ULTRASONIC IRRADIATION
OF CHEMICAL COMPOUNDS
IN AQUEOUS SOLUTIONS

Thesis by

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Στους γονείς μου Γιώργο - Λίτσα

Dedicated to my parents George – Litsa
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Abstract

The ultrasonic irradiation of para-nitrophenol, S(-II), and parathion is studied in aqueous solutions at 20 kHz and ≈ 75 W·cm⁻². Para-nitrophenol was degraded primarily by denitrification and secondarily by ·OH radical attack to yield NO₂⁻, NO₃⁻, benzoquinone, hydroquinone, 4-nitrocatechol, formate and oxalate. These reaction products and the kinetic observations are consistent with a model involving high-temperature reactions of p-nitrophenol in the interfacial region of cavitation bubbles. The average effective temperature of the interfacial region surrounding the cavitation bubbles was estimated to be \( T \approx 800 \) K.

Ultrasonic irradiation of S(-II) is studied in aqueous solutions over the pH range 7 – 12. The reaction of HS⁻ with ·OH is the principal pathway for the oxidation of S(-II) at pH \( \geq 10 \); the oxidation products are SO₄²⁻, SO₃²⁻, and S₂O₃⁻. Upon prolonged sonication, SO₄²⁻ is the only observed product. At pH ≤ 8.5, thermal decomposition of H₂S within or near collapsing cavitation bubbles becomes the important pathway and elemental sulfur is found as an additional product of the sonolysis of S(-II). The sonolytic oxidation of H₂S at pH \( \geq 10 \) was successfully modeled with an aqueous-phase free-radical chemistry mechanism and assuming continuous and uniform ·OH input into solution from the imploding cavitation bubbles.

Parathion degradation occurred primarily by enhanced hydrolysis and secondarily by direct ·OH radical attack.

The effect of various physical and chemical parameters on sonolytic yields is examined. The observed effects are in qualitative agreement with the sonolysis mechanisms proposed for the chemicals of interest and the existing hydrodynamic
theories of acoustic cavitation.

The formation of iodine upon ultrasonic irradiation of potassium iodide solutions and the sonolysis of S(−II) are used as probes to compare the sonochemical efficiency of different experimental set-ups.

This work elucidates the mechanisms of the ultrasonic decomposition of typical organic and inorganic pollutants. It is shown that ultrasound has the potential to become a viable alternative for the destruction of chemical contaminants in water and wastewater. The current limitation of sonolysis is its low energy utilization efficiency, but there is room for improvement by optimizing reactor design and physical/chemical operation conditions. This work offers some recommendations and insight in that respect.
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**Thesis Overview and Summary**

In this work, the ultrasonic irradiation of selected inorganic and organic compounds is studied in aqueous solutions and under controlled laboratory conditions. Based on the observed kinetics and reaction products, mechanisms for the sonochemical degradation of these compounds are proposed. The effect of various physical and chemical parameters and different ultrasonic devices on sonochemical reaction yields is also examined. This research was motivated by the potential application of sonolysis for the elimination of chemical contaminants found in water.

Chapter 2 presents a literature review on acoustic cavitation, bubble dynamics and aqueous sonochemistry. Acoustic cavitation is the phenomenon where small bubbles (cavities) are formed in the solution under sonication in response to the passage of expansion and compression waves. Current hydrodynamic theories can model the dynamics of single bubbles and provide estimates for the high transient temperatures and pressures that result locally upon implosion of the cavities. It is these transient extreme conditions that lead to chemical transformations of the solvent and the chemical species present in the solution. The primary sonochemical reactions are high temperature reactions taking place in the gas phase, but there are also secondary reactions occurring in the liquid phase that involve species escaping from the gas phase into solution.

Unfortunately, the number and size distribution of cavitation bubbles and the physical conditions inside the bubble and its surrounding region upon collapse cannot be predicted. Furthermore, the existing theories cannot handle bubble fields, where many bubbles of different sizes interact with one another as well as with the sound field. Photographic and holographic methods coupled with sonoluminescence can be used to follow bubble dynamics and probe the intensity of
collapse and the spatial and temporal distributions of cavitation events. Applications of these methods indicate that, even though real bubble fields are very complex, overall behavior of bubble clouds agrees qualitatively with that predicted from hydrodynamic theories for single bubbles.

Para-nitrophenol (p-NP) was chosen as model organic compound since phenol and substituted phenols are significant environmental pollutants. Chapter 3 presents kinetic data and selected mechanistic observations for the sonochemical degradation of p-NP in water. In the presence of ultrasound (20 kHz, 84 Watts, ≈ 75 W·cm⁻²) p-NP was degraded primarily by denitrification to yield NO₂⁻, NO₃⁻, benzoquinone, hydroquinone, 4-nitrocatechol, formate and oxalate. These reaction products and the kinetic observations are consistent with a model involving high-temperature reactions of p-nitrophenol in the interfacial region of cavitation bubbles. The main reaction pathway appears to be carbon-nitrogen bond cleavage. Reaction with hydroxyl radical provides a secondary reaction channel. The average effective temperature of the interfacial region surrounding the cavitation bubbles was estimated to be T ≈ 800 K.

Sulfide [S(–II)] was chosen as model inorganic compound since reduced sulfur species are another class of pollutants commonly found in aquatic environment. Chapter 4 presents the results of an investigation of the kinetics and mechanism of the sonolysis of S(–II), where [S(–II)] = [H₂S] + [HS⁻] + [S²⁻], in oxic aqueous solutions over the pH range 7 – 12. Ultrasonic irradiation of S(–II) at 20 kHz and 75 W·cm⁻² resulted in its rapid oxidation. The reaction of HS⁻ with ·OH is the principal pathway for the oxidation of S(–II) at pH ≥ 10; the oxidation products are SO₄²⁻, SO₃²⁻, and S₂O₃²⁻. Upon prolonged sonication, SO₄²⁻ is the only observed product. At pH ≤ 8.5, thermal decomposition of H₂S within or near collapsing
cavitation bubbles becomes the important pathway and elemental sulfur is found as an additional product of the sonolysis of S(−II). Oxidation of S(−II) by ultrasonic irradiation may present an alternative method for the control of H₂S in water and wastewater systems.

In Chapter 5, a comprehensive aqueous phase mechanism that describes the free radical chemistry of the S(−II) + hydroxyl radical (·OH) system in the presence of oxygen is developed. The oxidation of S(−II) is initiated by reaction with ·OH but it is further propagated by a free–radical chain sequence involving O₂. This chemical mechanism is used to model the ultrasonic irradiation of S(−II); ·OH input from the imploding cavitation bubbles into the aqueous phase is assumed to be continuous and uniform.

This simplified approach can model adequately the observed sonolytic degradation of S(−II) in air saturated aqueous solutions at high pH but underpredicts the rate of S(−II) disappearance at pH ≤ 8.5. These results are in agreement with the pathways for S(−II) sonolysis proposed in Chapter 4 and they indicate that the action of ultrasonic waves on aqueous solutions containing species that are not susceptible to thermal decomposition can be predicted based on the knowledge of the free–radical chemistry of the species. It is also shown that even though aqueous–phase sonochemical reactions are initiated by ·OH transfer into the aqueous phase from the cavities, molecular oxygen present in the solution can be the main oxidant if it can propagate a free–radical chain reaction. This observation is important with respect to the application of ultrasound for the control of chemicals in trace amounts in water and wastewater systems.

Chapter 6 presents the results of ultrasonic irradiation of iodide and parathion. The main motivation behind the iodide experiments was to perform a
visual inspection of the ultrasonic field to detect possible inhomogeneities and to obtain all the background information needed for later use of KI as a dosimeter for different ultrasonic apparatus. It is concluded that the mechanism of KI sonolysis could be more complicated than the simple reaction of \( \Gamma^- \) with 'OH. Molecular oxygen clearly plays an important role in this free radical oxidation. High temperature reactions of \( \Gamma_2 \) in the gas phase were suspected but the effect of dissolved gases on \( \Gamma_2 \) yield seems to indicate otherwise. Potassium iodide can be used as an overall sonochemical dosimeter but a closed system is necessary, since considerable amounts of \( \Gamma_2 \) produced can be lost through evaporation. The \( \Gamma_2 \) yield is independent of pH in the neutral to alkaline region.

Parathion is a commonly used organophosphate pesticide that is fairly persistent in natural systems (\( \tau_{1/2} = 108 \) days at 20 °C and pH 7.4). Its chemical structure is similar to that of many nerve gases. Ultrasonic irradiation of a parathion-saturated aqueous solution at 20 kHz and 75 W/cm\(^2\) resulted in complete destruction of parathion within 2 hours. The observed products include inorganic species (sulfate, nitrate, phosphate) and simpler organic compounds (mainly p-NP and organic acids) that are known to degrade further under the action of ultrasound. Clearly, ultrasonic irradiation (US) has an advantage versus catalyzed hydrolysis of organophosphates; US results in harmless products, while many of the hydrolytic products (e.g., substituted phenols) may be toxic or cause taste and odor problems in water systems.

Chapter 7 presents the effects of different parameters on the sonolysis yields of the above mentioned chemicals. The observed effects are in agreement with the sonolysis mechanisms proposed in the previous chapters and the existing acoustic cavitation theory. It is shown that specific ions (e.g., halogens) can have significant
catalytic or inhibitory effects for the sonolysis of chemicals. These effects are attributed to high temperature reactions at or near the interfacial region, or reactions with 'OH.

Sonolysis is relatively inefficient with respect to the input energy. It is calculated that only a small portion of the total energy supplied to the direct immersion horn system results in "useful" free-radical reactions. Different commercial ultrasonic apparatus is tested and continuous flow operation is compared to batch experiments. It is suggested that sonication units with larger radiating surfaces (e.g., cup–horn type) are a better choice than localized application of high intensity ultrasound (direct immersion horn type). The operation of both types of sonicators in the flow–through mode does not greatly decrease the sonochemical efficiency of the unit. Sonication of S(−II) in wastewater indicates that sonochemical free–radical reactions are not significantly affected by the complex wastewater matrix.

The main conclusions of this work are summarized in Chapter 8. It is concluded that ultrasound has the potential to be a viable alternative for the destruction of chemical contaminants in water and wastewater. Its low energy utilization efficiency would currently limit its potential use to applications where higher cost could be offset by one or more of the advantages that this novel treatment method presents (e.g., rapid decomposition of otherwise persistent organics, harmless decomposition products, relatively "clean" and "easy" operation). For instance, application of sonolysis for groundwater remediation, or for low–flow pretreatment of industrial wastes could be envisioned for the near future. Furthermore, there is room for improvement of sonolysis by optimizing reactor design and physical/chemical operation conditions.
Appendix A and Appendix B present the results of investigations for novel chemical reagents for the control of S(−II) in water and wastewater. The motivations for this work were i) the existing need for new cost–effective methods for the control of hydrogen sulfide in water and wastewater systems, and ii) the desire to compare ultrasonic degradation of S(−II) to improved chemical methods for the oxidation of that chemical.

The catalytic effectiveness of cobalt(II)–4,4',4'',4'''-tetrasulfophthalocyanine [Co(II)TSP] for the autoxidation of hydrogen sulfide, S(−II), is presented in Appendix A. At pH 7 and 25°C the rate of S(−II) oxidation is first–order with respect to [S(−II)]. A fractional order on the catalyst is observed. At oxygen concentrations 15 to 200 μM the oxygen dependence can be described by simple Michaelis–Menten kinetics with \( K = 63 \) μM. The uncatalyzed oxidation of sulfide by molecular oxygen is found to be faster in wastewater than in clean water. This difference is attributed to microbial oxidation of S(−II) and to catalytic action of transition metals present in wastewater.

Appendix B presents the results of S(−II) oxidation in wastewater by an alternative oxidant, peroxymonosulfate. Peroxymonosulfate, \( \text{HSO}_5^- \), is found to be a more rapid and efficient oxidant of S(−II) than either \( \text{H}_2\text{O}_2 \) or Fe(II). The combination of peroxymonosulfate and hydrogen peroxide is additive in terms of S(−II) oxidation, while the combination of peroxymonosulfate and Fe(II) results in a decrease in the effectiveness of Fe(II) as an oxidant. Peroxymonosulfate is shown to be a viable alternative to \( \text{H}_2\text{O}_2 \) for the control of sulfide–induced corrosion in concrete sewers.

The computer code of the mathematical model discussed in Chapter 5 is presented in Appendix C.
CHAPTER 1

INTRODUCTION
Motivation

The elimination and control of chemical contaminants in the environment have become a major regulatory issue in recent years. In order to address this problem, there has been a continuous search for innovative technologies for the removal of inorganic and organic pollutants from water and wastewater. In some situations urgent problems require fast, practical, and cost-effective solutions. The application of ultrasonic irradiation may provide a convenient method for the elimination of problematic pollutants.

Ultrasound is the name given to sound waves with frequencies higher than those to which the human ear can respond (> 16 kHz). The chemical effects of ultrasonic irradiation have been known for more than 50 years\textsuperscript{1}. But it is only in recent years that a considerable interest in sonochemistry has arisen. Several books\textsuperscript{2-4} and numerous review papers\textsuperscript{5-9} have appeared during the last few years. The similarities of sonochemistry to radiation and combustion chemistry have been recognized, and ultrasound has been used to induce or accelerate a variety of chemical reactions\textsuperscript{10-19}. Nevertheless, the mechanisms involved in sonochemical reactions are not fully understood. Even though ultrasound has currently a wide range of industrial applications\textsuperscript{2-3}, its potential as an alternative water and wastewater treatment method has only been explored at a preliminary level so far\textsuperscript{20-23}.

In this work, the ultrasonic irradiation of selected inorganic and organic compounds is studied in aqueous solutions under controlled laboratory conditions. Based on the observed kinetics and reaction products, mechanisms for the sonochemical degradation of these compounds are proposed. The effect of various
physical and chemical parameters and different commercial ultrasonic apparatus on sonochemical reaction yields is also examined. The motivation for this work is the potential application of ultrasound for the pyrolytic and oxidative control of hazardous chemicals in water systems. However, the primary focus is directed toward the fundamental chemistry of the sonolysis of chemicals.

Para-nitrophenol (p-NP) was chosen as model organic compound since phenol and substituted phenols are significant environmental pollutants. Small amounts of phenolic compounds can cause taste and odor problems in water supplies, especially after chlorination\textsuperscript{23}. Phenolic compounds are also relatively difficult to remove by conventional wastewater treatment methods, particularly when present at high concentrations. Phenols have been often used as model compounds for wastewater in experimental studies on the feasibility of wastewater treatment methods\textsuperscript{20-23}. There are data available in the literature on the degradation of phenolic compounds by thermal decomposition\textsuperscript{24} and radiolysis\textsuperscript{25-27}. Furthermore, information exists about the oxidation of phenol in an ultrasonic field\textsuperscript{28}. Even though this information is rather qualitative, it definitely suggests that phenolic compounds can be degraded sonochemically.

Sulfide [S(−II)] was chosen as model inorganic compound since reduced sulfur species are another class of pollutants commonly found in aquatic environment. They have both natural (geochemical and biological) and anthropogenic (fossil fuel refining and combustion) sources. Hydrogen sulfide (H\textsubscript{2}S) and mercaptans (RSH) have characteristically unpleasant odors and very low threshold concentrations (<1 ppbv). Even in very low concentrations, these compounds may create odor and taste problems in drinking water supplies\textsuperscript{29}. In natural waters, sulfides and mercaptans are toxic to many aquatic organisms\textsuperscript{30}. Odor and corrosion problems
associated with the presence of hydrogen sulfide are often encountered in geothermal power plants\textsuperscript{31} and oil refineries\textsuperscript{32}. Hydrogen sulfide is also a major contributor to objectionable odors and corrosion in wastewater collection and treatment facilities, and it represents a significant safety hazard to plant personnel\textsuperscript{33,34}. Despite extensive research that covers both laboratory and field scale\textsuperscript{35-46}, there is still an urgent need for novel cost-effective methods for the control of hydrogen sulfide in water and wastewater systems\textsuperscript{33,47}.

Research objectives
The main research objectives of this thesis were:

- To select model chemicals of environmental importance and examine their behavior in aqueous solution when exposed to ultrasonic irradiation.
- To understand the mechanisms of the sonolytic decomposition of the selected model chemical compounds.
- To study the effect of various physical and chemical parameters on the sonochemical reaction yields and attempt to correlate the experimental results with existing acoustic theory.
- To evaluate the feasibility of the use of ultrasound as an alternative for the destruction of chemicals in water and wastewater.
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CHAPTER 2

AN INTRODUCTION TO
THE PHYSICS OF SONOCHEMISTRY
Background

Ultrasound is the name given to sound waves having frequencies higher than those to which the human ear can respond (>16 kHz). The upper limit of ultrasonic frequency is not sharply defined but is usually taken to be 5 MHz for gases and 500 MHz for liquids and solids\(^1\).

When a sound wave passes through a liquid or a gas the molecules of the medium vibrate longitudinally in the direction of the wave propagation. Pressure variations (rarefaction and compression cycles) are associated with the movement of the molecules. For a sinusoidal sound source, the acoustic pressure at any time \(t\) is given by \(P(t) = P_a \cdot \sin 2\pi ft\), where \(P_a\) = maximum pressure amplitude, \(f\) = frequency of the sound wave. The following relationship exists between the intensity of the sound source (\(I = \text{energy per unit area per unit time}\)) and \(P_a\):

\[
I = \frac{P_a^2}{2\rho c}
\]

where \(\rho\) = density of the medium, \(c\) = velocity of sound in that medium (\(c = f\lambda\), where \(\lambda\) is the wavelength of the sound wave; \(c \approx 1450\) m/s for water). For water (\(\rho = 1\) kg/m\(^3\)), equation (2.1) gives \(P_a \approx 1.7 \times 10^{-5}\), where \(P_a\) is in atm and \(I\) in W/cm\(^2\).

The intensity decreases with distance traveled by the wave (sound attenuation) due to energy losses. For the one-dimensional case, the intensity at a distance, \(l\), from the source is given by\(^1\):

\[
I = I_0 e^{-2\alpha l}
\]
where $I_0$ is the intensity at the source and $\alpha$ is an overall attenuation coefficient that includes frictional losses, thermal conduction losses, and other energy losses represented by the bulk viscosity. For constant $T$, $\alpha$ is proportional to $f^2$, and a value of $\alpha/f^2 = 21.5 \times 10^{-17} \text{ sec}^2 \cdot \text{cm}^{-1}$ was observed experimentally for a wide variety of frequencies in water$^1$. On the basis of this value, 1% loss in the intensity will be noticed in $\approx 600$ m, 23 m and 23 cm at 20 kHz, 100 kHz and 1 MHz, respectively. Therefore, higher frequency ultrasound is associated with higher energy losses. For 20 kHz sound waves, energy losses are negligible for short distances.

Following the existing nomenclature, the terms sonication, insonation, and ultrasonic irradiation are used in this work interchangeably, and they all refer to the introduction of ultrasound into a medium.

**Acoustic cavitation**

**Introduction**

The term cavitation refers to the formation and the subsequent dynamic life of bubbles in liquids. These bubbles will be filled with vapor and/or gases present in the liquid. Cavitation is brought about by tension produced by pressure variations and may be of hydrodynamic, thermal or acoustic origin. It can occur in many fluids such as water, organic solvents, biological fluids, liquid helium and molten metals$^2$.

Acoustic cavitation, i.e., cavitation taking place when a medium is subjected to ultrasonic irradiation is accepted to be the most important physical mechanism involved in sonochemistry$^{1-4}$. This section focuses on acoustic cavitation in water.
Initiation of acoustic cavitation

The tensile strength of a pure liquid is determined by the attractive intermolecular forces which maintain its liquid state. In order for a cavity to form during sonication of a pure liquid, the total pressure during the rarefaction cycle must overcome the tensile strength of the medium. The tensile strength of water in the complete absence of impurities has been calculated to be in excess of 1000 atm\(^3\). However, cavitation thresholds (i.e., acoustic pressure amplitudes to which the liquid is exposed when cavitation is first detected) of the order of 1 atm are measured for water without protracted purification\(^2\).

It is generally accepted that inhomogeneities in water serve as preferential sites for liquid rupture\(^1\)-\(^6\). Furthermore, free gas bubbles present in a liquid in small numbers (i.e., not near gas saturation) are not accepted as the main source of nucleation sites\(^1\)-\(^2\), since theoretical calculations show that small bubbles will dissolve very fast due to surface tension\(^7\) while large bubbles will rise to the surface\(^8\). Therefore, mechanisms that prevent dissolution of microbubbles have been postulated and they have been reviewed by Crum\(^6\) and more recently by Atchey & Crum\(^8\). The two main models are: i) the organic skin model, that assumes that surface–active–organic molecules form "skins" on the surface of the gas bubbles preventing them from dissolving, and ii) the crevice model that accepts the existence of gas pockets in crevices of hydrophobic solid impurities present in water; during the rarefaction cycle (and if a critical "vacuum" threshold is exceeded) the gas pocket grows releasing small free bubbles into the solution or, it undergoes violent collapse itself. A mathematical description of the crevice model where the acoustic cavitation threshold is primarily a function of surface tension
and dissolved gas concentration has been presented\textsuperscript{6}.

Atchley & Crum\textsuperscript{8} have summarized the results of a number of cavitation threshold measurements in water. The observed cavitation threshold decreases with increasing amount of dissolved gases and increasing number and size of solid contaminants, is directly proportional to the hydrostatic pressure applied to the liquid and varies inversely with surface tension and temperature.

Assuming ideal gas behavior, the following expression can be calculated\textsuperscript{3-4} for the minimum rarefaction pressure (i.e., "vacuum"), $P_b$, that must be applied in order to create a bubble of radius $R_o$ (refs. 1, 2, and 3 among others):

$$P_b = P_h + \frac{2}{3} \left[ \frac{(2\sigma/R_o)^3}{3(P_h-P_v+2\sigma/R_o)} \right]^{0.5} \quad (2.3)$$

where $\sigma =$ surface tension (76 dynes/cm for pure water, $\approx$ 72 dynes/cm for tap water), $P_h =$ ambient pressure, and $P_v =$ saturation vapor pressure ($\approx$ 0.03 atm at 25 $^\circ$C for water). $P_b$ is known as Blake's threshold pressure since it was first introduced by Blake\textsuperscript{9} (with $P_v = 0$).

In most sonochemical experiments a gas saturated solution is used, and the question of inception of cavitation does not arise since enough nuclei are present to initiate bubble formation. Figure 2.1 is reproduced from Katz & Acosta\textsuperscript{10} and summarizes measured nuclei distributions from various sources. The term nuclei is used here to denote free-gas bubbles; sometimes "nuclei" is used as a generic term and includes all inhomogeneities that can result in the formation of a cavity. The number density distribution function, $N(R)$, is defined so that the total number of nuclei with sizes between $R_o$ and $R_o+dR$ is $N(R_o)dR_o$ per unit volume. Gavrilov\textsuperscript{11}
Figure 2.1  Nuclei distribution from various sources. Figure is reproduced from Ref. 12 and was presented originally by Katz and Acosta (1982)
used thermodynamic arguments to conclude that $N(R)$ must be proportional to $R^{-3}$. As it can be seen in Fig. 2.1, the experimental data of various investigators can be represented by

$$N(R) = A/R^n$$ (2.4)

where $A$ is a constant and the value of $n$ is around 3. Gavrilov$^{11}$ suggested the use of eq. (2.4) with $A = 10^{-9}$ cm$^{-4}$ and $n = 3$ (R in cm) for water allowed to settle for a long time. It is noted that various acoustical, optical and electrical methods have been used in order to perform measurements of the number and size distribution of gas bubbles. A review of those methods can be found in Ref. 12.

After the onset of cavitation, imploding bubbles will also contribute to the number of available nucleation sites by adding smaller bubbles into the solution. It is expected that the number of nuclei is increased by several orders$^{13}$ and that the relative distribution changes too. However, there are no experimental data that give $N(R)$ under sonication. Hansson et al.$^{14}$ have presented numerical calculations of the expected total number and average diameter of bubbles during sonication with an ultrasonic probe at 20 kHz near a solid surface. Their analysis assumes a continuum of single size bubbles (all bubbles present in the solution before sonication are assumed to be of the same size, and that size changes with sonication). Such an assumption may be justified when the total volume of gas is of interest, e.g., for determining the compressibility of the medium. However, the actual bubble size distribution is important for sonochemical applications since the size of a bubble will determine its fate and, consequently, the type and intensity of the resulting chemical phenomena.
**Single bubble dynamics**

The formulation of the general hydrodynamic problem of a single bubble in a liquid exposed to a time variable pressure involves: 
i) writing the equations of conservation of mass, momentum, and energy for both the gas and the liquid phases, 
ii) matching of these equations at the interface between the gas and the liquid, and 
iii) using the proper equations of state for the gas and the liquid. The pressure and velocity fields and the motion of the bubble wall could then be determined by solving the system of the non-linear differential equations. However, the general problem is too complicated to solve and the use of simplifying assumptions is necessary in order to arrive to a system that is amenable to numerical or even analytical solution.

The following equation for the motion of the bubble wall is commonly used for bubble cavitation:

\[
RR+(3/2)R^2=(1/\rho)[(P_o+2\sigma/R_o-P_v)(R_o/R)^{3k}-P_o-P_a\sin\omega t-2\sigma/R-(4\mu R)/R] \tag{2.5}
\]

where: \( R \) = bubble radius, \( R_o \) = initial radius, \( \rho \) = liquid density, \( P_o \) = ambient pressure, \( P_a\sin\omega t \) = acoustic pressure, \( P_v \) = vapor pressure, \( \sigma \) = surface tension, \( \mu \) = viscosity, \( k \) = polytropic exponent [between 1 (isothermal) and \( \gamma \) (adiabatic)], and dots indicate differentiation with respect to time.

This equation is usually referred to as the Rayleigh–Plesset equation, but the name R.P.N.N.P. used by Neppiras\textsuperscript{15} seems more appropriate since it refers to all of the basic contributors: Rayleigh\textsuperscript{16}, Plesset\textsuperscript{17}, Nolting & Neppiras\textsuperscript{18,19}, and Poritsky\textsuperscript{20}. It assumes incompressible liquid, constant gas content, sound
wavelength large compared with bubble dimensions, \( \rho \), \( \kappa \) of liquid small compared with that of gas, and spatially uniform conditions within the bubble, and neglects damping (because of thermal conduction or acoustic radiation), heat and mass transfer, body forces (e.g., gravity), and loss of spherical shape.

There is a generally accepted division of cavitation phenomena in homogeneous liquids into\(^2\): \( i \) stable cavitation, in which a bubble oscillates many times with limited change about its equilibrium radius, and \( ii \) transient cavitation, in which a short lived small bubble undergoes violent radial pulsations in a few acoustic cycles and may terminate in violent collapse. Both forms of cavitation may occur simultaneously in a solution and a bubble undergoing stable cavitation may change to transient cavitation.

Stable cavitation is commonly the case for low sound intensities (1–3 W/cm\(^2\)) and bubbles are believed to contain mainly gas (since they live long enough for gases to diffuse into them). The resonance frequency, \( f_{\text{res}} \), of a bubble of radius \( R \) is given by\(^{45}\):

\[
f_{\text{res}} = \left[ \frac{1}{(2\pi R)} \right] \left\{ [3\kappa (P_o + (2\sigma/R)) - (2\sigma/R)]/\rho \right\}^{0.5}
\]  \( (2.6) \)

where \( \rho \), \( \kappa \), and \( P_o \) are as for equation (2.5). It can be calculated that at 20 kHz and 1 MHz the resonance size of cavities is \( \approx 170 \) \( \mu \text{m} \) and 3.3 \( \mu \text{m} \) respectively. If surface tension is neglected (large bubble), equation (2.6) is simplified to:

\[
f_{\text{res}} = \left[ \frac{1}{(2\pi R)} \right] (3\gamma P/\rho)^{0.5}
\]  \( (2.7) \)

where \( P = \) pressure inside the bubble. For air bubbles in water at 1 atm, eq. (2.6)
gives \( f_{\text{res}} \cdot R \approx 3 \) (\( f_{\text{res}} \) in Hz, \( R \) in m).

Transient cavitation is believed to occur in liquids exposed to high sound intensities (>10 W/cm\(^2\))\(^4\) and transient gas bubbles are mostly filled with vapor: this leads to violent collapse since there is not much gas present to cushion the impact of the implosion. Assuming adiabatic conditions upon collapse, the following equations have been developed for the time of collapse, \( \tau \), the maximum pressure, \( P_{\text{max}} \), the maximum temperature, \( T_{\max} \), and the maximum Mach number, \( M_{\text{max}} \):\(^{15}\)

\[
\tau = 0.915 R_{\text{max}} (\rho/P_m)^{0.5}(1+Q/P_m) \tag{2.8}
\]

\[
P_{\text{max}} = Q \left[ \frac{P_m(k-1)}{Q} \right]^{\frac{k}{k-1}} = Q Z^k \tag{2.9}
\]

\[
T_{\max} = T_0 \left[ \frac{P_m(k-1)}{Q} \right] = T_0 Z^{k-1} \tag{2.10}
\]

\[
M_{\text{max}} = (0.015 (R_{\text{max}}/R_{\text{min}})^{1.5}(P_m/Q), \text{ for } R_{\text{max}}/R_{\text{min}} \geq 4 \tag{2.11}
\]

where: \( R_{\text{max}}, R_{\text{min}} \) = maximum and minimum bubble radius (at start and end of collapse), \( P_m \) = liquid pressure at collapse, \( Q \) = initial gas pressure, \( k \) = polytropic exponent, \( Z \) = volume compression ratio = \((R_{\text{max}}/R)^3\).

The polytropic exponent is again used in the place of \( \gamma \) (ratio of specific heats). The assumptions of eq. (2.5) are also implied. The incompressibility assumption is valid for \( M \leq \sim 0.2 \), that corresponds to \((P_m/Q) \leq \sim 100\)\(^{15}\). The above equations should only be used as an approximation to get the order of magnitude for \( T, P \) upon bubble collapse. However, they demonstrate the importance of the dissolved gas (\( \gamma \) is 5/3, 7/5, and 4/3 for monoatomic, diatomic,
and triatomic gases), and of the vapor pressure (affects \( Q; P_v \) increases with increasing temperature and gas solubility).

Modifications of eq. (2.5) have been proposed where some of the assumptions have been relaxed (and usually replaced by others that are more justified). For example, Gilmore\(^{21}\) included the compressibility of the liquid by using the Kirkwood–Bethe approximation\(^{22}\) (wave propagates with velocity equal to the sum of the sound and the fluid velocity) and neglected the effect of surface tension and viscosity. Heat conduction was added by Hickling & Plesset\(^{23}\), who showed that Gilmore's approximation is in general justified. Margulis & Dmitrieva recently included heat exchange\(^{24}\) and presented calculations for cavitation bubbles containing air, Ar, He, and water vapor\(^{25}\). The overall collapse time did not differ much from that given from eq. (2.8). However, rate of collapse and maximum temperature were shown to be about twofold lower than those calculated from eqs. (2.9) and (2.10), and the minimum \( R \) attained is about twofold higher than that of adiabatic collapse.

The growth of small microbubbles to bubbles of larger size can be explained by the mechanism of rectified diffusion, i.e., unequal mass transfer across the gas–water interface during bubble oscillation. Not all bubbles initially present in the solution will cavitate. Furthermore, cavitating bubbles will be either stable or transient, or will go from one type of cavitation to the other. Cavitation thresholds can be found by setting criteria for the onset of transient cavitation and with the use of eq. (2.5) or even a more simplified non–linear equation of motion. The increase of the radius of the bubble to approximately double its original size, or wall velocity approaching the velocity of sound in water are the two most commonly used criteria for the onset of transient cavitation. Apfel\(^{26}\) has presented
cavitation prediction charts that combine thresholds for gas nucleation [Blake threshold, eq. (2.1)], rectified diffusion (using Safar's analysis\textsuperscript{27}), and transient cavitation ($R_{\text{max}} = 2.3 \cdot R_0$ is used as the threshold condition). The expressions used for the minimum and maximum rectified diffusion threshold, and the maximum radius controlled by inertia are given in Table 2.1.

Table 2.1 summarizes the parameters that are relevant to sonication in water at 20 kHz and 75 W cm\textsuperscript{-2} (conditions used in most of the experiments presented in the following chapters). It can be seen that only bubbles between 40 nm and 460 \mu m are expected to contribute in transient cavitation under these conditions.

**Bubble fields—photographic studies**

The dynamics of a single bubble are relatively well understood and can be modeled mathematically. However, many bubbles of different sizes are present in bubble fields encountered in practice. High speed photography, cinematography and holography have been used to visually observe the dynamics of single bubbles and bubble fields.

Ellis\textsuperscript{28} did pioneering work using a drum camera and a Kerr Cell as the shutter. Lauterborn and co–workers\textsuperscript{29–32} have reported observations of cavities that are produced by focusing an intense light beam from a ruby laser. They have studied stable and transient bubbles and bubble fields, and they reported interesting features of bubble–bubble interactions (e.g., bubbles of similar size coalesce, bubbles of significantly different sizes develop jets before coalescence), bubble–wall interactions, and the dynamics of clouds originating from the collapse of a single bubble. Figure 2.2 presents the recorded growth and collapse of a bubble in water. Several other researchers have also used similar techniques to study
Table 2.1  
Sonication in water at 20 kHz, 75 W·cm⁻²

<table>
<thead>
<tr>
<th>Variable</th>
<th>value</th>
<th>formula used</th>
</tr>
</thead>
<tbody>
<tr>
<td>sound wavelength</td>
<td>7.25 cm</td>
<td>$\lambda = c/f$</td>
</tr>
<tr>
<td>resonant radius</td>
<td>165 µm</td>
<td>$\omega^2 = \left[ \frac{3k(P_o+2\sigma/R_r)-2\sigma/R_r}{\rho R_f^2} \right]$</td>
</tr>
<tr>
<td>min radius corresponding to Blake's threshold</td>
<td>0.04 µm</td>
<td>$P_a = P_o+8\sigma/9 \left[ \frac{3\sigma}{2(P_o+2\sigma/R_b)R_b^3} \right]$</td>
</tr>
<tr>
<td>RD min threshold</td>
<td>0.06 µm</td>
<td>$\frac{P_a}{P_o} = \frac{(3k(1+X)-X)(1-(f/f_a)^2)(1-C-X)^{0.5}}{6(1+X)^{0.5}}$</td>
</tr>
<tr>
<td>RD max threshold</td>
<td>830 µm</td>
<td>$\frac{(\frac{4}{3\omega})(P_a-P_o)(\frac{2}{\rho P_a})^{0.5}}{[1+\frac{2}{3P_o}(P_a-P_o)]}$</td>
</tr>
<tr>
<td>Max inertial R</td>
<td>460 µm</td>
<td>$0.3/f(\Delta P/\rho)^{0.5}$</td>
</tr>
<tr>
<td>collapse time</td>
<td>4 µs</td>
<td>$0.915R_{\text{max}}(\rho/P)^{0.5}$</td>
</tr>
</tbody>
</table>

where: $\Delta P = 2/3P_o(P_a-1)$, $X = 2\sigma/(P_oR)$, $P = P_a+P_o$, $C =$ gas saturation (0–1), $f_b =$ resonance frequency of bubble, $P_a$, $P_o$, and $f$ as defined in the text. Values used: $\sigma = 7.25\cdot10^{-2}$ N/m, $\kappa = 1.4$ (air), $\rho = 1$ kg/m³, $c = 1450$ m/s, $P_o = 1$ atm, $P_a = 14.7$ atm.
Figure 2.2 Growth and collapse of a bubble in water. Photographs taken at 20,000 frames/s (time between consecutive photographs = 50 $\mu$s). Frame sequence from top to bottom and from left to right. (Reproduced from ref. 30; Lauterborn, 1974)
bubble dynamics. Recently, Sanada et al.\textsuperscript{33} used holography in order to observe the interaction of a small air bubble with a shock wave and obtained an estimate of about 4000 atm for the impact pressure induced by the collapse of a 1.7 mm bubble.

In general, these type of studies have revealed surface deformations and loss of spherical shape of individual bubbles (sometimes followed by release of microbubbles into solution), complex interactions between bubbles, and the existence of bubble clouds, streamers, shock waves, and jets. On the other hand, overall behavior of bubble clouds has been observed to be similar qualitatively to that of single bubbles, at least with reference to collapse and rebound\textsuperscript{31}, or cavitation noise\textsuperscript{32}.

The need for mathematical description of the complex dynamics of bubble fields has become apparent, and considerable efforts are under way in that area (e.g., refs. 14, 34–37).

Sonochemistry

The term sonochemistry includes all chemical effects that occur upon ultrasonic irradiation of a medium. Sonochemistry is attributed to the high temperatures and pressures associated with acoustic cavitation\textsuperscript{1,2}. Transient cavitation is considered to be the main contributor to the observed sonochemical effects, but stable cavitation may also be important\textsuperscript{4}.

Sonochemical reactions could be categorized as: \textit{i}) primary reactions, involving thermal decomposition of solvent, solute, or gases present in solution as a result of the high temperatures and pressures attained upon bubble collapse, and \textit{ii}) secondary reactions, involving radicals from primary reactions and other species;
reactions of those radicals may occur in the gas phase within the hot bubble, the bubble/water interface, or the bulk aqueous phase.

A schematic representation of the regions of sonochemical reactions is given in Figure 2.2. It is noted that conflicting estimates of the temperatures attained upon collapse exist currently. The temperature estimates shown in Fig. 2.2 have been reported for sonication of metal carboxyls in mixtures of hydrocarbons\textsuperscript{38}. It is reasonable to expect that these temperatures will be lower in the case where water is the solvent (because of the lower vapor pressure and the higher thermal conductivity of water). An average effective temperature of \( \approx 800 \) K is estimated for the interfacial region during sonication in water at 20 kHz in this work (see Chapter 3). It is also stressed that Fig. 2.2 is only an idealization since cavitation bubbles will lose their spherical shape upon collapse.

It is noted that the observed destructive, cleaning, or mixing action of sonication on various systems (e.g., macromolecules, organometallic chemistry, catalysis) is partly due to hydrodynamic phenomena, such as jets and shock waves, that take place during sonication. However, hydrodynamic phenomena could not account for sonochemistry, since they could not result in direct breaking of chemical bonds\textsuperscript{2}.

Spin trapping methods combined with ESR have provided evidence for the formation of H atoms and \(^\cdot\)OH radicals in the cavitation bubbles produced by ultrasound in Ar saturated water\textsuperscript{39}. The formation of H and \(^\cdot\)OH is attributed to thermal dissociation of water vapor present in the cavities during the compression phase\textsuperscript{1-4}. Table 2.2 shows the principal reactions that appear to be involved in water sonolysis in the presence of Ar, O\(_2\), N\(_2\), and air\textsuperscript{2}. These reactions have been proposed by analogy to combustion and shock tube chemistry following evidence
Figure 2.3  Schematic representation of the regions of sonochemical reactions in aqueous sonochemistry (see text for comments).
Table 2.2
Reactions involved in water sonolysis

1) Under Ar:

\[
\begin{align*}
H_2O \underset{\text{US}}{\rightarrow} & H^+ + OH^- \\
\cdot OH + \cdot H \underset{\text{M}}{\rightarrow} & H_2O \\
2 \cdot OH & \rightleftharpoons \cdot O + H_2O \\
2 \cdot OH \underset{\text{M}}{\rightarrow} & H_2O_2 \\
2 H^+ \underset{\text{M}}{\rightarrow} & H_2 \\
2 O^- \underset{\text{M}}{\rightarrow} & O_2 \\
O_2 + H^+ & \rightarrow HO_2 \\
HO_2 + H^+ & \rightarrow H_2O + O^-.
\end{align*}
\]

2) Under O₂:

\[
\begin{align*}
O_2 & \rightarrow 2 O^- \\
O_2 + H^- & \rightarrow HO_2 (or \cdot OH + O) \\
2 HO_2 & \rightarrow H_2O_2 + O_2 \\
O^- + HO_2 & \rightleftharpoons 2 \cdot OH
\end{align*}
\]

3) Under N₂:

\[
\begin{align*}
N_2 + \cdot OH & \rightarrow N_2O + H^- \\
N_2 + O^- \underset{\text{M}}{\rightarrow} & N_2O \\
N_2 + O^- & \rightleftharpoons NO + N^- \\
N_2O + O^- & \rightarrow N_2 + O_2 \\
NO + H^- & \rightarrow N^- + \cdot OH
\end{align*}
\]

4) Under air:

as in 2 and 3 plus \( N_2 + O_2 \rightarrow 2 \text{NO} \)
provided by isotopic scrambling (e.g., refs. 40, 41). In the absence of 'OH scavengers the main product of the sonolysis of water is H₂O₂.

No direct studies on the conditions inside and in the vicinity of cavitating bubbles exist (e.g., measurements of temperature, pressure, or concentrations of chemical species). This is due to the dynamic nature of acoustic cavitation and the small time and length scales involved in the collapse of the cavities (see Table 2.1). Indirect methods such as sonoluminescence (SL) and comparative rate thermometry⁴² have been used to probe the intensity of collapse and the spatial and temporal distribution of cavitation events. An excellent review article on the phenomenon of SL and its use as sonication probe has been presented by Walton & Reynolds⁴³; a more recent review of SL was presented by Verral & Sehgal².

Sonoluminescence (SL) refers to the emission of light when a liquid is sonicated. It is now accepted that SL originates from recombination of free radicals (e.g., H⁺ + OH⁻ → H₂O) and de-excitation of excited species⁴⁴ (e.g., H₂O⁺, OH⁺). Its intensity and spectrum depend on the factors that affect cavitation, i.e., nature of solvent and solute (including dissolved gas), sound frequency, temperature, pressure (ambient, acoustic)⁴³. SL can be detected with the use of photomultipliers or image intensifiers. Luminol (o-aminophthalhydrazide) can be used to enhance the natural water SL⁴³ (because of its reaction with H₂O₂). A high-gain image intensifier system has been used to obtain visual observations of ultrasonic fields⁴⁵,⁴⁶.

In conclusion, sonochemistry can be seen as a third-order phenomenon of ultrasonic irradiation. The introduction of sound waves into the system results in cavitation. Conditions "suitable for chemistry" develop in a small fraction of the total number of cavities (e.g., high T, P upon collapse of transient cavities). These conditions then result in various tertiary chemical effects.
References


8. Atchley, A. A.; Crum, L. In reference 2, Chapter 1.


16. Lord Rayleigh. Phil. Mag., 34, 94 (1917).


CHAPTER 3

ULTRASONIC IRRADIATION
OF p–NITROPHENOL
IN AQUEOUS SOLUTION

ABSTRACT

The kinetics and mechanism of the sonochemical reactions of p-nitrophenol have been investigated in oxygenated aqueous solutions. In the presence of ultrasound (20 kHz – 84 Watts) p-nitrophenol was degraded primarily by denitrification to yield NO$_2^-$, NO$_3^-$, benzoquinone, hydroquinone, 4-nitrocatechol, formate and oxalate. These reaction products and the kinetic observations are consistent with a model involving high-temperature reactions of p-nitrophenol in the interfacial region of cavitation bubbles. The main reaction pathway appears to be carbon–nitrogen bond cleavage. Reaction with hydroxyl radical provides a secondary reaction channel. The average effective temperature of the interfacial region surrounding the cavitation bubbles was estimated to be T ≈ 800 K.
Introduction

The action of ultrasonic waves in liquids can induce or accelerate a wide variety of chemical reactions.\textsuperscript{1} The chemical effects of ultrasound have been explained in terms of reactions occurring inside, at the interface or at some distance away from cavitating gas bubbles.\textsuperscript{1–3} In the interior of a collapsing bubble, extreme but transient conditions are known to exist. Temperatures approaching 5000 K have been determined\textsuperscript{4} and pressures of several hundred atmospheres have been calculated.\textsuperscript{5} Temperatures on the order of 2000 K have been determined for the interfacial region.\textsuperscript{4} These and other important results such as the direct observation of cavitation dynamics\textsuperscript{6} and the ESR\textsuperscript{7} detection of H\textsuperscript{·} and OH radicals from the thermal decomposition of water have generated an increasing interest in sonochemistry. Much of the current interest in sonochemistry has arisen because of the utilization of sonolysis in catalysis\textsuperscript{1} and synthesis.\textsuperscript{8}

Sonochemical reactions are characterized by the simultaneous occurrence of pyrolysis and radical reactions especially at high solute concentrations.\textsuperscript{9} Any volatile solute will participate in the former reactions because of its presence inside the bubbles during the oscillations or collapse of the cavities.\textsuperscript{9–11} In the solvent layer surrounding the hot bubble, both combustion and free radical reactions (e.g. involving OH derived from the decomposition of H\textsubscript{2}O) are possible. Pyrolysis (i.e. combustion) in the interfacial region is predominant at high solute concentrations,\textsuperscript{11a,12} while at low solute concentrations free radical reactions are likely to predominate.\textsuperscript{12} In the bulk solution phase the reaction pathways are similar to those observed in aqueous radiation chemistry.\textsuperscript{11a,12,13} However, evidence for combustion reactions at low solute concentrations with non–volatile
surfactants and polymers has been presented.\textsuperscript{14}

In this paper we present kinetic data and selected mechanistic observations for the sonochemical degradation of para-nitrophenol (PNP) in water. We were motivated in part by the potential application of sonolysis for the elimination of chemical contaminants found in water.

Experimental

The ultrasonic irradiation of aqueous solutions of PNP was carried out with a Branson 200 sonifier that was operated at 20 kHz and with an output of electrical power-to-converter equal to 84 W. Reactions were performed in a stainless-steel continuous-flow reaction cell operated in the batch mode (Sonics & Materials). The total volume of the cell was 50 ml; the sonicated volume was 25 ml. The reactor was encased in a self-contained water jacket and was cooled with water at 15 °C. The measured reaction temperature inside the cells was 30 °C. All reactions were carried out with air-saturated solutions. Two openings on the upper part of the reactor allowed for a continuous exposure to air during the course of sonication. Unless otherwise stated experiments were performed with aqueous solutions adjusted to an initial pH of 5.

Quantification of PNP and 4-nitrocatechol (4–NC) was achieved by the measurement of their respective absorbancies in alkaline solution (0.1 M NaOH) at λ = 401 nm (ε = 19200 M\textsuperscript{-1}cm\textsuperscript{-1} for PNP) and 512 nm (ε = 12300 M\textsuperscript{-1}cm\textsuperscript{-1} for 4–NC).\textsuperscript{15} The measured absorbance of PNP was corrected for the small contributions due to 4–NC at 401 nm (ε = 6500 M\textsuperscript{-1}cm\textsuperscript{-1}).\textsuperscript{15} The concentration of p-benzoquinone (p-BQ) was determined spectrophotometrically in a solution
containing 20% n-butylamine at \( \lambda = 345 \text{ nm} \). The measured absorbance at 345 nm was corrected for the contributions due to PNP and 4–NC (extinction coefficients in 20% n-butylamine: p–BQ, \( \epsilon_{345} = 26400 \text{ M}^{-1}\text{cm}^{-1} \); p–NP, \( \epsilon_{345} = 3800 \text{ M}^{-1}\text{cm}^{-1} \); 4–NC, \( \epsilon_{345} = 3300 \text{ M}^{-1}\text{cm}^{-1} \)).

Nitrite, nitrate, formate and oxalate were determined with a Dionex 2020i ion chromatograph and a Dionex AS4–A column. The IC eluents were 2.2 mM CO\(_3^{2-}\), 2.8 mM HCO\(_3^-\) and 5 mM B\(_4\)O\(_7^{2-}\). The concentration of H\(^+\) was determined with a Radiometer autotitration system. Ionic strength was adjusted after sonication to 1 mM with Na\(_2\)SO\(_4\). Hydrogen peroxide was determined iodometrically and fluorometrically as described previously. Kinetic runs were carried out by sonication of a sample for a desired length of time. At that time an aliquot was withdrawn for complete chemical analysis. Kinetic experiments were continued after cleaning the cell thoroughly and filling it with fresh solution. Before analysis all samples were filtered with 0.2 \( \mu \text{m} \) HPLC filters (from Gelman) to remove Ti particles produced during sonication by erosion of the Ti tip of the sonication horn. Loss of PNP or its degradation products by adsorption to the HPLC filters was not observed. The water employed in all preparations was purified by a Milli–Q/RO system (18 Mohm resistivity) produced by Millipore. Absorption spectra were measured with a Shimadzu MPS–2000 UV–VIS spectrophotometer and fluorescence analyses were performed with a Shimadzu RF–540 spectrofluorimeter.

Results

Exposure of 25 ml solutions of 100 \( \mu \text{M} \) p–NP to ultrasound in the presence of
air resulted in a decrease in the absorption due to PNP at 401 nm and the subsequent formation of a new absorption band at 512 nm corresponding to 4–NC. The evolution of the absorption spectra with time is presented in Figure 3.1. Two near (but not exact) isosbestic points were observed at \( \sim 460 \) and \( \sim 335 \) nm. At sonication times longer than 40 min., these apparent isosbestic points were lost. Figure 3.2 shows the concentration vs. irradiation time profiles for PNP and 4–NC. The initial increase in the [4–NC] was linear with time. A maximum concentration of 4–NC was observed after 40 min. of sonication. The concentration of PNP decreased exponentially with sonication time.

Figure 3.3 shows a first-order plot of ln [PNP] vs. time. The ultrasonic degradation of PNP followed apparent first-order kinetics for at least four half-lives. A first-order rate constant of \( k_1 = 3.7 \times 10^{-4} \) s\(^{-1}\) was determined from the slope of this plot.

Nitrite and nitrate were found as primary nitrogen-containing products of the degradation of PNP. The time-dependent variations in the concentrations of these ions are shown in Figure 3.4a. \( \text{NO}_2^- \) appears to be the main product at short sonication times; it reached a maximum concentration of 57 \( \mu \)M after 42 min. of sonication. The concentration of \( \text{NO}_3^- \) increased continuously with time. The results of Figure 3.4a were obtained by analyzing the samples immediately after sonication. However, if the IC analysis were repeated on the same sample aliquot after several hours, \( \text{NO}_3^- \) was found as the main product and only traces (\( \sim 6 \) \( \mu \)M) of nitrite were detected. These results suggest that \( \text{NO}_2^- \) is the principal product of the decay of PNP by ultrasound.

It is well known that nitrite and nitrate are generated by the ultrasonic oxidation of \( \text{N}_2 \) in air–saturated aqueous solutions\(^1\). Sonication of pure water under
Figure 3.1  Absorption spectra evolution with sonication time where peak at 401 nm corresponds to p–NP while the broad band at 512 nm corresponds to 4–NC.
Figure 3.2  
[p-NP] and [4-NC] versus sonication time at pH 5
Figure 3.3 First-order plot of $\ln[p\text{-NP}]$ vs. time for the sonochemical decay of $p\text{-NP}$ at pH 5.
Figure 3.4  
(a, top) NO$_2$ and NO$_3$ formation during sonication of p–NP. (b, bottom) First–order plot of NO$_3$ formation at pH 5.
the same experimental conditions used for the PNP solutions produced substantial concentrations of these ions. The determination of the $[\text{NO}_3^-] + [\text{NO}_2^+]$ produced by the decay of PNP was possible by subtracting $[\text{NO}_3^-] + [\text{NO}_2^+]$ produced in the control reaction with purified water from the sum of the concentrations of these ions in the PNP solutions, for each irradiation time as follows:

$$
\left( [\text{NO}_3^+]_\text{PNP}^t + [\text{NO}_2^+]_\text{PNP}^t \right) - \left( [\text{NO}_3^+]_\text{H}_2\text{O}^t + [\text{NO}_2^+]_\text{H}_2\text{O}^t \right) = (\text{NO}_3^- + \text{NO}_2^-)
$$

(3.1)

where $[\text{NO}_x^-]_\text{PNP}^t$ represents the amount of NO$_x^-$ produced by sonication of PNP solutions and $[\text{NO}_x^-]_\text{H}_2\text{O}^t$ represents the amount of NO$_x^-$ formed by sonication of water at time $= t$. The results of this calculation are included in Figure 3.4a. From these results we see that NO$_x^-$ (i.e. NO$_3^-$ + NO$_2^-$) increased exponentially with irradiation time between 0 and 60 min. The corresponding first-order plot of these results is shown in Figure 3.4b. A first-order rate constant for the formation of (NO$_2^- + $NO$_3^-$) of $k_1 = 4 \times 10^{-4}$ s$^{-1}$ was obtained from these data (Fig. 3.4b).

As shown in Figure 3.5, H$_2$O$_2$ was produced during the decay of PNP by sonication. These results were obtained by analyzing the PNP solutions immediately after sonication. Lower peroxide concentrations were detected when irradiated samples were left in the dark for several hours and then reanalyzed. The decrease of [H$_2$O$_2$] during the post-irradiation period can be attributed to the reaction of H$_2$O$_2$ with NO$_2$ to yield NO$_3$. No organic peroxides were detected with the iodide–difference method of Kormann et al. Both analytical methods for H$_2$O$_2$ gave identical results. Henglein has shown that H$_2$O$_2$ is generated by the action of ultrasonic waves on pure water. Under our experimental conditions sonolysis of the solvent alone led to a linear increase of [H$_2$O$_2$] vs. irradiation time
Figure 3.5 Hydrogen peroxide generation during sonication.
with a rate constant of $4 \times 10^{-8}$ M s$^{-1}$. Sonication of solutions containing PNP yielded initially the same result as shown in Figure 3.5. At longer irradiation times the observed concentrations of H$_2$O$_2$ were lower in PNP solutions than in pure water. The deviation from the results obtained with water alone increased with increasing initial concentrations of PNP. Also, this deviation occurred at earlier stages of the reaction in solutions containing high concentrations of nitrophenol. However, the initial rate of formation of H$_2$O$_2$ was the same as in pure water alone, regardless of the [PNP].

Hydrogen ions were formed by the action of ultrasound on a 100 $\mu$M PNP solution. Figure 3.6 shows the increase of proton concentrations in a PNP solution and in pure water as a function of sonication time. The increase of [H$^+$] was initially slow in both systems. However, after 10 minutes of irradiation, [H$^+$] increased. The sonolysis of pure water produced a linear increase of [H$^+$] as a function of time with an apparent zero–order rate constant of $8.3 \times 10^{-9}$ M min$^{-1}$. At sonication times $\geq 20$ min., [NO$_3^-$] + [NO$_2^-$]/[H$^+$] = 1. On the other hand, in sonicated PNP solutions the increase of [H$^+$] (at $t \geq 10$ min.) appeared to be first–order with an apparent first–order rate constant of $k_1 = 3 \times 10^{-4}$ s$^{-1}$ after correction of the [H$^+$] in manner analogous to the correction made for NO$_3^-$ + NO$_2^-$ (vide supra eq. 3.1).

Since the rate of production of H$^+$ was less than the rate of generation of NO$_3^-$ and NO$_2^-$ in PNP solutions, a pH–buffering effect by some of the products was indicated. IC analyses of the sonicated PNP solutions showed clearly that HCO$_3^-$ and C$_2$O$_4^{2-}$ were formed as a function of time (Figure 3.7). The [HCO$_3^-$] increased linearly with sonication time with an apparent zero–order rate constant of $4.2 \times 10^{-9}$ M s$^{-1}$. After an induction period of $\sim 10$ min., oxalate was produced with an
Figure 3.6  \([H^+]\) vs. time during sonication.
Figure 3.7  Formate and oxalate formation during sonication of $10^{-4}$ M p-NP.
apparent zero–order rate constant of $5 \times 10^{-9} \text{ M s}^{-1}$.

Para–benzoquinone (p–BQ) was also formed upon exposure of PNP solutions to ultrasound. The [p–BQ] vs. sonication time profile is shown in Figure 3.8. Concentrations of p–BQ increased during the first 30 min. of sonication to about 17 $\mu$M and remained nearly constant at longer reaction times. It should be noted that the n–butylamine method responds to p–BQ. However, hydroquinone is oxidized rapidly in air to p–BQ in alkaline n–butylamine solutions.\textsuperscript{16} Hence, the results depicted in Figure 3.8 correspond to summation of p–BQ and hydroquinone.

As mentioned above, PNP decayed in the presence of ultrasound via apparent first–order kinetics. However, the rate of PNP decay by sonication was found to be dependent on the initial concentration of PNP ([PNP]$_i$) as shown in Figure 3.9a. While PNP decayed exponentially with time irrespective of the PNP concentration, the apparent first–order rate constant decreased from $1.37 \times 10^{-2} \text{ s}^{-1}$ at [PNP]$_i$ = 10 $\mu$M to $6.17 \times 10^{-5} \text{ s}^{-1}$ at [PNP]$_i$ = 1 mM. A plot of log $k_1$ vs. log [PNP]$_i$ yielded a straight–line ($r^2 = 0.99$) relationship from which the following empirical equation, $k_1 = 3.83 \times 10^{-7} \text{ [PNP]}_i^{-0.7}$, was obtained.

The formation of 4–NC from PNP followed zero–order kinetics at short sonication times (Figure 3.2, [PNP]$_i$ = 100 $\mu$M) with an apparent rate constant of $k_0 = 6.17 \times 10^{-9} \text{ M s}^{-1}$. However, the rate of formation increased with increasing [PNP]$_i$. These results are illustrated in Figure 3.9b. The initial zero–order rate constant varied from $k_0 = 3.0 \times 10^{-9} \text{ M s}^{-1}$ at [PNP]$_i$ = 10 $\mu$M to $k_0 = 1.7 \times 10^{-8} \text{ M s}^{-1}$ at [PNP]$_i$ = 1 mM.

Changes in the initial pH (pH$_i$) of the PNP solutions also affected the decay of PNP as shown in Figure 3.10. PNP decayed exponentially with time at all pH values. The apparent first–order rate constant decreased from $k_1 = 3.67 \times 10^{-4} \text{ s}^{-1}$
Figure 3.8  
[p-BQ] vs. sonication time at pH 5 with [p-NP]₀ = 100 μM.
Figure 3.9  (a, top) Effect of \([p\text{-NP}]_0\) on the rate of \(p\text{-NP}\) degradation.  (b, bottom) Effect of \([p\text{-NP}]_0\) on the initial rate of 4-NC formation.
Figure 3.10  Effect of pH on the rate of p-NP degradation.
at pH<sub>i</sub> = 5 to k<sub>i</sub> = 2.0 × 10<sup>-4</sup> s<sup>-1</sup> at pH<sub>o</sub> = 8 and remained constant up to pH<sub>o</sub> = 10.

At pH<sub>o</sub> > 10 the apparent first–order rate constant increased slightly because of the slow thermal reaction between PNP and the products of the base–catalyzed decomposition of H<sub>2</sub>O<sub>2</sub>. This thermal reaction was detected as a post–irradiation decay of PNP in alkaline solutions, which extended for several hours. The post–irradiation effect was detected in all sonicated PNP solutions that were made alkaline for the analysis of the nitrophenoxide ion at 401 nm. No post–irradiation decay of PNP was observed in solutions that were acidified to pH = 1 immediately after sonication. The latter solutions were analyzed spectrophotometrically for PNP at λ = 317 nm (ε = 10190 M<sup>-1</sup>cm<sup>-1</sup>). In the experiments at high pH, only borax and phosphate buffers were used. This procedure was adopted to avoid possible interference from the buffers due to the scavenging of H<sup>+</sup> and OH<sup>-</sup> radicals. Similar results were obtained when experiments carried out in the presence of phosphate buffers were repeated with borax buffers.

A modest increase of k<sub>i</sub> was noticed when the pH was lowered with H<sub>2</sub>SO<sub>4</sub> from pH = 5 to pH = 4 (Figure 3.10). At pH < 4 the apparent first–order rate constant increased to 5.0 × 10<sup>-4</sup> s<sup>-1</sup> (pH = 3). However, at [H<sup>+</sup>] > 1 mM results were not reproducible. The increase of k<sub>i</sub> with increasing acid concentrations cannot be explained by ionic strength effects, since sonication of PNP solutions at pH = 5 in the presence of 0.5 mM Na<sub>2</sub>SO<sub>4</sub> or 1 mM NaNO<sub>3</sub> gave identical results to those obtained in the absence of these electrolytes.

4–NC was formed with an apparent zero–order rate of k<sub>o</sub> = 6.17 × 10<sup>-9</sup> M s<sup>-1</sup> which was found to be independent of pH over pH range of 4 to 10. At pH = 3 the rate of formation decreased to k<sub>o</sub> = 1.67 × 10<sup>-9</sup> M s<sup>-1</sup>. A similar effect was noticed in alkaline solutions where k<sub>o</sub> = 1 × 10<sup>-9</sup> M s<sup>-1</sup> at pH = 10.9 and k<sub>o</sub> = 6.67 × 10<sup>-10</sup><sup>-10</sup>
M s\(^{-1}\) at pH = 11.8.

Several experiments were performed in order to evaluate the sonochemical reactivity of some of the reaction products and their influence in the reactions of PNP. For this purpose, air-saturated solutions containing 20 \(\mu\)M 4-NC were exposed to ultrasound. The concentration of 4-NC decreased exponentially with time with an apparent first-order rate constant of \(k' = 9.83 \times 10^{-4}\) s\(^{-1}\). This result is very close to the rate constant obtained in a solution containing 20 \(\mu\)M PNP (\(k_1 = 8.83 \times 10^{-4}\) s\(^{-1}\)). Sonication of a mixture containing 100 \(\mu\)M PNP and 20 \(\mu\)M 4-NC resulted in an apparent first-order rate constant for the decay of PNP equal to \(k_1 = 2.5 \times 10^{-4}\) s\(^{-1}\). The concentration of 4-NC decreased continuously with sonication time. Under these conditions the decay of 4-NC was faster at all sonication times than its formation from PNP. However, 4-NC decayed in the presence of 100 \(\mu\)M PNP with an apparent first-order rate constant of \(2.83 \times 10^{-5}\) s\(^{-1}\); a value significantly lower than that obtained in the absence of PNP.

While \(\text{NO}_3^-\) did not interfere with the sonochemical reactions of PNP, \(\text{NO}_2^-\) appeared to affect the decay of p-nitrophenol. Irradiation of a solution containing 100 \(\mu\)M PNP and 100 \(\mu\)M \(\text{NaNO}_2\) with ultrasound resulted in a slower disappearance of PNP (\(k_1 = 2.0 \times 10^{-4}\) s\(^{-1}\)) when compared to a kinetic run in the absence of \(\text{NO}_2^-\) (\(k_1 = 3.67 \times 10^{-4}\) s\(^{-1}\)). In addition, we found that the formation of 4-NC was slower in the presence of \(\text{NO}_2^-\). The apparent zero-order rate constant for the formation of nitrocatechol was about one half (\(k_o = 3.0 \times 10^{-9}\) M s\(^{-1}\)) of the rate constant obtained in the absence of \(\text{NO}_2^-\) ions (\(k_o = 6.2 \times 10^{-9}\) M s\(^{-1}\)).

On several occasions the spectrophotometric determination of PNP at 401 nm in alkaline solutions was verified by measurements of \([\text{PNP}]\) in acid solution at 317 nm (\(\epsilon = 10200\) M\(^{-1}\)cm\(^{-1}\)). Excellent agreement (derivation < 5\%) between the
two methods was obtained after correcting the absorption at 317 nm for the small contributions of 4–NC ($\epsilon = 5700 \text{ M}^{-1}\text{cm}^{-1}$). No absorption at $\lambda = 348$ nm was detected in PNP solutions acidified to pH = 1 after sonication. Knowing that in acid solution neither PNP nor 4–NC absorb at this wavelength and that the absorption of 4–nitroresorcinol at low pH is strongest at $\lambda = 348$ nm ($\epsilon = 8850 \text{ M}^{-1}\text{cm}^{-1}$),\textsuperscript{18} it can be concluded that the concentration of nitroresorcinol was smaller than 5 $\mu$M at all sonication times. Products of the nitration of PNP such as 2,4–dinitrophenol were not detected in concentrations above the limit of detection of 7 $\mu$M.

The rate of disappearance of PNP was found to be independent of the volume of sonicated solution (20–40 ml). Sonication of air–saturated solutions, which were not exposed to air during the course of sonication, produced the same results as those obtained with air–equilibrated solutions. Furthermore, identical results were obtained by using continuous sonication or pulsed sonication (0.5 s. sonication per every second). The comparison was made using the net sonication times in the case of pulse experiments. No significant effects due to tip erosion were found.

Discussion

We have shown clearly that the action of ultrasound on PNP in aqueous solutions resulted in its degradation with the formation of $\text{NO}_2^-$, $\text{NO}_3^-$ and $\text{H}^+$ as primary products and with $\text{HCO}_2\nu$, $\text{C}_2\text{O}_4^{2-}$, 4–NC and $\text{H}_2\text{O}_2$ as secondary products. Several reaction mechanisms can be postulated to account for these observations. Since PNP boils at $T \geq 166 \, ^\circ\text{C}$,\textsuperscript{21} high temperature reactions of PNP vapor inside the cavitating bubbles can be discounted due to its low vapor pressure. Processes
leading to the denitrification of PNP are more likely to occur in the hot solvent layer surrounding the gas bubbles or in the bulk of the solution. A degradation mechanism that involves 'OH radical attack on PNP appears plausible.\textsuperscript{22} Results of radiation-chemistry investigations have shown that 'OH reacts rapidly with PNP to produce 4-NC, p-BQ and NO\textsubscript{2}.\textsuperscript{23-25} A plausible mechanism for the reaction of hydroxyl radicals with PNP is as follows:

\begin{equation}
\text{C}_6\text{H}_4\text{NO}_2 + \cdot \text{OH} \rightarrow \text{C}_6\text{H}_4\text{NO}_2\cdot \cdot \text{OH} \quad (X) \quad (1)
\end{equation}

\begin{equation}
X + \text{O}_x \rightarrow \text{HO}_x + \text{C}_6\text{H}_4\text{NO}_2\cdot \cdot \text{OH} \quad (2)
\end{equation}

\begin{equation}
X + \text{O}_2 \rightarrow \text{C}_6\text{H}_4\text{NO}_2\cdot \cdot \text{O}_2^{-} \rightarrow \text{C}_6\text{H}_4\text{NO}_2\cdot \cdot \text{OH} \quad + \text{HO}_2\cdot \quad (2a)
\end{equation}

\begin{equation}
\text{C}_6\text{H}_4\text{NO}_2 + \cdot \text{OH} \rightarrow \text{C}_6\text{H}_4\text{NO}_2\cdot \cdot \text{OH} \quad (Y) \quad (3)
\end{equation}
where $O_x$ in eq. 2 is an oxidant and $HO_x$ is the reduced form of $O_x$. Both radicals X and Y have been identified by ESR as the major products of 'OH attack on PNP. The unknown oxidant $O_x$ could be the benzoquinone radical produced by eq. 4 or products from the attack of 'OH in positions ortho (at the carbon atom of the ring bonded to the hydroxyl function) or meta. At pH = 5, about 15% of the 'OH radicals attack PNP via eqs. 1b through 5 to produce NO$_2^-$, whereas 70% of 'OH radicals react with formation of 4-NC according to eqs. 1a to 3.$^{23a,24}$ The ratio of yields for the products is p-BQ (+ hydroquinone):NO$_2^-$:4-NC = 1:1:4.7. At pH $\geq$ 8, however, 30% of the hydroxyl radicals react to produce nitrite and 5% of
the 'OH radicals reacts with PNP to form 4–NC.\textsuperscript{23a,24} Under these conditions, the ratio of yields for the different products is p–Bq (+ hydroquinone):NO\textsubscript{2}−:4–NC = 1:1:1.8.

In aerated solutions the products, X and Y, react with oxygen (k = 1.7 × 10\textsuperscript{6} M\textsuperscript{−1}s\textsuperscript{−1}\textsuperscript{25}) via eqs. 2a and 4a to yield the same products (and ratio of products) produced by eqs. 1 to 5 with the exception of hydroquinone. Instead, only p–BQ is produced, which is equivalent to the oxidation of hydroquinone by O\textsubscript{2} to produce hydrogen peroxide. In aerated solutions, the peroxy radicals formed by eqs. 2a and 4a will decay with generation of H\textsubscript{2}O\textsubscript{2}\textsuperscript{27}:

\[2 \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2\]  \hspace{1cm} (6)

For every pair of 'OH radicals which react with PNP one molecule of H\textsubscript{2}O\textsubscript{2} is produced. This means that in PNP solutions, the same amounts of peroxide are produced from hydroxyl radical reactions as by sonolysis of pure water. In the absence of PNP, 'OH recombines to form hydrogen peroxide\textsuperscript{22}:

\[2 \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2\]  \hspace{1cm} (7)

Hydrogen atoms are known to react with PNP but the rate constant of this reaction has not been measured.\textsuperscript{25} 'OH and 'H will react preferentially with scavengers present in the cavitation bubbles. The main scavenger for H atoms in the gas phase of the bubbles is oxygen. The reaction between H and O\textsubscript{2} at high temperatures is believed to produce oxygen atoms and OH radicals\textsuperscript{11b}: 
\[ H + O_2 \rightarrow \cdot OH + \cdot O \] (8)

According to this reaction, hydrogen atoms are converted to hydroxyl radicals and oxygen atoms before they can reach the solution and react with PNP. Oxygen atoms and hydroxyl radicals are expected to be partially scavenged by nitrogen in the gas bubbles.\(^{11a}\) These reactions lead to the formation of \( NO_2^- \) and \( NO_3^- \) in the sonolysis of air-saturated water. Only those radicals which escape into solution without reacting with \( N_2 \) will be scavenged by PNP. This argument implies that nitrate and nitrite are produced by two independent mechanisms during the sonolysis of PNP solutions: \( a \) via the same gas phase reaction which takes place in pure water and \( b \) from the decay of PNP molecules. The basic assumption that PNP did not interfere with the gas phase chemistry taking place inside the hot cavities is confirmed by the close agreement of \( k_1 \) calculated from the decay of PNP and the rate constants derived from the formation of \( NO_2^- \) and \( NO_3^- \) as well as from the H\(^+\) results.

However, a closer inspection of the results reveals that the sonochemical decay of PNP in aqueous solution cannot be explained only on the basis of reactions between \( \cdot OH \) and PNP in the bulk solution phase. For example, PNP decreased exponentially with sonication time, while PNP attack by \( \cdot OH \) in homogeneous solution follows zero-order kinetics.\(^{24,25}\) First-order kinetics have been observed in the sonication of thymine\(^2\) and phenol.\(^{28}\) In both cases the concentration decreased exponentially with time at initial concentrations of substrate ≤ 1 mM, whereas at higher concentrations the reactions followed zero-order kinetics.\(^2,28\) These results have been explained by assuming that thymine and phenol react preferentially in the interfacial region with free radicals.\(^2\) At low substrate concentrations (≤ 1 mM)
the rate-limiting step was considered to be the diffusion of substrate to the reaction zone, while the reaction of free radicals and substrate was assumed to occur very fast (diffusion controlled). At high solute concentrations (> 1 mM) the reactive radicals will be scavenged as they reach the interface; thus zero-order kinetics are observed. This model is only correct if the radical concentrations at the interface are very high, otherwise low concentrations of solute would be sufficient to scavenge most of the free radicals.

However, this model presents a simplified version of the events that occur during sonolysis. For example, solute–radical reactions in the bulk solution are not considered. Also, no allowance is made for thermal decomposition reactions of the solute in cavities as well as reactions in the hot surroundings of the cavities.

It is, therefore, not surprising that several observations made in sonolysis experiments with PNP solutions remained unexplained. The unexplained results are as follows:

1) According to the above model, the first-order decay of substrate is related to diffusion of substrate to the reaction zone. In the case of PNP this assumption implies that diffusion of the PNP molecules to the interface was highest at the lowest [PNP], since $k_1$ increased with decreasing concentration of the substrate (Figure 3.9a). Obviously, such a conclusion is not correct.

2) If p-BQ is formed exclusively via the sequence of eqs. 3 and 4a the measured concentrations of quinone represent only 13% of the products produced by reaction of 'OH with PNP. We observed that after 10 min of sonication $[p$-BQ] = 5.9 μM. The free–radical model predicts a change of [PNP] equal to $\Delta[PNP] = 45 \mu M$ for the same reaction time. The predicted value of $\Delta[PNP]$ does not agree with the experimental value of 17 μM.
3) The initial ratio of products from the sonolysis of PNP was p-BQ:NO$_2$:4-NC = 1:3:6:0.7. In contrast, the observed products of 'OH attack on PNP were formed initially with a ratio of p-BQ:NO$_2$:4-NC of 1:1:4.7.$^{23a,24}$ Note that in the case of phenol the ratio of products, at short reaction times, was the same at high$^{29}$ as well as at low$^{30}$ 'OH concentrations. By analogy, the initial ratio of products from hydroxyl radical attack on PNP is not expected to vary with changing ['OH]. The differences in the ratio of products suggest that the mechanism of reaction in the sonolysis of PNP is different from the mechanism represented by reactions 1 to 5. It might be argued that the different ratio of products in the sonolysis reflects a different selectivity of the 'OH attack at high temperatures. However, extensive investigations on high temperature reactions of 'OH with aromatic compounds have demonstrated that at T $\geq$ 400 K the main reaction pathway is hydrogen atom abstraction instead of addition to the aromatic ring.$^{31}$ Thus, the denitrification of PNP initiated by reaction 1 is not expected to be the main reaction pathway in the high temperature regions of the interface.

The relatively fast decay of PNP can be explained by the thermal decomposition of PNP in the near vicinity region of the hot collapsing gas cavities. The thermal instability of nitroaromatic compounds, which forms the basis for their use as explosives, is well documented.$^{21,32,33}$ As mentioned above, PNP is known to decay thermally at T $\geq$ 166 °C (439 K). While no kinetic information is available for PNP, closely related compounds such as nitrobenzene (NB) and p-nitrotoluene (p-NT) have been recently studied by shock-tube experiments.$^{33}$ Both compounds are decomposed at high temperatures by cleavage of the C-NO$_2$ bond. The analogous reactions for PNP are:
Assuming that NO and NO$_2$ are the precursors of NO$_2^-$ (vide infra), the unimolecular decay of PNP via eqs. 9 and 10 provides a plausible explanation for the observed first-order denitrification of PNP by the action of ultrasound. In order to understand the formation of 4-NC it has to be assumed that PNP decays by parallel zero- and first-order processes:

\[
-\frac{d[PNP]}{dt} = k'_0 + k_1[PNP]_t
\]

There $k_1$ represents $k_0 + k_{10}$ and $k'_0$ is the zero-order rate constant for the reaction between 'OH and PNP, which produces mainly 4-NC. The solution to eq. 11 is:

\[
[PNP]_t = \frac{-k'_0}{k_1} + \frac{-k'_0}{k_1} + [PNP]_0 e^{-k_1 t}
\]

Since approximately 70% of the 'OH radicals that react with PNP yield
4-NC, the value of $k'_0 \simeq k_0/0.7$. Given the experimental values of $k_0$ shown in Figure 3.9b, the values of $k'_0$ for different initial concentrations of PNP can be estimated. Using these results and the measured concentrations of PNP at different sonication times, the apparent first-order rate constants at different concentrations of PNP were calculated using a non-linear fitting procedure and are presented in curve 2 of Figure 3.9a. The calculated values of $k_1$ agree closely with the experimental values for $k_1$. Only kinetic data obtained at short sonication times [i.e. at low fractions of PNP destroyed ($1-F \leq 20\%$)] were used for this analysis. It can be concluded that the exponential decay of $[\text{PNP}]$ via eqs. 9 and 10 is the dominant process and that ·OH radical reactions contribute to PNP decay only at short reaction times. If this interpretation is correct, 4-NC is formed via a zero order process represented by reactions 1 and 2a and decays exponentially with time via reactions analogous to eqs. 9 and 10.

The present model can also account for the unusually high ratio of p-BQ to 4-NC of 1:0.7 observed from sonolysis compared to the ratio obtained from radiolysis of PNP (i.e. p-BQ:4-NC = 0.19:1).$^{23a,24}$ Tsang et al.$^{33}$ identified two different reaction channels for the pyrolysis of NB and p-NT; they were identified as 1) the direct loss of NO$_2$ and 2) the isomerization of bound NO$_2$ followed by elimination of NO. In our case these two reaction pathways are represented by eqs. 9 and 10, respectively. For NB and p-NT Tsang et al. estimated that the ratio of rate constants was $k_{\text{elimination}} : k_{\text{isomerization}} = 2:1$. Hence, the fraction of products formed by the isomerization channel is simply $k_{\text{isomerization}} / (k_{\text{elimination}} + k_{\text{isomerization}}) = 1/3$. Assuming a similar mechanism in our case, it appears that a reaction path involving first eq. 9 followed by eq. 5 contributed to the formation of p-BQ. From the pyrolysis mechanism it is predicted that $[\text{p-BQ}]_t \times (\Delta[\text{PNP}]_t)^{-1}$.
= 1/3 provided that the decay of p-BQ is negligible. After correcting both [p-BQ] and Δ[PNP] for the contributions from the ·OH radical reactions, the experimental ratio is 1/2.2 (at t = 10 min). The difference between the expected ratio and the experimental value can be explained by assuming that a fraction of the NO₂ reacted with the aromatic hydroxy radical generated via eqs. 9 and 13 followed by reaction 5.

\[ \text{OH} + \text{NO}_2 \rightarrow \text{OH} + \text{NO} \]  \hspace{1cm} (13)

Reaction 13 is analogous to the postulated mechanism for the attack of NO₂ on hydroxy-cyclohexadienyl radicals.³⁴ Thus, according to our model, p-BQ is produced mainly by pyrolysis of PNP while the formation of p-BQ by ·OH radical attack is of minor importance.

The proposed mechanism for the decomposition of PNP based on pyrolysis reactions not only explains our kinetic observations, but enables us to estimate the reaction temperatures in the interfacial region. Using the known rate expressions for model compounds and assuming a similar rate expression for the case of PNP, the average temperature in the reaction zone can be evaluated. This method, which is called chemical thermometry, has been used previously to estimate the temperature inside and in the surroundings of collapsing bubbles in hydrocarbon solvents.⁴ From the values of \( k_1 \) shown in Figure 3.9a and using \( k(C_6H_5NO_2 \rightarrow C_6H_5^- + NO_2) = 1.9 \times 10^{15}e^{-3306/T} \text{ s}^{-1} \),³³ the temperature of the interfacial region
was found to vary between \( T = 740 - 790 \text{ K} \) (see Table 3.1). The same results were obtained by using the rate expression for p–NT.\(^{33}\) Higher temperatures (\( \sim 2000 \text{ K} \)) were estimated for the interface of bubbles in hydrocarbon solvents.\(^4\) The difference in temperature between water and hydrocarbons can be explained by considering the different thermal conductivities of each solvent. Because of the higher thermal conductivity of \( \text{H}_2\text{O} \), heat will move faster in this water and the peak interfacial temperature is expected to be lower.\(^{35}\) The results presented in Table 3.1 are considered to be lower limits for the average temperature in the interfacial region, since \( k_1 \) is only an apparent first–order rate constant for the reaction.

In order to explain the chemical processes, which take place at the interface, it is necessary to understand, at least qualitatively, the sequence of events occurring in that region. The local temperature in the solvent surrounding the bubble will be a time–dependent spatial gradient during the collapse of the cavity as proposed earlier for hydrocarbon solvents.\(^4\) Thus, heat will move from the surface of the bubble toward the solution bulk. It is further assumed that \(^{\text{OH}}\) generated in the hot bubbles will diffuse to the solvent interface and subsequently through it at a speed similar to that of the front of the heat wave. In the solvent, \(^{\text{OH}}\) reacts with PNP. The OH–adducts will increase in thermal energy as the temperature of the solvent increases. At the same time PNP molecules situated at the interface having a thermal energy equivalent to or greater than 439 K will react by denitrification via eqs. 9 and 10. However, this reaction is not restricted to PNP molecules. Addition of OH radicals to the ring of PNP is not expected to increase the strength of the C–NO\(_2\) bond. Therefore, all OH–adducts with sufficient thermal energy will undergo denitrification via an analogous mechanism. The
Calculated first-order p-NP thermal decomposition rates and corresponding effective temperatures of the reaction zone.

<table>
<thead>
<tr>
<th>[p-NP] (μM)</th>
<th>$10^4 \cdot k$ (s$^{-1}$)</th>
<th>T (K)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8.50</td>
<td>782</td>
</tr>
<tr>
<td>20</td>
<td>8.33</td>
<td>781</td>
</tr>
<tr>
<td>50</td>
<td>4.83</td>
<td>771</td>
</tr>
<tr>
<td>100</td>
<td>2.33</td>
<td>758</td>
</tr>
<tr>
<td>250</td>
<td>0.96</td>
<td>743</td>
</tr>
<tr>
<td>500</td>
<td>0.70</td>
<td>738</td>
</tr>
<tr>
<td>1000</td>
<td>0.30</td>
<td>724</td>
</tr>
</tbody>
</table>

$^a$ Calculated assuming $k_1 = 1.9 \times 10^{15} e^{-33026/T}$
threshold temperature for the loss of NO$_2$ from "OH–PNP" adducts is expected to be similar to the minimum temperature for PNP.

The fate of the resulting OH adducts can be predicted from results gained in high temperature studies on hydroxyl radicals with aromatics.$^{31}$ These studies indicate that at T $\leq$ 325 K the addition reaction (eq. 14) dominates.

\[
\cdot\text{OH} + \text{aromatic} \longrightarrow (\text{OH} - \text{aromatic}) \quad (14)
\]

For T $\geq$ 400 K dissociation of the OH–adduct is very fast:

\[
(\text{OH} - \text{aromatic}) \longrightarrow \cdot\text{OH} + \text{aromatic} \quad (15)
\]

At T $\approx$ 1000 K hydroxyl radicals and hydrogen atoms react predominantly with phenol via hydrogen atom abstraction from the hydroxy group.$^{31a}$ In the case of PNP, the resulting phenoxy radicals are strong oxidants (E$^\circ$ = 1.2 V vs NHE)$^{36}$ and will probably reform PNP after oxidizing other products. The reaction of eq. 15 is very interesting because it implies that, after the release of the hydroxyl radical from the aromatic ring, the radical can further diffuse to colder regions of the solvent and react again with solute molecules. The temperature dependence of $k_{15}$ has been measured for benzene, bromobenzene and aniline.$^{37}$ For direct comparison with our results with PNP, aniline appears to be the most appropriate since the electron–donating properties of the –NH$_2$ and –OH are similar. Using the corresponding temperature dependence, $k_{15} = 6 \times 10^{14}e^{-8400/T}$ s$^{-1}$ $^{37}$, a half–life of 48 ns is calculated for eq. 15 at 790 K ($k_{15} = 1.5 \times 10^7$s$^{-1}$). This short half–life implies that PNP and probably most of the hydroxylated aromatic products
produced by the decay of PNP are relatively non-reactive toward \( \cdot \text{OH} \) in the high-temperature regions of the interface. This argument leads to the conclusion that formation of 4-NC and denitration of PNP via \( \cdot \text{OH} \) radical attack (reactions 2a and 4a) occurred in the cooler region of the interface (\( T < 439 \text{ K} \)).

Products of eqs. 9 and 10 are expected to decay further by pyrolysis and/or free radical reactions. The preferential formation of nitrite at short sonication times is an indication that the reaction between \( \text{NO}_2 \) and \( \cdot \text{OH} \) (eq. 16) to form nitric acid is not important. Nitrous acid (i.e. nitrite) is produced via eq. 17.\(^{38}\)

\[
\text{NO}_2 + \cdot \text{OH} \longrightarrow \text{HNO}_3 \tag{16}
\]

\[
\text{NO} + \text{OH} \longrightarrow \text{HNO}_2 \tag{17}
\]

Since eq. 9 is considered to be the main decay pathway for PNP, it appears that \( \text{NO}_2 \) was rapidly converted to \( \text{NO} \) presumably by combination of \( \text{NO}_2 \) with organic radicals produced by pyrolysis reactions in a reaction similar to eq. 10:

\[
\text{R}^* + \text{NO}_2 \longrightarrow \text{RO}^* + \text{NO} \tag{18}
\]

While \( \cdot \text{OH} \) reaction with aromatics followed by \( \text{O}_2 \) addition can lead to ring opening and formation of polycarboxylic acids,\(^{31b}\) formation of formate from these acids would require a concerted attack by several hydroxyl radicals. Thus, the generation of formate is consistent with a pyrolysis pathway. Oxalate was detected only after an induction period of about 10 min. Oxalate could be produced by \( \text{OH} \) radical attack on formate as has been found in the sonolysis of aqueous formate.
solutions under Ar.\textsuperscript{11c} However, the sonolysis of oxygenated formate solutions generates CO\textsubscript{2} and not oxalate.\textsuperscript{11c} Reaction of \textquoteleft OH with formic acid at high temperatures also leads to CO\textsubscript{2} in the absence of O\textsubscript{2}.\textsuperscript{31b} Since at short sonication times only 50\% of the degraded PNP is accounted for by the appearance of 4–NC, p–BQ and HCO\textsubscript{2}–, the remainder could be postulated to be polycarboxylic acids formed as intermediates. The delayed formation of oxalate can be explained if the polycarboxylic acids are formed as precursors.

According to our model PNP was denitrated mainly by pyrolysis reactions but the detected products resulted from pyrolysis and free radical reactions. The concentration of PNP near the surface of the bubbles, which is the zone of the interface where pyrolysis is expected to take place, is assumed to increase with increasing PNP concentration in solution. However, once the interface is saturated with PNP molecules, no further increase of [PNP] in this region will result upon increasing [PNP] in the solution. It seems that the limiting concentration of PNP at the interface is achieved at [PNP]\textsubscript{i} \approx 500 \textmu M, since P (percentage of PNP converted to 4–NC) was nearly independent of concentration in the range 10 \leq [PNP]\textsubscript{i} \leq 500 \textmu M (see Figure 3.11; Appendix). At [PNP]\textsubscript{i} = 1 mM the fraction P increased abruptly to 30\%, indicating that [PNP] was still increasing in regions far away from the bubble surface. This in turn allowed PNP to compete successfully with pyrolysis products for \textquoteleft OH. The decrease of k\textsubscript{1} in solutions containing PNP and 4–NC or NO\textsubscript{2} is explained, in part, assuming that 4–NC and NO\textsubscript{2} were able to displace some PNP molecules from the interface. In addition, both NO\textsubscript{2} and 4–NC decay at the interface with formation of NO\textsubscript{2}. Nitrite is oxidized by OH radicals to NO\textsubscript{2} according to eq. 19:\textsuperscript{22}
\[
\text{NO}_2^-/\text{HNO}_2 + \cdot \text{OH} \rightarrow \text{NO}_2^- + \text{OH}^-/\text{H}_2\text{O}
\] (19)

The additional formation of NO$_2$ at the interface by reactions other than eq. 9 will increase the probability of the reverse reaction (eq. 9). This second-order reaction will become faster with increasing [NO$_2$] resulting in the apparent retardation of PNP decay. The same explanation holds for the results shown in Figure 9a. At low concentrations of PNP only small amounts of NO$_2^-$, 4–NC and products from eq. 9 are generated by sonication. Thus, the back reverse reaction of eq. 9 is expected to be very slow and the unimolecular decay of PNP dominates. As [PNP]$_i$ increased k$_i$ decreased due to the increasing amounts of products from eq. 9 and from the increasing concentrations of NO$_2^-$ and 4–NC; which produced higher [NO$_2$] and accelerated the reverse of eq. 9.

The concentration of PNP in the high temperature zone of the interface is expected to depend also on solution pH. Evidence gathered in earlier studies suggests that the bubbles are hydrophobic and that hydrophobic compounds can accumulate in the hot surroundings of the interfacial region where they undergo high temperature reactions. The hydrophobic nature of the aromatic ring should drive PNP molecules to the interfacial zone, whereas the polar NO$_2$ and OH groups will be repelled from the interface. At pH > pK$_a$ the [PNP] at the interface is expected to be smaller than the concentrations attained at lower pH values, due to the increased repulsion from the interface generated by the phenoxide ion. Furthermore, delocalization of electrons from the deprotonated hydroxyl groups into the aromatic ring will increase the stability of the C–NO$_2$ bond by increasing the sp$^2$ character of that bond:
An increase in the stability of the C–NO₂ bond will lead to an increase in the thermal stability of PNP. The decrease of [PNP] at the interface at pH > 7 (pKₐ of PNP = 7.05), together with the increased stability of the nitrophenoxide ion explains the low values of k₁ found in alkaline solutions. The fact that k₁ is relatively constant between 8 ≤ pH ≤ 11.8 and is independent of the nature of the buffer (phosphate or borax) provides support for our interpretation.

In conclusion, the application of ultrasound for the control of oxidizable trace contaminants in water has the potential to become a competitive technology with semiconductor photodegradation. For example, the relative efficiency of ultrasound in terms of the total power consumed per mole of p-nitrophenol degraded per liter of water is far superior to photolysis. In our investigation of the ultrasonic oxidation of H₂S, we have found a direct linear relationship between the applied power at a fixed frequency and the observed rate of loss of S(–II). Thus, a continuous-flow stirred-tank (CSTR) probe reactor can attain significant conversion efficiencies at relatively high volumetric flow rates. Our initial tests
indicate that the use of large high-powered sonicators in the CSTR mode can result in viable degradation efficiencies.

An attractive alternative to the flow-through probe system is the high intensity flat-plate reverberatory sonicator or the near-field acoustical processor (NAP). The NAP reactor system consists of two sonicated metal plates that form two sides of a rectangular flow-through pipe; one plate has a set of transducers operated at 16 kHz while the opposing plate has a similar set of transducers operated at 20 kHz. In this configuration, a liquid flowing between the plates, which may be as large as 0.5 m × 3 m with a plate separation of 0.08 m, is exposed to an ultrasonic intensity that is greater than that expected from a simple doubling of a single plate due to reverberation of the ultrasound. This technology has already been used on a large scale for the extraction of oil from oil shale. In the near future, we plan to explore the feasibility of a NAP system for high capacity water purification. Commercial systems have been constructed to handle process streams with volumetric flow rates approaching 265 L min⁻¹.
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51, 1123.


Appendix

The action of 20–kHz ultrasound on aqueous solutions of p–NP resulted in an exponential decrease of [PNP] as shown in Figures 3.1, 3.2 and 3.3. Small amounts of 4–NC were produced as the result of the decay of PNP. The formation of 4–NC led to the quasi isosbestic point at about 460 nm (Figure 3.1). The presence of isosbestic points in the absorption spectra of products and reactants implies that, after a certain reaction time, the absorption of unreacted PNP plus the absorption of all products is, at a particular wavelength, equal to the initial absorption of the PNP solution. This condition is represented by eq. a1 (for \( \ell = 1 \text{ cm} \)).

\[
\left( [\text{PNP}]_0 - [\text{PNP}]_t \right) \epsilon_{\text{PNP}}^{460} = \sum_i \left( [\text{P}_i]_t \epsilon_{\text{P}_i}^{460} \right) \tag{a1}
\]

where \([\text{PNP}]_0\) and \([\text{PNP}]_t\) are the concentrations of PNP at reaction times 0 and \(t\), respectively; and \(\epsilon_{\text{P}_i}^{460}\) is the extinction coefficient of PNP at 460 nm. Similarly, \([\text{P}_i]_t\) represents the concentration of the product \(i\) after a reaction time \(t\) and \(\epsilon_{\text{P}_i}^{460}\) is the extinction coefficient of product \(i\) at 460 nm. Since identical [PNP]'s were obtained from analyses in basic and in acid solutions (at 401 and 317 nm respectively), it can be assumed that 4–NC is the only product which absorbs above 400 nm in alkaline solutions. If the term in parenthesis on the left hand side of eq. a1 is substituted by \(\Delta[\text{PNP}]_t\), then equation can be rearranged to eq. a2:

\[
\frac{\epsilon_{\text{PNP}}^{460}}{\epsilon_{4-\text{NC}}^{460}} = \frac{[4-\text{NC}]_t}{\Delta[\text{PNP}]_t} = P \tag{a2}
\]

In eq. a2, \(\Delta[\text{PNP}]_t\) is the amount of PNP which has disappeared after a sonication
time t and [4–NC]_t represents the concentration of 4–NC formed after the same period of time. Hence, the term on the right hand side of this equation corresponds to the percentage (P) of decomposed PNP which has been converted into 4–NC, after a reaction time t. According to eq. a2, this percentage should remain constant with reaction time if an isosbestic point is to be observed. From ε^{46.0}_{PNP} = 1600 M^{-1}cm^{-1} and ε^{46.0}_{4–NC} = 7300 M^{-1}cm^{-1} (in 0.1 M NaOH) it is calculated by eq. a2 that about 22% of the reacted PNP was converted to 4–NC in a 100 μM solution of PNP sonicated at pH = 5. In order to verify the validity of the assumptions which led to eq. a2, calculation of P was made from the known concentrations of 4–NC and PNP at different reaction times. To allow for an easy comparison of results obtained under different conditions, the values of P were plotted as function of the fraction of PNP destroyed (F) instead of sonication time (Figure 3.11). Line 1 in Figure 3.11 shows the evolution of P with reaction times for a 100 μM solution of PNP sonicated at pH = 5. P decreased slightly with increasing F; when only small amounts of PNP have decayed (F = 0.13) the fraction P is 24.5% whereas after one half life (F = 0.5) P amounts to 19%. The results presented in line 1 of Figure 3.11 help to explain the small shifts towards longer λ, with increasing sonication times, of the point where the spectrum of the unsonicated solution is intersected by the spectrum of the sonicated solution. As P decreased slightly with increasing F, equation a2 predicts a shift of the intersection point towards longer wavelengths, since ε^{46.0}_{PNP} decreases but ε^{λ}_{4–NC} increases with increasing λ. Because of the large difference in the extinction coefficients of PNP and 4–NC the shifts in the intersection points were very small, resulting in a broad (Δλ ≈ 2 nm) isosbestic point centered at 460 nm. Note that the "mean" value of P in line 1 of Figure 3.11 is 22%, in good agreement with the calculation using eq. a2. The quasi–isosbestic
Figure 3.11 Percentage of p-NP decayed converted to 4-NC.
points were close to 460 nm for the experiments carried out at pH = 5. This is not surprising since, at [PNP]_i < 1 mM, the dependence of P on F did not change appreciably by changing [PNP]_i. An example of this is the result obtained by sonication of a 20 μM solution of PNP (line 2 in Figure 3.11). Only at [PNP]_i = 1 mM the quasi isosbestic point shifted to shorter wavelengths because P increased to about 30%. Sonication of PNP solutions at pH = 8.1 led to an isosbestic point at λ ≈ 455 nm. From the extinction coefficients at that wavelength (ε_{PNP} = 2700 M^{-1}cm^{-1} and ε_{4−NC} = 6400 M^{-1}cm^{-1}) it is calculated that P = 42%, whereas the mean value of P in Figure 3.11 is about 43%. At pH = 3, P is essentially independent of F and P ≈ 5% (Figure 3.11, line 4). From the extinction coefficients at the quasi-isosbestic point at 370 nm (ε_{PNP} = 530 M^{-1}cm^{-1}, ε_{4−NC} = 8700 M^{-1}cm^{-1}) a mean value of P = 6% is derived. These examples are a further confirmation of our explanation of the isosbestic points and provide support for the assumption that no product other than 4−NC interfered with the spectrophotometric determinations of [PNP]. This conclusion, in turn, implies that the exponential decay of PNP with sonication time is not an artifact of the analytical methods. The exponential increase of [NO_2] with sonication time (Figure 3.4, curve 1) is also consistent with this conclusion.
CHAPTER 4

OXIDATION OF HYDROGEN SULFIDE IN AQUEOUS SOLUTIONS BY ULTRASONIC IRRADIATION

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ABSTRACT

The kinetics and mechanism of the sonolysis of S(−II), where \([S(−II)] = [H_2S] + [HS^-] + [S^2^-]\), have been investigated in oxic aqueous solutions over the pH range 7 – 12. Ultrasonic irradiation of S(−II) at 20 kHz and 75 W·cm\(^{-2}\) results in its rapid oxidation. The reaction of HS\(^-\) with \('OH\) is the principal pathway for the oxidation of S(−II) at pH ≥ 10; the oxidation products are SO\(_4^{2-}\), SO\(_3^{2-}\), and S\(_2\)O\(_3^{2-}\). Upon prolonged sonication, SO\(_4^{2-}\) is the only observed product. At pH ≤ 8.5, thermal decomposition of H\(_2\)S within or near collapsing cavitation bubbles becomes the important pathway and elemental sulfur is found as an additional product of the sonolysis of S(−II). Oxidation of S(−II) by ultrasonic irradiation may present an alternative method for the control of H\(_2\)S in water and wastewater systems.
Introduction

In 1933, Flosdorf and Chambers (1) reported that metal sulfides were oxidized in the presence of audible sound (1–15 kHz) while investigating the bactericidal action of audible sound. However, Schmitt et al. (2) were the first researchers to observe the rapid oxidation of dissolved $\text{H}_2\text{S}$ gas to colloidal sulfur during sonication at 750 kHz with a 250 W power source. They reported that an increase in the total pressure of the system ($P_{\text{O}_2}$) led to higher oxidation rates up to a limiting pressure. This critical pressure depended on the amount of dissolved $\text{H}_2\text{S}$ gas and the intensity of irradiation.

Wawrzyczek et al. (3) observed the oxidation of $\text{H}_2\text{S}$ dissolved in water containing Ar or O$_2$ at 27 kHz and an ultrasonic intensity of 5 W/cm$^2$. The primary oxidation product was found to be elemental sulfur (i.e., $S_8$). The reaction yield in their experiments was found to be 25% higher in the presence of Ar as compared to that obtained in oxygenated solutions. The overall reaction was thought to proceed via reactions of $\text{HS}^-$ with OH radicals and $\text{HO}_2$ or $\text{H}_2\text{O}_2$. A secondary pathway involving the direct decomposition of $\text{H}_2\text{S}$ to $\text{HS}^-$ and $\text{H}^+$ was also proposed.

Cauwet et al. (4) studied the ultrasonic decomposition of $\text{H}_2\text{S}$ into H$_2$ and $S^\circ$ at various frequencies up to 600 kHz and at a voltage amplitude of 40 V. They found a continuous increase in H$_2$ production during sonication of $\text{H}_2\text{S}$ with increasing ultrasonic power and they found that the yield of H$_2$ doubled in solutions containing 10% diethanolamine (a possible surface tension effect).

The chemical effects of ultrasound result from the phenomenon of acoustic cavitation (5–7). Sound waves with frequencies higher than 16 kHz traveling through a liquid can force the growth and subsequent collapse of small bubbles in
response to the passage of expansion and compression waves. In the interior of the collapsing bubbles (cavities) extreme transient conditions exist; temperatures approaching 5000 K have been determined experimentally (8) and pressures of several hundred atmospheres have been calculated (5,9). At 20 kHz and typical ultrasonic immersion-horn intensities (10–100 W/cm²) the radius of the bubble prior to collapse can be estimated to be on the order of several hundred μm (400–500 μm) (10). The time scale for the collapse of the bubble is <100 ns and the time scale for heat diffusion in the surrounding liquid is a few microseconds with a corresponding diffusion length of a few hundred nanometers (8).

The primary chemical effects are realized during and immediately after collapse of the cavity as a result of the transient high pressures and temperatures. For instance, when the solvent is water, water vapor present in the cavities undergoes thermal dissociation to give hydrogen atoms (H⁺) and hydroxyl radicals (·OH) (11). Solute present near the bubble/water interface can also undergo thermal decomposition (12). Secondary reactions take place in the liquid phase between solute molecules and excited species, mainly ·OH in the case of aqueous solutions, escaping from the gas phase into solution. ·OH is a powerful and efficient chemical oxidant in both the gas and liquid phase. In the aqueous phase, ·OH has a one-electron oxidation potential of \( E^0 = +1.8 \text{ V} \) in neutral solution (\( \text{·OH} + \text{e}^- \rightarrow \text{OH}^- \)) and 2.7 V in acidic solution (\( \text{·OH} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} \)) (13). Reactions of ·OH with inorganic and organic substrates are often near the diffusion-controlled rate (14).

Although ultrasound has currently a number of industrial uses (5), its potential for water and wastewater treatment has not been fully explored. A few preliminary studies have indicated that ultrasonic irradiation is effective for the
oxidation of organics and the disinfection of water and wastewater either as the sole means of treatment (15), or in combination with ozonation (16) and UV irradiation (17).

In this paper we present the results of an investigation of the ultrasonic irradiation of S(−II) in oxic aqueous solutions over the pH range 7 – 12 at 20 kHz over a range of applied power. Our work was motivated in part by the potential application of sonolysis for the treatment of H₂S in wastewater. The ultrasonic decomposition of H₂S may prove to be an efficient way for the removal of this gas from fossil fuel refining wastes or geothermal power plants with commercial applications similar to that of the Claus process (18).

Experimental

The ultrasonic irradiation of aqueous sulfide solutions was conducted with a Branson 200 sonifier, operating at 20 kHz. The ultrasonic intensity at the titanium tip of the 1/2-in. sonication probe was about 75 W/cm² (corresponding power input ≈ 85 W). Reactions were performed in a water–jacketed–stainless steel cell from Sonics & Materials. The cell is shown schematically in Fig. 4.1; its total volume is 50 ml and it is similar to ultrasonic reactors used in other studies (5–6). The temperature inside the reaction vessel was kept constant at 25 °C. All irradiations were carried out in air saturated solutions at t = 0. The sample ports of the stainless steel reactor were sealed with rubber septa during the course of sonication and no attempt was made to control the pressure in the headspace (volume of headspace = volume of sonicated solution = 25 ml, initial headspace pressure = atmospheric).

Sulfide concentrations were measured with a sulfide ion specific electrode,
Figure 4.1  Ultrasonic apparatus (Direct immersion horn/SS cell)
ISE (ORION 94–16 Ag/Ag₂S with double junction reference electrode), coupled to an ORION 801–A ion analyzer. Oxygen concentrations were measured with an ORION 97–08–00 oxygen electrode, and pH measurements were performed with a RADIOMETER pH electrode and a PHM84 pH meter. A K–type thermocouple connected to a FLUKE 75 multimeter via a FLUKE 80TK thermocouple module was used for temperature measurements. A HAAKE A80 water circulation and temperature controlling system was used for temperature control. Spectrophotometric measurements were performed on an HP 8450A UV/VIS spectrophotometer. Nitrite, nitrate, sulfate, sulfite and thiosulfate ions were determined with a Dionex 2020i ion chromatograph and a Dionex AS4–A column. The eluent consisted of a mixture of 2.2 mM carbonate and 2.8 mM bicarbonate. Hydrogen peroxide was analyzed fluorometrically as described earlier (19).

Kinetic runs were carried out by sonication of a sample for the desired length of time, followed by sample withdrawal and multiple analysis. Experiments were continued after cleaning the cell thoroughly and filling it with fresh solution. Prior to any analysis, all samples were filtered with 0.2 μ HPLC filters (from Gelman) to remove Ti particles produced during sonication by erosion of the Ti tip of the sonifier. No adsorption of S(–II) or any of the sonication products on the HPLC filters was observed. The water employed in all preparations was purified by a Milli–Q/RO system from Millipore. Mono and disodium phosphate salts (Mallinckrodt) or sodium borate (Spectrum) were used for the preparation of the buffers.

Results

Ultrasonic irradiation of 25 ml solutions of bivalent sulfur at pH 10 (borate
buffer, 1=0.06 M) resulted in a linear decrease of [S(−II)] with sonication time. Figure 4.2a shows the concentration of S(−II), where [S(−II)] = [H₂S] + [HS⁻] + [S²⁻], remaining vs sonication time for an experiment at pH 10 and [S(−II)]₀ ≈ 200 μM. The zero–order rate for this particular experiment was 7.5 μM·min⁻¹. The rate of [S(−II)] disappearance was also followed spectrophotometrically (ε₂₃₀ = 7950 M⁻¹·cm⁻¹ for HS⁻) and the zero–order rate constants obtained using the absorbance data were in agreement with those obtained from the ISE measurements. The products of S(−II) sonolysis at pH 10 were found to be SO₄²⁻ (sulfate), SO₃²⁻ (sulfite) and S₂O₃²⁻ (thiosulfate) as shown in Figure 4.2b. These products were initially formed in the mole ratio 2.2:2.7:1, respectively. An overall mass balance (i.e. [S(−II)]ₜ = [S(−II)]₀ − [SO₄²⁻]ₜ − [SO₃²⁻]ₜ − 2·[S₂O₃²⁻]ₜ) was achieved within the limits of analytical error.

A post–irradiation oxidation of sulfite to sulfate was observed and was attributed to the subsequent thermal reaction of HS⁻ with H₂O₂. Hydrogen peroxide is known to form during the sonolysis of water (5). In order to verify this hypothesis, sonicated S(−II) solutions were analyzed for H₂O₂. These concentrations were compared to those measured in sonicated Milli–Q water buffered at pH 10. In the control experiments a linear increase of [H₂O₂] vs sonication time was observed with a zero–order rate constant of 2.52 μM·min⁻¹. This measured rate of H₂O₂ production during sonolysis of deionized water agreed with our previously reported results (20). However, [H₂O₂] was found to be lower for the S(−II) sonicated solutions as shown in Figure 4.3. The difference can be attributed to the thermal reactions of HS⁻, SO₃²⁻ and S₂O₃²⁻ with H₂O₂.

NO₂ and NO₃ were also found as products of the sonolysis of water. Figure 4.4 shows the total concentrations of these ions ([NO₂] + [NO₃] = [NOₓ]) in
Figure 4.2 Sonication of S(−II) at pH 10, T_b = 25 °C, 75 W/cm², [S(−II)]_o = 196 µM. (a, top) S(−II) decrease with sonication time. (b, bottom) Sonication products distribution; S_{ox} = \left[SO_4^{2-}\right] + \left[SO_3^{2-}\right] + 2 \cdot \left[S_2O_3^{2-}\right].
Figure 4.3. Hydrogen peroxide formation versus sonication time.
Figure 4.4  NO$_y$ formation during sonication.
sonicated solutions as a function of time. From these results it can be seen that the presence of S(−II) did not affect the rate of NO\textsubscript{y} formation which was found to be 1 μM·min\textsuperscript{-1}.

As mentioned above, the oxidation of S(−II) at pH 10 was found to be zero–order with respect to [S(−II)]. However, the zero–order rate constant, k\textsubscript{0}, was found to depend on the initial concentration of S(−II) as shown in Figure 4.5. It can be seen that k\textsubscript{0} increased linearly with [S(−II)]\textsubscript{o} up to [S(−II)]\textsubscript{o} ≈ 450 μM and then remained practically constant for higher [S(−II)]. This behavior of k\textsubscript{0} vs [S(−II)]\textsubscript{o} is quite interesting and will be discussed further in the discussion part of this paper.

In order to determine the sonochemical reactivity of the intermediate product S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}, thiosulfate solutions were sonicated at pH 10 under the same conditions used for S(−II). A linear decrease of [S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}] vs time was observed, and the oxidation products were found to be SO\textsubscript{4}\textsuperscript{2−} and SO\textsubscript{3}\textsuperscript{2−}. Those products were initially formed with a stoichiometry 1:1, but SO\textsubscript{3}\textsuperscript{2−} was later oxidized to SO\textsubscript{4}\textsuperscript{2−}. Figure 4.6 shows the distribution of the products for [S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}]\textsubscript{o} = 100 μM. A limited number of experiments showed that the zero–order rate for S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} oxidation, k\textsubscript{ot}, had a dependency on [S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}]\textsubscript{o} similar to that described above for S(−II) (i.e., k\textsubscript{ot} increased with [S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}]\textsubscript{o}).

Additional experiments were performed at pH > 10 (with a phosphate buffer) and [S(−II)]\textsubscript{o} = 100 μM. As in the earlier experiments described above the ultrasonic oxidation of S(−II) followed apparent zero–order kinetics and the oxidation products were found to be SO\textsubscript{4}\textsuperscript{2−}, SO\textsubscript{3}\textsuperscript{2−} and S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}. The zero–order rate decreased from 5.4 μM·min\textsuperscript{-1} at pH 10 to 4.0 μM·min\textsuperscript{-1} at pH 11 and remained constant thereafter. Figure 4.7 presents the results of two experiments performed
Figure 4.5 Dependence of $k_0$ on $[S(-II)]_0$ at pH 10.
Figure 4.6  \( \text{S}_2\text{O}_3^{2-} \) sonication product distribution at pH 10.
Figure 4.7  S(−II) sonication products distribution in borate and phosphate buffer at pH 10.6. (a, top) S(−II) vs time. (b, bottom) Products.
at pH 10.6, \([S(-II)]_0 = 100 \mu M\), and with different buffers. It can be seen that the overall rate of the ultrasonic oxidation of \(S(-II)\) is the same in both borate and phosphate buffers (Figure 4.7a). The distribution of the products (Figure 4.7b) indicates a catalytic effect of the phosphate buffer on the oxidation of \(SO_3^{2-}\) to \(SO_4^{2-}\). Phosphate buffer catalysis has been reported previously by Hoffmann and Edwards (21) and Mader (22).

Experiments performed at \(pH < 10\) revealed an apparent change in the observed reaction kinetics. The rate of ultrasonic oxidation of \(S(-II)\) was found to be first-order with respect to \([S(-II)]\) at \(pH \leq 8.5\). The rate of oxidation of \(S(-II)\) increased with decrease in pH. However, the measured concentrations of \(SO_4^{2-}\), \(SO_3^{2-}\) and \(S_2O_3^{2-}\) could not account for the total observed decrease in \(S(-II)\), especially at short sonication times. This difference is shown in Fig. 4.8 where \([S(-II)], [S_{ox}]^{identified} (= [SO_4^{2-}] + [SO_3^{2-}] + 2 \cdot [S_2O_3^{2-}])\) and \([S_{un}] (= [S(-II)]_0 - [S(-II)] - [S_{ox}]^{id})\) are plotted vs sonication time for a typical experiment at pH 7.4. In subsequent experiments \(H_2O_2\) (in excess of \(4 \cdot [S(-II)]_0\)) was added in samples from the sonicated \(S(-II)\) solutions and was allowed to react with the reduced sulfur present in the samples before analyzing for \(S_{ox}\). As expected, only \(SO_4^{2-}\) was present in the \(H_2O_2\)-treated samples. In Fig. 4.9 the \([SO_4^{2-}]\) measured in \(H_2O_2\)-treated sonicated solutions at pH 7.4 and \([S(-II)]_0 = 92 \mu M\) is compared to that measured in \(H_2O_2\)-treated blanks taken out from the cell before sonication (control). Even though both sets of data showed some scatter compared to the expected value of 92 \(\mu M\) (solid line in Fig. 4.9) (this is attributed to poor pH control during \(H_2O_2\) addition) no significant difference was found between the sonicated samples and the control case. Therefore, the possibility of \(H_2S\) degassing, at least in considerable amounts, during sonication was discounted; this conclusion
Figure 4.8 S(−II) sonication product distribution at pH 7.4, and $[S(−II)]_0 = 82 \mu M$. 
Figure 4.9  \( \text{SO}_4^{2-} \) measured in \( \text{H}_2\text{O}_2 \) treated S(−II) solutions ([S(−II)]_0 \approx 82 \mu\text{M}) before and after sonication at pH 7.4.
is also supported by calculations based on the known gas-transfer rates for H₂S that show that a negligible change in [S(−II)] in solution (in the order of 1 μM) is expected due to H₂S gas escaping into the headspace during the course of the experiment. Thus, the discrepancy between the [S_{ox}] measured and [S_{ox}] expected is attributed to the formation of elemental sulfur (S₈) which was not determined analytically but was observed qualitatively as an increased turbidity of the solution.

The rate of the sonolysis of low S(−II) concentrations was found to be independent of the volume of solution between 20 and 35 ml and showed some decrease for solution volume of 40 ml (this volume is close to the reactor cell capacity). Fig. 4.10 shows the fraction of [S(−II)]₀ remaining after 10 min. of sonication as a function of solution volumes (20–40 ml) at pH 10 and [S(−II)]₀ = 100 μM. The total input power (as measured by calorimetry; see below) increased from ≈ 65 W to ≈ 103 W for sonication of 20 ml and 35 ml, respectively and remained at ≈ 103 W for solution volume 40 ml. It was calculated that the amount of S(−II) oxidized per unit energy offered to the system was similar for all sonicated volumes; a maximum efficiency of 3.9⋅10⁻¹¹ moles/J corresponded to 35 ml sonication volume, and the efficiency for 20, 25, 30, and 40 ml was 3.3⋅10⁻¹¹, 3.4⋅10⁻¹¹, 3.7⋅10⁻¹¹, and 3.6⋅10⁻¹¹ moles/J, respectively.

Fig. 4.10 also shows the agreement between [S(−II)] values calculated from the sulfide ISE measurements and the absorbance data. Identical results were obtained with continuous or pulsed sonication with duty cycles (% of time that sonicator is on every second) ranging from 30% to 70%. The comparison was made using the net sonication time in the case of pulsed experiments.

A series of experiments were conducted in which the output power was varied
Figure 4.10 Effect of sonicated solution volume; pH 10, \([S(-\text{II})]_o = 100 \ \mu\text{M},\
\text{t}_{\text{son}} = 10 \ \text{min}.\)
within the limitations of the power unit. Power values were determined from the rise in temperature, \( T \), of a known volume of water with sonication time, \( t \), in the absence of cooling. Using a simplified heat transfer analysis, the rate of energy input to the system (power = \( Q \), in Watts) is given by

\[
Q = M \cdot C_p \cdot dT/dt + U \cdot A_w \cdot (T - T_{amb}) \tag{4.1}
\]

where \( T_o \) and \( T_{amb} \) are the initial temperature of the solution and the ambient temperature respectively, \( A_w \) is the wetted area (total wall area of the reaction vessel that is wetted by the sonicated liquid; 43 cm\(^2\) for our SS cell at 25 ml), \( M \) is the mass of sonicated water, \( C_p \) is the specific heat of water (4.18 J/gr/K), and \( U \) is a bulk heat loss coefficient (units of Watts/m\(^2\)/K). Integrating eq. (4.1) we obtain:

\[
T = \{T_o - T_{amb} - Q/(U \cdot A_w)\} \cdot \exp\{- U \cdot A_w \cdot t/(M \cdot C_p)\} + T_{amb} + Q/(U \cdot A_w) \tag{4.2}
\]

and \( Q \) and \( U \) can be calculated by fitting the temperature data numerically.

If heat losses are neglected, power \( Q \) can be calculated from

\[
Q = M \cdot C_p \cdot dT/dt \tag{4.3}
\]

where \( dT/dt \) is the initial slope of the \( T \) vs \( t \) curve. Analysis of the data showed that \( Q \) values obtained using eq. (4.3) differ less than 10% from the values obtained using eq. (4.2). The ultrasonic intensity at the titanium tip is equal to \( Q/A_t \), where \( A_t \) ( = 1.2 cm\(^2\)) is the surface area of the tip. Figure 4.11 shows that the
Figure 4.11  Effect of input power on S(−II) sonication; pH 10, [S(−II)]_o = 100 μM.
observed zero-order rate ($k_0$, in $\mu$Mmin$^{-1}$) for sonication of 25 ml solution at pH 10 increased linearly with Q in the range studied (i.e. up to 100 W).

The rate of S(–II) oxidation at alkaline pH was found to be practically independent of bulk solution temperature, $T_{\text{bulk}}$. Figure 4.12 shows the observed $k_0$ as a function of $T_{\text{bulk}}$ for three different values of power input.

Potassium iodide (KI) has been used by other investigators as a 'sonochemical dosimeter' (23–26). It has been proposed that $I^-$ reacts in the liquid phase with products of the sonolysis of water (mainly 'OH) and possibly with oxygen atoms coming from the thermal decomposition of $O_2$ (24) and produces $I_2$ which can be detected spectrophotometrically in the form of $I_3^-$ $[I_2 + I^- \xrightarrow{} I_3^-, \text{K} = 770 \text{ (25)}; \epsilon_{350} = 2.6 \cdot 10^4 \text{ M}^{-1}\text{sec}^{-1} \text{ for } I_3^-(19,24)].$ When starch is added to the KI solution, this system can be used for qualitative inspection of a sonochemical reactor system (if the system produces a field that is enough to 'do chemistry' there will be a rapid change in the color of the solution: the initially clear liquid will become deep blue). Sonication of a 1 M solution of KI using the same experimental set-up as for S(–II) sonication resulted in a linear increase in $I_3^-$ of $d[I_3^-]/dt = 13.9 \mu$M$\cdot$min$^{-1}$.

The oxidation of ferrous sulfate to ferric sulfate, known as the Fricke dosimeter, has been also used to probe ultrasonic cavitation activity (28–31). Acidic solutions of 1 mM $\text{Fe(NO}_3\text{)}_2(\text{SO}_4)_{2}$ (0.8 N $\text{H}_2\text{SO}_4$, pH $\simeq$ 0.5) were sonicated and formation of $\text{Fe}^{3+}$ was followed spectrophotometrically $[\epsilon_{305} = 2197 \text{ M}^{-1}\text{cm}^{-1} \text{ (30)}]$. The linear increase in $[\text{Fe}^{3+}]$ with time was found to be $d[\text{Fe(III)}]/dt = 24.4 \mu$Mmin$^{-1}$. 
Figure 4.12  Effect of bulk solution temperature on S(−II) sonication; pH 10, \([S(−II)]_o = 100 \mu\text{M}\).
Discussion

The total sulfide, S(−II), is present in the form of H₂S, HS⁻ or S²⁻. The relative amounts of these three species depend on the pH of the solution based on the acid/base sulfide equilibria:

\[
\begin{align*}
H_2S & \leftrightharpoons pK_{a1} \rightarrow HS^- & \leftrightharpoons pK_{a2} \rightarrow S^2- \\
& \pm H^+ & \pm H^+
\end{align*}
\]

(4.4)

where \(K_{a1}, K_{a2}\) are the first (\(pK_{a1} \approx 7.00\)) and second (\(pK_{a2} \approx 17\)) acid–dissociation constants for \(H_2S\), respectively. The value of \(pK_{a2}\) was previously accepted to be \(\approx 14\) (32), but a later spectrophotometric study (33) reported it as 17.00. It now seems clear that \(pK_{a2}\) is much higher than 14 and that \(S^2-\) is not present at appreciable concentrations even in basic solutions (34). Therefore, the species \(S^2-\) can be neglected for all practical purposes, and the concentrations of \(H_2S\) and \(HS^-\) are given by:

\[
\begin{align*}
[H_2S] & = \alpha_0[S(-II)] \\
[HS^-] & = \alpha_1[S(-II)]
\end{align*}
\]

(4.5) (4.6)

where

\[
\alpha_0 = \frac{[H^+]^2}{([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})} \approx \frac{[H^+]}{[H^+] + K_{a1}}
\]

(4.7)

\[
\alpha_1 = \frac{K_{a1}[H^+]}{([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})} \approx \frac{K_{a1}}{[H^+] + K_{a1}}
\]

(4.8)

Therefore, the fraction of the total sulfide, \([S(-II)]\), that is in the form of \(HS^-\) increases with increasing pH. At pH around neutral, 50% of the total \(S(-II)\) is
present in the form of HS−; and at pH ≥ 9 practically all [S(−II)] is present in the form of HS−. HS− represents 99.9% of the total S(−II) at pH 10.

Natroshvili et al. (35) have studied the γ-radiolysis of Na2S at 10¹⁶ eV/ml·sec at pH 11.8 in the presence of air. They found SO₃²⁻ and S₂O₆²⁻ to be the products of the oxidation of HS− by ·OH radicals; these two products had practically the same G values (i.e. they were formed with a mole ratio of 1:1). The same investigators also studied the products of the γ-radiolysis of S₂O₆²⁻ in the presence of air; SO₄²⁻, S and SO₃²⁻ were formed with a mole ratio of 5:3:5:1. Under their experimental conditions they observed the complete scavenging of ·OH radicals by HS− and S₂O₆²⁻. They did not observe the formation of H₂O₂.

Our results in alkaline solution are in good agreement with the above results from radiation chemistry. The higher SO₄²⁻ ratios that we observed can be explained by further oxidation of the reaction intermediates by H₂O₂. Hoffmann (36) reported the following rate law for the oxidation of S(−II) by H₂O₂:

\[ \frac{d[S(−II)]}{dt} = k_1[H₂S][H₂O₂] + k₂[HS⁻][H₂O₂] \]

where \( k_1 = 0.5 \text{ M}^{-1}\text{s}^{-1} \), \( k_2 = 29 \text{ M}^{-1}\text{s}^{-1} \). Based on this expression the half life for \([S(−II)]\) at [H₂O₂] = 20 μM and at pH 10 is 1.2 min. It is also known that in alkaline solutions the main product of S(−II) oxidation by [H₂O₂] is SO₄²⁻.

It is therefore reasonable to assume that ultrasonic oxidation of S(−II) in alkaline solutions is the result of the direct reaction of HS− with ·OH. The generation of ·OH during water sonolysis has been established (5–6, 11) and the second-order reaction constants for the reaction of ·OH with reduced sulfur compounds are known to be extremely fast (14): \( k(\text{OH}+\text{HS}−) = 9×10^9 \text{ M}^{-1}\text{s}^{-1} \) [or \( 5.5×10^9 \text{ M}^{-1}\text{s}^{-1} \) (39)], \( k(\text{OH}+\text{SO}_3^{2−}) = 5.5×10^9 \text{ M}^{-1}\text{s}^{-1} \), \( k(\text{OH}+\text{S}_2\text{O}_6^{2−}) = 7.8×10^9 \text{ M}^{-1}\text{s}^{-1} \), \( k(\text{OH}+\text{H}_2\text{S}) = 1.5×10^{10} \text{ M}^{-1}\text{s}^{-1} \). These rate constants are comparable to the
self–reaction rate constant for 'OH radical recombination \([5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} (38)]\).

The apparent zero–order dependence on \([S(–\text{II})]\) suggests that the rate–determining step in the overall reaction is the availability of 'OH radicals (i.e. 'OH is scavenged by HS\(^-\) and the oxidation intermediates in the liquid phase as soon as it diffuses out of the cavitation bubbles). This interpretation of the experimental results is in line with our observation that the reaction rate was the same in both the borax and the phosphate buffered systems. The second–order reaction constants \(k[\text{OH}+\text{B(OH)}_2] < 10^6 \text{ M}^{-1}\text{s}^{-1}\) and \(k(\text{OH}+\text{PO}_4^{3-}) < 10^7 \text{ M}^{-1}\text{s}^{-1}\) (14) are much lower than \(10^9 \text{ M}^{-1}\text{s}^{-1}\) and thus neither of these ions is expected to interfere with the reactions of 'OH with the reduced sulfur species. On the other hand, a decrease in the rate of \(\text{S}_2\text{O}_3^{2-}\) sonolysis was observed in the presence of high concentrations (> 1 mM) of carbonate/bicarbonate buffer which is in line with the relatively high value of \(k(\text{OH}+\text{CO}_3^{2-}) = 4 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}\) (14).

The dependence of the zero–order rate on \([S(–\text{II})]_0\) is similar to what has been reported for the ultrasonic oxidation of ferrous sulfate (28). The oxidation of \(\text{Fe}^{2+}\) to \(\text{Fe}^{3+}\) during sonolysis has been shown to be zero–order; the zero–order rate, however, increased with increasing initial \(\text{Fe}^{2+}\) concentration up to \([\text{Fe}^{2+}]_0 \simeq 0.5\) mM and remained constant thereafter. This phenomenon is also similar to what was observed by Makino et al. (11) during experiments designed to spin–trap 'OH and 'H radicals during aqueous solution sonolysis at 50 kHz and 0.06 W·cm\(^{-2}\). DMPO (5,5–dimethyl–1–pyrroline 1–oxide) was used to trap 'OH with the formation of the adduct 'OH–DMPO. In air–saturated solutions, the concentration of ['OH–DMPO] increased linearly with time. However, the rate of the formation of ['OH–DMPO] increased with increasing [DMPO] \(_0\) reaching a plateau at [DMPO] \(_0\) \(\simeq 1\) mM.
A standard free radical competition model (see for example reference 39) for the scavenging of OH radicals by HS\(^{-}\) and by \('\)OH (recombination) would lead to the following relationship between the initial zero–order rate constant, \(k_{o}\), and \([S(-II)]_{o}\) :

\[
k_{o} = \frac{k_{S} \left[ S(-II) \right]_{o}}{k_{S}[S(-II)]_{o} + k_{rf}[OH]_{ss}} \quad (4.9)
\]

where \(k_{S}\) and \(k_{r}\) are the second–order rate constants for reaction of \('\)OH with S\((-II)\) and \('\)OH respectively, and \(k_{rf}\) is the rate at which \('\)OH is made available for solution reactions.

Using the experimental data of Figure 4.5, a plot of \(1/k_{o}\) vs \(1/[S(-II)]_{o}\) can be approximated by a straight line \(r^2 = 0.96\) and the following empirical relationship is obtained:

\[
k_{o} = \frac{13.7 \left[ S(-II) \right]_{o}}{[S(-II)]_{o} + 121.1} \quad (4.10)
\]

Comparing equations (4.9) and (4.10) and using \(k_{r}/k_{S} = 0.56 \ (5 \times 10^{9} \ \text{M}^{-1}\text{s}^{-1}/9 \times 10^{9} \ \text{M}^{-1}\text{s}^{-1})\), we get: \(k_{rf} = 13.7 \ \mu\text{M}\cdot\text{min}^{-1}\) and \([\cdot\text{OH}]_{ss} \approx 218 \ \mu\text{M}\). This calculated steady–state concentration for \('\)OH radical is extremely large and cannot be explained by the calculated \(k_{rf}\). This fact suggests that the oxidation of S\((-II)\) proceeds via a chain reaction that is initiated by \('\)OH and involves an additional oxidant (e.g., \(O_2\)).

It is known that the mechanism for the reaction of S\((-II)\) with \('\)OH in the aqueous phase is initiated as follows (14):
\[
\begin{align*}
\text{HS}^- + \cdot \text{OH} & \rightarrow \text{HSO}_2^- \quad (4.11) \\
\text{H}_2\text{S} + \cdot \text{OH} & \rightarrow \text{HS}^- + \text{H}_2\text{O} \quad (4.12)
\end{align*}
\]

The subsequent intermediate steps may include a variety of radical reactions. Some of the reactions of \(\text{HS}^-\) have been studied by pulse radiolysis (37) and electron spin resonance (40). In these studies the formation of the transients \(\text{SO}_2^-\) and \(\text{O}_2^-\) has been observed in the presence of oxygen. Information also exists about the mechanisms of the oxidation of sulfite, \(\text{S(IV)}\), by \(\cdot \text{OH}, \text{H}_2\text{O}_2\) and \(\text{O}_2\) because of its importance in aqueous-phase atmospheric chemistry (41-43). The main reaction species involved in the free-radical chemistry of sulfite are \(\text{SO}_3^-\), \(\text{SO}_5^-\) and \(\text{SO}_4^-\) (41-44). Although no data could be found in the literature concerning reaction of these radicals with \(\text{S(-II)}\), it is reasonable to believe that \(\text{SO}_3^-\) and \(\text{SO}_4^-\) will react with \(\text{HS}^-\) very fast with the formation of \(\text{HS}^-\) and \(\text{SO}_3^2^-\) and \(\text{SO}_4^2^-\), respectively.

Based on the above, we propose that the main reactions involved in the oxidation of \(\text{S(-II)}\) by \(\cdot \text{OH}\) in the presence of \(\text{O}_2\) are as follows:

\[
\begin{align*}
2 \cdot \text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad (4.13) \\
\text{HSO}_2^- + \text{HS}^- & \rightarrow \text{H}_2\text{S}_2^- + \text{OH}^- \quad (4.14) \\
\text{HS}^- + \text{HS}^- & \leftrightarrow \text{H}_2\text{S}_2^- \quad (4.15) \\
\text{HSO}_2^- + \text{O}_2 & \rightarrow \text{SO}_2^- + \text{H}_2\text{O} \quad (4.16) \\
\text{HS}^- + \text{O}_2 & \rightarrow \text{HSO}_2^- \quad (4.17) \\
\text{HSO}_2^- & \leftrightarrow \text{H}^+ + \text{SO}_2^- \quad (4.18) \\
\text{H}_2\text{S}_2^- + \text{O}_2 & \rightarrow \text{H}_2\text{S}_2^- + \text{O}_2^- \quad (4.19) \\
\text{H}_2\text{S}_2^- & \leftrightarrow \text{H}^+ + \text{HS}_2^- \quad (4.20)
\end{align*}
\]
\[ \text{HS}_2^- + \text{O}_2 \rightarrow \text{SO}_2^- + \text{HS}^- \quad (4.21) \]
\[ \text{SO}_2^- + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}_2^- \quad (4.22) \]
\[ \text{SO}_2^- + \text{HS}^- \rightarrow \text{SO}_4^{2-} + \text{HS} \quad (4.23) \]
\[ \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_2\cdot\text{H}_2\text{O} \quad (4.24) \]
\[ \text{SO}_2\cdot\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HSO}_3^- \quad (4.25) \]
\[ \text{HSO}_3^- \rightarrow \text{H}^+ + \text{SO}_3^{2-} \quad (4.26) \]
\[ \text{HS}_2 + \text{SO}_3^{2-} \rightarrow \text{HS}^- + \text{S}_2\text{O}_3^{2-} \quad (4.27) \]
\[ \text{SO}_3^{2-} + \cdot\text{OH} \rightarrow \text{SO}_3^- + \cdot\text{OH}^- \quad (4.28) \]
\[ \text{SO}_3^- + \text{HS}^- \rightarrow \text{SO}_3^{2-} + \text{HS} \quad (4.29) \]
\[ \text{SO}_3^- + \text{O}_2 \rightarrow \text{SO}_5^- \quad (4.30) \]
\[ \text{SO}_5^- + \text{SO}_5^- \rightarrow \rightarrow \text{SO}_4^- + \text{SO}_4^{2-} + \text{O}_2 \quad (4.31) \]
\[ \text{SO}_4^- + \text{HS}^- \rightarrow \text{SO}_4^- + \text{HS} \quad (4.32) \]
\[ 3 \text{O}_2^- + \text{HS}^- \rightarrow \rightarrow \text{SO}_4^- + 2 \cdot\text{OH}^- \quad (4.33) \]
\[ \text{HSO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{HSO}_4^- + \text{H}_2\text{O} \quad (4.34) \]
\[ \text{HS}^- + 4 \text{H}_2\text{O}_2 \rightarrow \rightarrow \text{SO}_4^{2-} + 4 \text{H}_2\text{O} + \text{H}^+ \quad (4.35) \]

It must be noted that some of the above reactions are not elementary steps. Furthermore, since we are primarily interested in the neutral to alkaline pH region, species with low pK\text{a} values are shown only in the deprotonated form and \text{S(II)} appears in the form of \text{HS}^-: Equations 4.14, 4.15, 4.23, 4.29, 4.32, 4.33, and 4.35 can also be written for \text{H}_2\text{S}, with an additional proton appearing in the right hand side.

A more detailed mechanism involving a set of 47 reactions and 22 species has been developed and is presented in Chapter 5. Rate constants for most of the reactions were found in the literature (mainly references 14, 37, 41-43, 45) and in the few cases where no data were available estimates of the rate constants based on
kinetic/thermodynamic considerations were used. The set of the 22 stiff ODE's was solved numerically using an Ordinary Differential Equation System Solver (EPISODE, 46) to find the concentrations of the different species with time. It was assumed that there is a continuous constant input of ‘OH in the system (from the cavities), $k_{rf}$. The experimental results at alkaline pH can be modeled with $k_{rf} = 3.5 \mu\text{M} \cdot \text{min}^{-1}$ and the corresponding average bulk liquid steady-state concentration is low ($['\text{OH}]_{ss} \leq 0.1 \mu\text{M}$).

The observed dependence of the initial zero–order rate constant, $k_o$, on $[S(-\text{II})]_0$ (Figure 4.5) is in line with the above described $S(-\text{II})$ oxidation mechanism. A qualitative explanation is as follows: Because of the low $['\text{OH}$ reaction (4.13) is negligible, and initially, all of the ‘OH introduced into solution reacts with $S(-\text{II})$ (eqs. 4.11 and 4.12). The $['\text{OH}]_{ss}$ is then inversely proportional to $[S(-\text{II})]_0$ (i.e., $['\text{OH}]_{ss} \approx (k_{rf})/(k[S(-\text{II})]_0)$, where $k = k_{12}\alpha_1 + k_{12}\alpha_0$ and $\alpha_1, \alpha_0$ are given by eqs. 4.8 and 4.7 respectively. The steady–state concentration of radical species that react with $S(-\text{II})$ in the free–radical $S(-\text{II})$ oxidation chain is practically independent of $[S(-\text{II})]_0$ and depends mainly on the available oxygen. If oxygen is not depleted, the expected dependence of $k_o$ ($= \frac{d[S(-\text{II})]}{dt} \big|_{t=0}$) on $[S(-\text{II})]_0$ is of the form: $k_o = A + B \ [S(-\text{II})]_0$, where $A$ depends on the ‘OH input to the system ($k_{rf}$) and $B$ depends on $[O_2]$. Assuming that $[O_2]$ is continuously replenished so that it remains constant at the air saturation value (i.e., $[O_2] \approx 240 \mu\text{M}$) the following values were found using our free–radical mechanism and $k_{rf} = 3.5 \mu\text{M} \cdot \text{min}^{-1}$: $A = 4.4 \mu\text{M} \cdot \text{min}^{-1}$, $B = 0.016 \text{ min}^{-1}$. These values were used to draw the solid line in Figure 4.5, and it can be seen that the experimental data fall on this line for low $[S(-\text{II})]_0$. Above $[S(-\text{II})]_0 \approx 400 \mu\text{M}$ the rate of $S(-\text{II})$ oxidation is limited by $O_2$. 
It is noted that, even though our reaction vessel was sealed from the atmosphere during the experiments, we had a significant volume of headspace (headspace volume ≈ solution volume = 25 ml). In order to explain the experimental results, it is necessary to assume oxygen transfer from the headspace to solution during sonication. If an overall reaeration coefficient, $K_{LO_2}$, is used the rate of $O_2$ addition to the system is $K_{LO_2}([O_2]_{sat} - [O_2])$, where $[O_2]_{sat}$ is the oxygen saturation concentration at the given temperature and pressure and $[O_2]$ is the actual oxygen concentration in solution. The reaeration coefficient that explains our experimental results is $3.7 \cdot 10^{-4}$ s$^{-1} = 32$ d$^{-1}$ (assuming constant $[O_2]_{sat}$, i.e., neglecting the depletion of $O_2$ in the headspace; see also Chapter 5). The oxygen transfer coefficient was measured experimentally for sonication of 35 ml of water in a glass vessel open to the atmosphere. The surface area of the vessel was similar to that of the stainless steel (SS) reaction cell used for the S(II) sonication experiments ($\approx 10$ cm$^2$). The procedure commonly used for measuring oxygen transfer from aeration equipment and described in Standard Methods (47) was used. The value of $K_{LO_2}$ in that vessel was found to be $4.5 \cdot 10^{-3}$ s$^{-1}$, i.e., about 10 times higher than the above theoretically derived value for the SS cell. Nevertheless, this discrepancy can be attributed to the differences in geometry, bulk solution temperature and pressure between the two cells, and the fact that the SS cell was not open to the atmosphere and therefore the oxygen of the headspace was depleted with time. It is also interesting to note that the oxygen transfer coefficient measured for the glass vessel during sonication was about 5 times higher than the oxygen transfer coefficient determined for a similar glass vessel for simple mixing with a stirrer. This enhancement of oxygen transfer upon sonication could be very important for practical applications of ultrasound for treatment and has been
previously reported by Dahi (16). In his experiments, where ultrasound was used in combination with ozonation, he observed a 15–45% increase in the overall aeration constant for oxygen injection during sonication.

The observed decrease in the apparent zero–order rate constant at pH > 10 can be partly explained by the dissociation of OH in alkaline solutions:

\[ \cdot \text{OH} + \text{OH}^- \rightleftharpoons \text{O}^{2-} + \text{H}_2\text{O} \quad (4.36) \]

where \( k_f = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \), \( k_b = 9.3 \times 10^7 \text{s}^{-1} \). \( \text{O}^{2-} \) reacts more slowly with the same substrates than \( \cdot \text{OH} \) (14, 38, 39). It is also possible that the deprotonation of \( \text{HS}^- \) decreases the rate of reaction of that species with oxygen (eq. 4.21). The pK_a's of \( \text{H}_2\text{S}_2 \) are \( \text{pK}_{a1} = 5 \), \( \text{pK}_{a2} = 9.7 \) (36) and \( \text{S}_2^{2-} \) is the principal \( \text{H}_2\text{S}_2 \) species at pH \( \geq 10 \).

The free–radical mechanism presented above underpredicts the rate of S(−II) disappearance at pH \( \leq 8.5 \). Near pH 7, \( \text{H}_2\text{S} \) present in the liquid phase will readily go into the gas phase upon formation of vapor cavities. Combustion reactions inside the collapsing cavities are known to occur during sonication of volatile solutes or dissolved gases (5). Thus we propose that thermal decomposition of \( \text{H}_2\text{S} \) occurs within the collapsing cavitation bubbles or within the gas–liquid interface where temperatures on the order of 800 K have been previously calculated for our experimental conditions (20) at low pH]. The thermal decomposition of \( \text{H}_2\text{S} \) at high temperatures (\( > \sim 1700 \text{ K} \)) (48–50) is first–order process with respect to [\( \text{H}_2\text{S} \)] and the main products are \( \text{H}_2 \) and \( \text{S}_2 \) (or \( \text{SO}_2 \) in the presence of \( \text{O}_2 \)). Thus the thermal decomposition of \( \text{H}_2\text{S} \) can be invoked to explain the observed increase in the oxidation rate of [S(−II)] with decreasing pH, the change in the apparent
reaction kinetics from zero-order to first-order with respect to \([S(-II)]\), and the appearance of \(S_8\) at \(pH < 9\).

The possible elementary reactions involved in the high-temperature pyrolysis of \(H_2S\) within the collapsing bubble or within the interfacial region of the bubble are as follows:

\[
\begin{align*}
H_2S & \longrightarrow H^+ + HS^- \quad (4.37) \\
HS^- + HS^- & \longrightarrow H_2 + S_2 \quad (4.38) \\
HS^- + S & \longrightarrow H^+ + S_2 \quad (4.39) \\
H_2S + H^+ & \longrightarrow H_2 + HS^- \quad (4.40) \\
H^+ + O_2 & \longrightarrow HO_2^- \quad (4.41) \\
H_2S + 'OH & \longrightarrow HS^- + H_2O \quad (4.42) \\
H_2S + O^- & \longrightarrow HS^- + 'OH \quad (4.43) \\
HS^- + O_2 & \longrightarrow HSO_2^- \quad (4.44) \\
HSO_2^- + 'OH & \longrightarrow SO_2 + H_2O \quad (4.45) \\
HSO_2^- + O_2 & \longrightarrow HSO_4^- \quad (4.46) \\
HSO_4^- + H^+ & \longrightarrow H_2SO_4 \quad (4.47) \\
SO_2 + H_2O & \longrightarrow SO_2\cdot H_2O \quad (4.48) \\
SO_2\cdot H_2O + 'OH & \longrightarrow HSO_3^- + H_2O \quad (4.49) \\
HSO_3^- + 'OH & \longrightarrow SO_3 + H_2O \quad (4.50) \\
HSO_3^- + HO_2^- & \longrightarrow SO_3 + H_2O_2 \quad (4.51) \\
SO_3 + H_2O & \longrightarrow 2 H^+ + SO_4^{2-} \quad (4.52)
\end{align*}
\]

Since \(S(-II)\) is destroyed via two different pathways during sonication, i.e., oxidation by \('OH\) (rate constant \(k_0\)) and thermal decomposition (rate constant \(k_1\)),
the overall rate of \([S(-\text{II})]\) disappearance with time can be written as:

\[
\frac{d[S(-\text{II})]}{dt} = -k_o - k_1 [S(-\text{II})]
\]  

(4.53)

Integration of eq. (4.53) yields:

\[
[S(-\text{II})] = \left[ [S(-\text{II})]_0 + \frac{k_o}{k_1} \right] e^{-k_1 t} - \frac{k_o}{k_1}
\]  

(4.54)

The experimental data for \([S(-\text{II})]_0 = 100 \ \mu\text{M}\) as a function of pH were analyzed using eq. (4.10) to obtain values of \(k_o\) and \(k_1\). Figure 4.13 shows the calculated rate constants over the pH range of 7.4 to 12.0. As expected, \(k_1\) is near zero between pH 12 and 10 and increases with decreasing pH. The solid line in Fig. 4.13 represents \(\alpha_o\) (eq. 4.7). Since the values of \(k_1\) qualitatively follow this curve, the relationship between \(k_1\) and \(H_2S\) is strengthened. \(k_o\) values were found to decrease with decreasing pH. This may be partly due to the decrease in the concentration of total sulfide available for free–radical solution reactions and to lower concentrations of \(OH^-\) radical. As \(H_2S\) fills the gas–phase within the bubbles, it will 'cushion' the implosion resulting in lower temperatures upon bubble collapse and thus lower \([OH^-]\) (5).

In conclusion, the ultrasonic irradiation of \(S(-\text{II})\) in water results in its rapid oxidation. Reaction of \(HS^-\) with \(OH^-\) is the main pathway for the oxidation of \(S(-\text{II})\) at \(pH \geq 10\). When \(O_2\) is present, the rate of \(S(-\text{II})\) oxidation increases linearly with initial sulfide concentration. At \(pH \leq 8.5\), thermal decomposition of \(H_2S\) within or near collapsing cavitation bubbles becomes the important pathway.
Figure 4.13  Calculated zero–order and first–order rate constants for S(–II) sonolytic oxidation.
The limitation of sonolysis for the control of H₂S and other trace contaminants in water is that it is relatively inefficient with respect to the input energy. Calculations presented in the Appendix show that only a small portion of the total energy supplied to the system results in "useful" free–radical reactions. The formation of free–radicals upon sonication has been traditionally used to define the "chemicoacoustic" or "sonoacoustic" efficiency (29–31, 51, 52) of ultrasonic irradiation. Since our previous (20) and current work showed that the ultrasound–induced elimination of trace contaminants in water is the result of free–radical reactions and thermal decomposition it seems that it would be more appropriate to define the efficiency of sonication for the control of chemicals (i.e., the percentage of the total energy supplied to the system that is effectively used in the decomposition of each particular chemical compound) as a "sonolytic" efficiency. The sonolytic efficiency would then depend on the chemical compound of interest and could be higher than the "chemicoacoustic" efficiency as defined previously (e.g., in the case of S(–II) decomposition at low pH). Nevertheless, since both the above mentioned sonolytic mechanisms result from the transient high temperatures that result from cavitation, chemicoacoustic efficiency should still be a good estimate for the order of magnitude of the overall sonolytic efficiency of an ultrasonic irradiation system.

In this regard we point out that the commercial immersion–horn sonifier that was used in this study is not the optimum reactor configuration for the efficient generation of transient cavitation. The high intensity sound waves generated at the tip of the horn result in intense local cavitation (53) as can be seen visually using sonoluminescence (54) but the large number of bubbles formed can cause a 'blanketing effect' (55) that reduces the sonication efficiency. Preliminary
experiments with a larger 3-in. diameter surface radiating at 20 kHz showed that free-radical H₂S oxidation proceeds at a faster rate even at ultrasonic intensities that are one order of magnitude lower than those used with the direct-immersion horn. These results are in agreement with the findings of a recent study (27) where the rate of I₂ formation was shown to be about fivefold higher using a quartz plate oscillating at 1 MHz as compared to a commercial 20 kHz immersion-horn with a tenfold higher intensity. Our current research is focused on a study of the optimum reactor configurations for sonolytic degradations.

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References


Appendix

Our experimental conditions (≈ 3.2 W.ml⁻¹) are equivalent to total energy input of $2 \times 10^{19} \text{ eV} \cdot \text{ml}^{-1} \cdot \text{sec}^{-1}$ (or a delivered dose of $3.2 \times 10^5 \text{ rad} \cdot \text{s}^{-1}$). At pH 11–12 the ultrasonic oxidation of S(−II) is attributed to the reaction of HS⁻ with 'OH radical and the zero–order rate is $4 \mu \text{M} \cdot \text{min}^{-1} = 2 \times 10^{-7} \text{ M} \cdot \text{s}^{-1}$. Natroshvili et al (35) working at $10^{16} \text{ eV} \cdot \text{ml}^{-1} \cdot \text{sec}^{-1}$ and at pH 11.8 found a $G(-\text{HS}^-) = 0.37$ (i.e. 0.37 molecules of HS⁻ were destroyed per 100 eV) for the γ–radiolysis of S(−II). This G value translates to a zero–order rate of $6.1 \times 10^{-8} \text{ M} \cdot \text{s}^{-1}$. Therefore, it can be seen that under our experimental conditions a three–fold higher rate was achieved but at the expense of a 2000–fold higher energy input. The higher energy input is due to low acoustic efficiency [i.e. a small amount of the total ultrasonic energy is transformed to cavitation power $W_{\text{cav}} (29)$]. Using the above mentioned $G(\text{HS}^-)$ value we can calculate a "sonoacoustic efficiency" (51, 52) of 0.054%. This sonoacoustic efficiency represents the portion of the total energy supplied to the system that was used in bulk solution free–radical reactions similar to those observed in radiation chemistry. The zero order rate of Fe⁺³ formation during irradiation of Fe⁺² (24.4 $\mu \text{Mmin}^{-1}$) gives a sonoacoustic efficiency of 0.03% if a $G(\text{Fe}^{+3})$ value of 3.9 (29) is used. The above estimates of the sonoacoustic efficiency of our system are of the same order of magnitude as those reported by other investigators (31, 52) working under different sonication conditions. This is in agreement with Todd's (29) finding that the yields of water sonolysis depended only on the total energy deposited and were independent of the frequency and intensity distribution of the ultrasonic field. Using a sonochemical efficiency of 0.05% and the estimate for the rate of 'OH release into solution calculated in the
main text (3.5 μM·min⁻¹) a G(OH) = 0.14 can be found for our experimental conditions. This value is in general agreement with the G(OH) = 0.35 ± 0.15 reported by Todd (29).
CHAPTER 5

MATHEMATICAL MODELING OF THE FREE RADICAL CHEMISTRY OF THE S(–II) + OH SYSTEM AND APPLICATION TO THE ULTRASONIC IRRADIATION OF S(–II)
ABSTRACT

A comprehensive mechanism for aqueous-phase oxidation of S(−II), where 
[S(−II)] = [H₂S] + [HS⁻] + [S²⁻], by ‘OH radical in the presence of oxygen is 
developed. The oxidation of S(−II) is initiated by reaction with ‘OH but it is 
further propagated by a free-radical chain sequence involving O₂. This mechanism 
can model adequately the observed oxidation of S(−II) in air saturated aqueous 
solutions sonicated at 20 kHz and 75 W·cm⁻² at pH ≥ 10. At this pH range, 
practically all S(−II) is present in the form of HS⁻ and cannot undergo thermal 
decomposition. Thus, it is shown that the action of ultrasonic waves on aqueous 
solutions containing species that are not susceptible to thermal decomposition can 
be predicted based on the knowledge of the free-radical chemistry of the species. It 
is also shown that even though aqueous phase sonochemical reactions are initiated 
by ‘OH escaping in the aqueous phase from the cavities, molecular oxygen present 
in the solution can be the main oxidant if it can sustain a free-radical chain 
reaction. This observation is important with respect to the application of 
ultrasound for the control of chemicals in trace amounts in water and wastewater 
systems.
Introduction

As discussed in Chapter 4, ultrasonic irradiation of alkaline oxic aqueous solutions of bivalent sulfur, S(−II), at 20 kHz resulted in the rapid, linear decrease in S(−II) concentration. The observed distribution of the oxidation products was similar to that reported for γ-radiolysis of S(−II). The ultrasound-induced oxidation of S(−II) in alkaline solutions was attributed to the reaction of HSO− with OH−. Although the experimental results appear to be qualitatively consistent with our proposed mechanism, there are questions that still remain unanswered. They concern the amount of ·OH released into the aqueous phase and the existence and relative importance of additional oxidants.

In order to address these questions, a comprehensive aqueous phase mechanism that describes the free radical chemistry of the S(−II) + ·OH + O2 system has been developed. This mechanism has been subsequently used to model the ultrasonic oxidation of S(−II) in alkaline pH.

S(−II) + ·OH + O2 system mechanism formulation

The free radical chemistry of the sulfur system is very complicated and includes a variety of species and reactions. In this work, we tried to develop a mechanism that can accurately model the overall behavior of the S(−II) + ·OH + O2 system with the minimum number of intermediates. Furthermore, we limited our interest in the neutral to alkaline pH region that is the region where the ultrasonic irradiation of S(−II) experiments were performed.

The chemical species that are included in the mechanism are shown in Table
5.1. It is noted that S(−II), S(−I) and S(IV) are 'group species', representing the sum of reactant species that are in rapid acid/base equilibrium. Equilibrium reactions relevant to our system are shown in Table 5.2. Only the upper part (above the broken line) of this table is actually used in the mathematical model. The pK values for the reactions of the remaining part of the table are considerably outside the pH region of interest, thus allowing us to neglect one of the two species involved in these equilibria (e.g., $S^{2-}$; $SO_{2}^{−} \cdot H_{2}O$).

The 47 reactions that are included in the mathematical modeling of the system are shown in Table 5.3. Broken arrows indicate multistep (i.e., nonelementary) reactions. In the few cases where no data were available estimates of the rate constants based on kinetic/thermodynamic considerations were used.

By analogy with the reactions of 'OH with $H_{2}S$ and $HS^{−}$, the rate constant for the reaction of $HS^{−}$ with $H_{2}S$ (R5) is expected to be of the same order of magnitude as the rate constant for $HS^{−} + HS^{−}$ (R6); a value of $5.5 \cdot 10^{9}$ M$^{-1}$s$^{-1}$ is therefore used. The choice of $k_{r5}$ is not critical for our application since $H_{2}S$ is not the main S(−II) species at alkaline pH.

The rate constant for the reaction of $HSOH^{−−}$ with $O_{2}$ (R11) is expected to be of the same order of magnitude as for the reaction of $HSOH^{−−}$ with $HS^{−}$ (R9) and lower than the rate constants for the reaction of $HS^{−}$ with those species (R7, R6); the value of $10^{9}$ M$^{-1}$s$^{-1}$ is therefore used for (R11). The overall rate of S(−II) oxidation does not seem to be sensitive to $k_{r11}$. At pH 10 and $[S(−II)]_{o} = 200$ $μM$, the kinetics and product distribution remained the same even when $k_{r11}$ was set to $5 \cdot 10^{9}$ M$^{-1}$s$^{-1}$.

Although $S_{2}O_{3}^{2−}$ is a known product of the radiolysis of S(−II) (14), no pathways that lead to its formation have been proposed. We included two possible
Table 5.1
Chemical species

<table>
<thead>
<tr>
<th>Non-radical species</th>
<th>Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S(\text{-II}) = H_2S + HS^-$</td>
<td>\text{\textbullet OH}</td>
</tr>
<tr>
<td>$O_2$</td>
<td>\text{HS}^-$</td>
</tr>
<tr>
<td>$S(\text{-I}) = H_2S_2 + HS_2^- + S_2^2-$</td>
<td>\text{H}_2\text{S}_2^-$</td>
</tr>
<tr>
<td>$S(\text{IV}) = \text{HSO}_3^- + \text{SO}_3^{2-}$</td>
<td>\text{HSOH}^-</td>
</tr>
<tr>
<td>\text{S}_2\text{O}_3^{2-}</td>
<td>\text{SO}_2^-</td>
</tr>
<tr>
<td>\text{SO}_4^{2-}</td>
<td>\text{\textbullet S}_2\text{O}_3\text{OH}^{2-}</td>
</tr>
<tr>
<td>\text{H}_2\text{O}_2</td>
<td>\text{\textbullet S}_4\text{O}_6^-</td>
</tr>
<tr>
<td>\text{NO}_2^-</td>
<td>\text{O}_2^-</td>
</tr>
<tr>
<td>\text{NO}_3^-</td>
<td>\text{SO}_3^-</td>
</tr>
<tr>
<td></td>
<td>\text{SO}_4^{2-}</td>
</tr>
<tr>
<td></td>
<td>\text{HS}_2</td>
</tr>
<tr>
<td></td>
<td>\text{H}_2\text{S}_2\text{O}^-</td>
</tr>
<tr>
<td></td>
<td>\text{NO}_2^-</td>
</tr>
</tbody>
</table>
Table 5.2  
Equilibrium reactions

<table>
<thead>
<tr>
<th>Equilibrium Reaction</th>
<th>pK</th>
<th>ΔH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O(l) ⇄ H⁺ + OH⁻</td>
<td>14.00</td>
<td>13.34</td>
<td>(1)</td>
</tr>
<tr>
<td>H₂S ⇄ H⁺ + HS⁻</td>
<td>7.02</td>
<td>-5.30</td>
<td>(1)</td>
</tr>
<tr>
<td>HSO₃⁻ ⇄ H⁺ + SO₃²⁻</td>
<td>7.18</td>
<td>3.00</td>
<td>(1)</td>
</tr>
<tr>
<td>HS⁻ ⇄ H⁺ + S₂⁻</td>
<td>9.70</td>
<td></td>
<td>(2)</td>
</tr>
<tr>
<td>H₂S₂ ⇄ H⁺ + HS₂⁻</td>
<td>5.00</td>
<td></td>
<td>(2)</td>
</tr>
<tr>
<td>HS⁻ ⇄ H⁺ + S²⁻</td>
<td>17.1</td>
<td>-12.00</td>
<td>(3)/(1)</td>
</tr>
<tr>
<td>SO₂⁻⋅H₂O ⇄ H⁺ + HSO₃⁻</td>
<td>1.91</td>
<td>4.00</td>
<td>(1)</td>
</tr>
<tr>
<td>HSO₄⁻ ⇄ H⁺ + SO₄²⁻</td>
<td>1.99</td>
<td>5.40</td>
<td>(1)</td>
</tr>
<tr>
<td>HS₂O₅⁻ ⇄ H⁺ + S₂O₅²⁻</td>
<td>1.60</td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>H₂O₂ ⇄ H⁺ + HO₂⁻</td>
<td>11.65</td>
<td>-7.40</td>
<td>(1)</td>
</tr>
<tr>
<td>HNO₂ ⇄ H⁺ + NO₂⁻</td>
<td>3.15</td>
<td>-2.00</td>
<td>(1)</td>
</tr>
<tr>
<td>HO₂ ⇄ H⁺ + O₂⁻</td>
<td>4.46</td>
<td></td>
<td>(4)</td>
</tr>
<tr>
<td>HSO₂⁻ ⇄ H⁺ + SO₂⁻⁻</td>
<td>≤ 2</td>
<td></td>
<td>(5)</td>
</tr>
<tr>
<td>HSO₃⁻ ⇄ H⁺ + SO₃⁻⁻</td>
<td>≤ 2</td>
<td></td>
<td>(5)</td>
</tr>
<tr>
<td>HSO₄⁻ ⇄ H⁺ + SO₄⁻⁻</td>
<td>≤ 2</td>
<td></td>
<td>(5)</td>
</tr>
</tbody>
</table>
# Table 5.3
Sulfur chemistry

<table>
<thead>
<tr>
<th>id#</th>
<th>Reaction</th>
<th>( k ) M(^{-1})s(^{-1} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>.OH + .OH ( \rightarrow ) H(_2)O(_2)</td>
<td>5.5 \times 10(^9)</td>
<td>(6)</td>
</tr>
<tr>
<td>R2</td>
<td>H(_2)S + .OH ( \rightarrow ) HS(^-) + H(_2)O</td>
<td>1.5 \times 10(^{10})</td>
<td>(6)</td>
</tr>
<tr>
<td>R3</td>
<td>HS(^-) + .OH ( \rightarrow ) HSOH(^-)</td>
<td>9.0 \times 10(^9)</td>
<td>(6)</td>
</tr>
<tr>
<td>R4</td>
<td>HS(^-) + HS(^-) ( \rightarrow ) H(_2)S(_2)</td>
<td>6.5 \times 10(^9)</td>
<td>(7)</td>
</tr>
<tr>
<td>R5</td>
<td>HS(^-) + H(_2)S ( \rightarrow ) H(_2)S(_2)(^-) + H(^+)</td>
<td>5.5 \times 10(^9)</td>
<td>EST*</td>
</tr>
<tr>
<td>R6</td>
<td>HS(^-) + H(_2)S(^-) ( \rightarrow ) H(_2)S(_2)(^-)</td>
<td>5.4 \times 10(^9)</td>
<td>(7)</td>
</tr>
<tr>
<td>R7</td>
<td>HS(^-) + O(_2) ( \rightarrow ) HSO(_2)(^-)</td>
<td>7.5 \times 10(^9)</td>
<td>(7)</td>
</tr>
<tr>
<td>R8</td>
<td>HS(^-) + H(_2)S(_2)(^-) ( \rightarrow ) H(_2)S(_2) + HS(^-)</td>
<td>9.0 \times 10(^9)</td>
<td>(7)</td>
</tr>
<tr>
<td>R9</td>
<td>HSOH(^-) + HS(^-) ( \rightarrow ) H(_2)S(_2)(^-) + OH(^-)</td>
<td>2.0 \times 10(^9)</td>
<td>(7)</td>
</tr>
<tr>
<td>R10</td>
<td>HSOH(^-) + H(_2)S ( \rightarrow ) H(_2)S(_2)(^-) + H(_2)O</td>
<td>3.0 \times 10(^9)</td>
<td>(7)</td>
</tr>
<tr>
<td>R11</td>
<td>HSOH(^-) + O(_2) ( \rightarrow ) SO(_2)(^-) + H(_2)O</td>
<td>1.0 \times 10(^9)</td>
<td>EST</td>
</tr>
<tr>
<td>R12</td>
<td>H(_2)S(_2)(^-) + H(_2)S(_2)(^-) ( \rightarrow ) H(_2)S(_2) + 2 HS(^-)</td>
<td>9.5 \times 10(^8)</td>
<td>(7)</td>
</tr>
<tr>
<td>R13</td>
<td>H(_2)S(_2)(^-) + O(_2) ( \rightarrow ) H(_2)S(_2) + O(_2)(^-)</td>
<td>4.0 \times 10(^8)</td>
<td>(7)</td>
</tr>
<tr>
<td>R14</td>
<td>HS(_2) + SO(_3)(^2)(^-) ( \rightarrow ) S(_2)O(_3)(^2)(^-) + HS(^-)</td>
<td>1.0 \times 10(^7)</td>
<td>EST</td>
</tr>
<tr>
<td>R15</td>
<td>HS(_2) + O(_2) ( \rightarrow ) SO(_2)(^-) + HS(^-)</td>
<td>5.0 \times 10(^7)</td>
<td>EST</td>
</tr>
<tr>
<td>R16</td>
<td>SO(_2)(^-) + O(_2) ( \rightarrow ) SO(_2) + O(_2)(^-)</td>
<td>1.0 \times 10(^8)</td>
<td>(6)</td>
</tr>
<tr>
<td>R17</td>
<td>SO(_3)(^2)(^-) + .OH ( \rightarrow ) SO(_3)(^-) + OH(^-)</td>
<td>5.5 \times 10(^9)</td>
<td>(6)</td>
</tr>
<tr>
<td>R18</td>
<td>HSO(_3) + .OH ( \rightarrow ) SO(_3)(^-) + H(_2)O</td>
<td>4.5 \times 10(^9)</td>
<td>(6)</td>
</tr>
<tr>
<td>R19</td>
<td>S(_2)O(_3)(^2)(^-) + .OH ( \rightarrow ) S(_2)O(_3)OH(^2)(^-)</td>
<td>7.8 \times 10(^9)</td>
<td>(8)</td>
</tr>
<tr>
<td>R20</td>
<td>S(_2)O(_3)OH(^2)(^-) + S(_2)O(_3)(^2)(^-) ( \rightarrow ) S(_4)O(_6)(^3)(^-) + OH(^-)</td>
<td>6.0 \times 10(^8)</td>
<td>(8)</td>
</tr>
<tr>
<td>R21</td>
<td>S(_4)O(_6)(^3)(^-) + (\frac{3}{4}) H(_2)O ( \rightarrow ) (\frac{1}{2}) SO(_3)(^2)(^-) + (\frac{7}{4}) S(_2)O(_3)(^2)(^-) + (\frac{3}{2}) H(^+)</td>
<td>2.5 \times 10(^6)</td>
<td>(8)</td>
</tr>
<tr>
<td>R22</td>
<td>O(_2)(^-) + .OH ( \rightarrow ) O(_2) + OH(^-)</td>
<td>1.0 \times 10(^9)</td>
<td>(6)</td>
</tr>
<tr>
<td>R23</td>
<td>SO(_3)(^-) + O(_2) ( \rightarrow ) SO(_5)(^-) ( \rightarrow ) (\frac{1}{2}) SO(_4)(^2)(^-) + (\frac{1}{2}) SO(_3)(^2)(^-) + O(_2)</td>
<td>1.0 \times 10(^8)</td>
<td>(9)</td>
</tr>
<tr>
<td>R24</td>
<td>SO(_4)(^2)(^-) + HSO(_3) ( \rightarrow ) SO(_4)(^2)(^-) + SO(_3)(^2)(^-) + H(^+)</td>
<td>1.3 \times 10(^9)</td>
<td>(10)</td>
</tr>
<tr>
<td>id#</td>
<td>Reaction</td>
<td>( k )</td>
<td>Reference</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>R25</td>
<td>( \text{SO}_4^{2-} + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_3^{-} )</td>
<td>( 2.0 \cdot 10^9 )</td>
<td>(5)</td>
</tr>
<tr>
<td>R26</td>
<td>( \text{SO}_4^{2-} + \text{O}_2^{-} \rightarrow \text{SO}_4^{2-} + \text{O}_2 )</td>
<td>( 5.0 \cdot 10^9 )</td>
<td>(10)</td>
</tr>
<tr>
<td>R27</td>
<td>( \text{SO}_4^{2-} + \text{OH}^{-} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} )</td>
<td>( 7.0 \cdot 10^7 )</td>
<td>(5)</td>
</tr>
<tr>
<td>R28</td>
<td>( \text{SO}_4^{2-} + \text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{O}_2^{-} + 2 \text{H}^+ )</td>
<td>( 1.2 \cdot 10^7 )</td>
<td>(5)</td>
</tr>
<tr>
<td>R29</td>
<td>( \text{S(IV)} + \text{O}_2^{-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} + \text{OH}^{-} )</td>
<td>( 1.0 \cdot 10^5 )</td>
<td>(4)</td>
</tr>
<tr>
<td>R30</td>
<td>( \text{S(IV)} + \text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} )</td>
<td>0.2</td>
<td>(11)</td>
</tr>
<tr>
<td>R31</td>
<td>( \text{S}(-\text{II}) + \text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 4 \text{H}_2\text{O} + \text{H}^+ )</td>
<td>0.483</td>
<td>(2)</td>
</tr>
<tr>
<td>R32</td>
<td>( \text{S}_2\text{O}_3^{2-} + 4\text{H}_2\text{O}_2 \rightarrow 2\text{SO}_4^{2-} + 3\text{H}_2\text{O} + 2\text{H}^+ )</td>
<td>0.025</td>
<td>(12)</td>
</tr>
<tr>
<td>R33</td>
<td>( \text{S}(-\text{II}) + 3 \text{O}_2^{-} \rightarrow \text{SO}_4^{2-} + 2 \text{OH}^{-} )</td>
<td>( 1.5 \cdot 10^6 )</td>
<td>(6)</td>
</tr>
<tr>
<td>R34</td>
<td>( 2\text{SO}_3^{-} \rightarrow \text{S}_2\text{O}_6^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_3^{2-} + 2\text{H}^+ )</td>
<td>( 5.3 \cdot 10^8 )</td>
<td>(5)</td>
</tr>
<tr>
<td>R35</td>
<td>( \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^{-} + \text{H}_2\text{O} )</td>
<td>( 2.7 \cdot 10^7 )</td>
<td>(6)</td>
</tr>
<tr>
<td>R36</td>
<td>( \text{NO}_2^{-} + \cdot \text{OH} \rightarrow \text{NO}_2^{-} + \text{OH}^{-} )</td>
<td>( 1.0 \cdot 10^{10} )</td>
<td>(4)</td>
</tr>
<tr>
<td>R37</td>
<td>( \text{NO}_2^{-} + \cdot \text{OH} \rightarrow \text{NO}_3^{-} + \text{H}^+ )</td>
<td>( 1.3 \cdot 10^9 )</td>
<td>(4)</td>
</tr>
<tr>
<td>R38</td>
<td>( 2\text{NO}_2 + \text{S(IV)} + \text{H}_2\text{O} \rightarrow 2\text{NO}_2 + \text{SO}_4^{2-} + 3\text{H}^+ )</td>
<td>( 1.7 \cdot 10^7 )</td>
<td>(13)</td>
</tr>
<tr>
<td>R39</td>
<td>( \text{SO}_4^{2-} + \text{S}(-\text{II}) \rightarrow \text{SO}_4^{2-} + \cdot \text{HS} )</td>
<td>( 1.0 \cdot 10^9 )</td>
<td>EST</td>
</tr>
<tr>
<td>R40</td>
<td>( \text{H}_2\text{S}_2^{2-} \rightarrow \text{HS}^{-} + \text{HS}^{-} )</td>
<td>( 5.3 \cdot 10^5 )</td>
<td>(7)</td>
</tr>
<tr>
<td>R41</td>
<td>( \text{SO}_2^{-} + \text{HS}^{-} \rightarrow \text{SO}_4^{2-} + \text{HS} )</td>
<td>( 1.0 \cdot 10^8 )</td>
<td>EST</td>
</tr>
<tr>
<td>R42</td>
<td>( \text{SO}_3^{2-} + \text{HS}^{-} \rightarrow \text{SO}_4^{2-} + \text{HS} )</td>
<td>( 1.0 \cdot 10^8 )</td>
<td>EST</td>
</tr>
<tr>
<td>R43</td>
<td>( \text{S}_2\text{O}_3^{2-} + 2 \text{O}_2^{-} \rightarrow \text{SO}_4^{2-} + \text{SO}_3^{2-} )</td>
<td>( 1.0 \cdot 10^5 )</td>
<td>EST</td>
</tr>
<tr>
<td>R44</td>
<td>( \text{HS}_2^{-} + \cdot \text{OH} \rightarrow \text{HS}_2 + \text{OH}^{-} )</td>
<td>( 1.0 \cdot 10^9 )</td>
<td>EST</td>
</tr>
<tr>
<td>R45</td>
<td>( \text{HS}_2 + \text{OH} \rightarrow \text{H}_2\text{S}_2\text{O} )</td>
<td>( 1.0 \cdot 10^9 )</td>
<td>EST</td>
</tr>
<tr>
<td>R46</td>
<td>( \text{HS}_2 + \text{HSOH}^{-} \rightarrow \text{H}_2\text{S}_2\text{O} + \cdot \text{HS} )</td>
<td>( 1.0 \cdot 10^9 )</td>
<td>EST</td>
</tr>
<tr>
<td>R47</td>
<td>( \text{H}_2\text{S}_2\text{O} + 4 \cdot \text{OH} \rightarrow \text{S}_2\text{O}_3^{2-} + 2 \text{OH}^{-} + 4 \text{H}^+ )</td>
<td>( 1.0 \cdot 10^9 )</td>
<td>EST</td>
</tr>
</tbody>
</table>

*EST: estimated (see text); † rate constant in s\(^{-1}\)
pathways: a) reaction of HS\textsubscript{2} with SO\textsubscript{3}\textsuperscript{2−} (R14) and b) oxidation of HS\textsubscript{2} by 'OH (R44) followed by successive addition and abstraction reactions (R45 and multistep R47). The rate constant of R14 is not expected to be higher than the rate constant for the reaction of SO\textsubscript{3}\textsuperscript{2−} with NO\textsubscript{2} (R38) and was therefore set at 10\textsuperscript{7} M\textsuperscript{−1}s\textsuperscript{−1}. The rate constants for reactions R44–R47 are expected to be near the diffusion–controlled limit and were set at 10\textsuperscript{9} M\textsuperscript{−1}s\textsuperscript{−1}. Even if k\textsubscript{r14} = 10\textsuperscript{8} M\textsuperscript{−1}s\textsuperscript{−1} and k\textsubscript{r44–47} = 5\cdot10\textsuperscript{9} M\textsuperscript{−1}s\textsuperscript{−1}, the above mentioned reactions cannot account for the observed formation of S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−}; but the values of these rate constants are not critical for the overall rate of S(−II) oxidation.

The rate constant for the reaction of HS\textsubscript{2} with O\textsubscript{2} (R15) is expected to be higher than the rate constant for the reaction of HS\textsubscript{2} with SO\textsubscript{3}\textsuperscript{2−} (R14); a value of 5\cdot10\textsuperscript{7} M\textsuperscript{−1}s\textsuperscript{−1} was therefore used for k\textsubscript{r15}. Sulfate radical is a very strong oxidant and is expected to react with S(−II) near the diffusion–controlled limit; the value of k\textsubscript{r39} was set at 10\textsuperscript{9} M\textsuperscript{−1}s\textsuperscript{−1}. Sulfur dioxide and sulfite radicals are expected to react with S(−II) slower than SO\textsubscript{4}\textsuperscript{2−} and a value of 10\textsuperscript{8} M\textsuperscript{−1}s\textsuperscript{−1} was used for k\textsubscript{r41} and k\textsubscript{r42}.

The model parameters are shown in Table 5.4. The model accepts a constant and continuous input of 'OH, H\textsubscript{2}O\textsubscript{2}, and NO\textsubscript{2} (OH\textsubscript{input}, H\textsubscript{2}O\textsubscript{2input}, and NO\textsubscript{2input}) so that it can simulate the continuous release of those species from the collapsing bubbles during sonication. Provision has been made for reaeration of the solution; an overall oxygen transfer coefficient [K\textsubscript{1}(O\textsubscript{2})] is used, and the rate of O\textsubscript{2} addition to the system is K\textsubscript{1}(O\textsubscript{2})\cdot([O\textsubscript{2}]\textsubscript{sat}−[O\textsubscript{2}]), where [O\textsubscript{2}]\textsubscript{sat} is the oxygen saturation concentration at the given temperature and pressure and [O\textsubscript{2}] is the actual oxygen concentration in solution.

The values of the model parameters shown in Table 5.4 are those that were found to represent the conditions of our sonication experiments. Their selection is
Table 5.4
Model Parameters

<table>
<thead>
<tr>
<th>Fixed Model Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH_{input}</td>
<td>3.5 \mu M/min</td>
</tr>
<tr>
<td>H_2O_{2input}</td>
<td>2.0 \mu M/min</td>
</tr>
<tr>
<td>NO_2_{input}</td>
<td>1.0 \mu M/min</td>
</tr>
<tr>
<td>K_1(O_2)</td>
<td>3.7 \cdot 10^{-4} \text{ s}^{-1}</td>
</tr>
<tr>
<td>T</td>
<td>298 K</td>
</tr>
<tr>
<td>P</td>
<td>1 \text{ atm}</td>
</tr>
<tr>
<td>pH</td>
<td>10.0</td>
</tr>
</tbody>
</table>
discussed in the next section of this chapter.

Since activation energies for most of the reactions of Table 5.3 were not available, T and P are fixed at standard conditions. The pH is also treated as a fixed variable in order to simulate our buffered sonication experiments. The computer code can be modified to correct the rate constants for different T or P (assuming that the necessary thermodynamic data for the reactions of Table 5.3 become available), or to treat pH as a variable species (by including H⁺ as a 23rd chemical species).

Given the initial conditions (concentrations of the 22 chemical species at t=0), the concentrations of the chemical species with time are found by solving numerically the set of the 22 stiff ODE's. An Ordinary Differential Equation System Solver (EPISODE, 15) is used. The method chosen for the numerical solution of the system includes variable-step size, variable-order backward differentiation and a chord or semi-stationary Newton method with an internally computed finite difference approximation to the Jacobian.

The computer program (USMODEL) was written in FORTRAN 77 and the code can be found in Appendix C. The ODE Solver subroutine (EPIS) is also included in Appendix C. This is the modification of the original EPISODE code prepared by Warren (16).

Model Application to Ultrasonic Irradiation of S(−II)

During ultrasonic irradiation of aqueous solutions, 'OH radicals are produced from dissociation of water vapor upon collapse of cavitation bubbles. A fraction of these radicals that are initially formed in the gas phase diffuse into solution.
Cavitation is a dynamic phenomenon and the number and location of bursting bubbles at any time cannot be predicted a priori. Nevertheless, the time scale for bubble collapse and rebound is orders of magnitude smaller than the time scale for the macroscopic effects of sonication on chemicals (i.e., nanoseconds to microseconds vs minutes to hours). Therefore, a simplified approach for modeling the liquid–phase chemistry resulting from sonication of a well mixed solution is to view the ·OH input into the aqueous phase as continuous and uniform. The implicit assumption in this approach is that the kinetics of the aqueous phase chemistry are not controlled by diffusion limitations of the substrates reacting with ·OH.

The mathematical model that is presented above was first used to simulate the oxidation of S(−II) at pH=10, [S(−II)]_o = 196 μM, and [O_2]_o = 240 μM (air saturation). These initial conditions correspond to the conditions of the sonication experiment shown in Figure 4.2. The rates of H_2O_2 and NO_2 input to the system (i.e., H_2O_2_{input} and NO_2_{input}) were set at the experimentally observed zero–order formation rates for those species in deionized water buffered at pH 10 (see Chapter 4). Various runs were performed with different values of OH_{input}.

Figure 5.1 shows the evolution of total sulfide with time for six different ·OH input values. As expected, the initial S(−II) oxidation rate increases with increasing OH_{input}. But that initial linear decrease of [S(−II)] is 'halted' at [S(−II)] \approx 55 μM in all cases. Figure 5.2 explains why: the main oxidant in our system turns out to be molecular oxygen present in the solution. The ratio of [O_2]_{depleted}:[S(−II)]_{oxidized} is about 1.7 in all cases, showing that most of the oxygen contained in the oxidized forms of sulfur that are the final products (i.e., SO_4^{2−}, SO_3^{2−} and S_2O_5^{2−}) comes from O_2 and not ·OH. Figure 5.3 shows schematically
Figure 5.1  
[S(-II)] profiles for various OH_{input} values; pH 10, \([S(-II)]_o = 196 \, \mu\text{M}, [O_2]_o = 240 \, \mu\text{M}.\)
Figure 5.2  \([O_2]\) profiles for various \(\text{OH}^{-}\) input values; pH 10, \([S(-II)]_0 = 196 \mu\text{M}\), \([O_2]_0 = 240 \mu\text{M}\).
Figure 5.3  Main pathways for the S(–II) + OH system in the presence of O₂ at alkaline pH.
the reactions and species that proved to be the most significant. The oxidation of S(−II) is initiated by reaction with 'OH but is further propagated by a free-radical chain reaction sequence involving O₂.

The value of 'OH input that results in an initial rate of S(−II) oxidation equal to the experimentally observed oxidation rate at the above mentioned conditions (i.e., 7.5 μM·min⁻¹ at [S(−II)]₀ = 196 μM and pH = 10) is 3.5 μM·min⁻¹. In order to explain the experimentally observed linear S(−II) decrease even after all of the initial O₂ should have been depleted, it is necessary to assume oxygen transfer from the headspace to solution during sonication. Figure 5.4 shows the calculated [S(−II)] and [O₂] profiles for 'OH input = 3.5 μM·min⁻¹ and 6 different values of the overall oxygen transfer coefficient K₁(O₂). It can be seen that the value of K₁(O₂) does not affect the initial oxidation rate but determines the subsequent form of the [S(−II)] curve. If not enough oxygen is added into solution, oxygen is depleted before all of the initial sulfide is oxidized resulting in a sudden decrease in the oxidation rate. If a lot of oxygen is added to the system, [O₂] near the end of the reaction is constantly higher than [S(−II)] and a slow-down of the rate of [S(−II)] oxidation occurs [the intermediate species involved in the chain mechanism will react preferably with O₂ and less with S(−II)]. The value of K₁(O₂) that results in a continuous linear [S(−II)] decrease is 3.7·10⁻⁴ s⁻¹ = 32 d⁻¹.

Subsequent experiments with the same direct-immersion horn that was used in S(−II) sonication but in a different vessel and at different conditions (higher T, vessel open to the atmosphere as opposed to the mere existence of headspace) determined oxygen transfer coefficient values that were even higher than that (see Chapter 4). Therefore, this value of K₁(O₂) was accepted to be reasonable and was used in all subsequent modeling work. It must be noted that the value of K₁(O₂) is
Figure 5.4  
(a, top)[S(−II)] profiles for different oxygen transfer coefficients; pH 10, OH\textsubscript{input} = 3.5 \(\mu\text{M} \cdot \text{min}^{-1}\), [S(−II)]\textsubscript{o} = 196 \(\mu\text{M}\), [O\textsubscript{2}]\textsubscript{o} = 240 \(\mu\text{M}\). (b, bottom) corresponding [O\textsubscript{2}] profiles.
vessel–specific, since reaeration will depend on the mixing pattern and the ratio of the surface area to the total volume of the solution.

Figure 5.5 compares the experimentally observed \([S(\ce{II})]\) profile (Figure 4.2a) with the model results using the parameter values shown in Table 5.4. It is noted that, in agreement with the experimental results, the values of \(\text{H}_2\text{O}_2\text{inpu}\)t and \(\text{NO}_2\text{inpu}\)t are not critical for the rate of \(S(\ce{II})\) oxidation. Therefore, the initially chosen values (i.e., 2.5 and 1.0 \(\mu\text{M} \cdot \text{min}^{-1}\) respectively) were not changed.

The parameters of Table 5.4 were then used to model the oxidation of \(S(\ce{II})\) at pH 10 and different initial sulfide concentrations, \([S(\ce{II})]_o\). The agreement with the experimental data was very good at low \([S(\ce{II})]_o\); the calculated \(S(\ce{II})\) profiles for \([S(\ce{II})]_o\) 7 \(\mu\text{M}\) and 45 \(\mu\text{M}\) are shown in Figure 5.6 together with the experimental \(S(\ce{II})\) profiles. As \([S(\ce{II})]_o\) increases, oxygen gets depleted before complete oxidation of the initial sulfide is achieved. Oxygen depletion results in a sudden decrease in the overall oxidation rate. Figure 5.7 shows the calculated \([S(\ce{II})]\) and \([\text{O}_2]\) profiles for \([S(\ce{II})]_o = 300 \ \mu\text{M}\) and two different values of the oxygen transfer coefficient; the solid line represents the case where \([\text{O}_2]\) is fixed at the initial air saturation value [by providing a very high \(K_l(\text{O}_2)\) value], and the broken line is expected to represent our experimental conditions (see above). For that value of \([S(\ce{II})]_o\), continuous aeration of the solution does not improve the \(S(\ce{II})\) oxidation rate significantly. The same is shown to be true up to \([S(\ce{II})]_o \approx 450 \ \mu\text{M}\) (Figure 5.8). At higher \([S(\ce{II})]_o\), the observed \(S(\ce{II})\) oxidation rate is lower than the rate at \([\text{O}_2]\) = constant = 240 \(\mu\text{M}\); Figure 5.9 illustrates that point for \([S(\ce{II})]_o = 955 \ \mu\text{M}\).

Figure 5.10 shows the agreement between the experimentally determined effect of \([S(\ce{II})]_o\) on the initial sulfide oxidation rate, \(k_o\), for \([S(\ce{II})]_o \leq \sim 450 \ \mu\text{M}\).
Comparison between \([S(-\text{II})]\) decrease predicted by the free--radical chemistry model and that observed upon ultrasonic irradiation of \(S(-\text{II})\) at pH 10, \([S(-\text{II})]_0 = 196 \mu\text{M}, \,[O_2]_0 = 240 \mu\text{M}.\)
Figure 5.6 Comparison between \([S(-II)]\) decrease predicted by the free-radical chemistry model and that observed upon ultrasonic irradiation of \(S(-II)\) at pH 10, \([O_2]_0 = 240 \mu M\) and two different \([S(-II)]_0\) low values (a, top) 45 \(\mu M\), and (b, bottom) 7 \(\mu M\).
Figure 5.7  
(a, top) Comparison of calculated [S(−II)] profiles with [O₂] kept constant at air saturation (solid line) and with the oxygen transfer coefficient of Table 5.4 (broken line) at pH 10, \( \text{OH}_{\text{inlet}} = 3.5 \ \mu M \cdot \text{min}^{-1} \), \([S(−II)]_o = 300 \ \mu M\), \([O_2]_o = 240 \ \mu M\). (b, bottom) corresponding [O₂] profiles.
Figure 5.8  
(a, top) Comparison of sonolysis data with calculated \([S(-II)]\) profiles with \([O_2]\) kept constant at air saturation (solid line) and with the oxygen transfer coefficient of Table 5.4 (broken line) at pH 10, \(O_{H\text{in}} = 3.5 \, \mu\text{M} \cdot \text{min}^{-1}, [S(-II)]_0 \approx 450 \, \mu\text{M}, [O_2]_0 = 240 \, \mu\text{M}.\) (b, bottom) corresponding calculated \([O_2]\) profiles.
Figure 5.9  Comparison of sonolysis data with calculated $[S(-II)]$ profiles with $[O_2]$ kept constant at air saturation (solid line) at pH 10, $OH_{\text{input}} = 3.5 \mu M \cdot \text{min}^{-1}$, $[S(-II)]_o \simeq 955 \mu M$, $[O_2]_o = 240 \mu M$. 
Figure 5.10  Effect of [S(−II)]₀ on initial zero-order S(−II) oxidation rate, k₀.
In both cases, $k_o$ increases linearly with $[S(-II)]_o$. The following linear relationship was found from the model:

$$k_o = 4.4 + 0.016 [S(-II)]_o \quad (5.1)$$

where, $k_o$ in $\mu M \cdot min^{-1}$, and $[S(-II)]_o$ in $\mu M$. As discussed in Chapter 4, the value of the intercept represents the contribution of $'OH$ while the slope is due to the free–radical chain sequence. For $[S(-II)]_o \geq \approx 300 \mu M$ the latter term exceeds the former (i.e., $O_2$ becomes the principal oxidant).

It must be noted that the two pathways that are used to model $S_2O_3^{2-}$ formation cannot outcompete the reaction of $H_2S_2$ with $O_2$. This results in an underprediction of $[S_2O_3^{2-}]$ as can be seen in Figure 5.11. Sulfite, on the other hand, is modeled rather well as can be seen also in Figure 5.12 where the profiles of $[S(-II)]$ and its oxidation products are presented for pH 10.6. Nevertheless, the free–radical chemistry mechanism describes adequately the overall oxidation of $S(-II)$ upon sonication at alkaline pH.

Figures 5.13, 5.14, and 5.15 present the $S(-II)$ and $S_{ox}$, where $S_{ox} = [SO_3^{2-}]+[SO_4^{2-}]+2[S_2O_3^{2-}]$, profiles observed upon sonication of $S(-II)$ aqueous solutions at pH 9.0, 8.5, and 7.4 respectively. The broken lines represent the corresponding concentrations of those species predicted by the free–radical chemistry mechanism. It can be seen that the free–radical mechanism underpredicts the rate of $S(-II)$ disappearance at pH $\leq 8.5$. Nevertheless, the total amount of the oxidized $S(-II)$ that was found in the form of the three species that form $S_{ox}$ is not much higher than the calculated $S_{ox}$. It must be noted that $S_{ox}$ represents the total amount of sulfide that has been oxidized in the case of the chemical model (since the three species from which $S_{ox}$ comprises of are the only final oxidation products), while in the case of the experimental data $S_{ox}$ represents
Figure 5.11  
[S(−II)] profile and oxidation product distribution at pH 10, 
[S(−II)]₀ = 196 μM·min⁻¹. Model results (solid and broken lines) 
and experimental data (symbols).
Figure 5.12  
[S(−II)] profile and oxidation product distribution at pH 10.6, 
[S(−II)]₀ = 96 μM·min⁻¹. Model results (solid and broken lines) 
and experimental data (symbols).
Figure 5.13  Comparison between \([S(-II)]\) decrease predicted by the free–radical chemistry model and that observed upon ultrasonic irradiation of \(S(-II)\) at pH 9.0, \([S(-II)]_0 = 91 \mu M\), \([O_2]_0 = 240 \mu M\).
Figure 5.14 Comparison between \([S(-II)]\) decrease predicted by the free-radical chemistry model and that observed upon ultrasonic irradiation of \(S(-II)\) at pH 8.5, \([S(-II)]_0 = 88 \text{ \(\mu\)M}, [O_2]_0 = 240 \text{ \(\mu\)M}.\)
Figure 5.15  Comparison between $[\text{S(II)}]$ decrease predicted by the free-radical chemistry model and that observed upon ultrasonic irradiation of $\text{S(II)}$ at pH 7.4, $[\text{S(II)}]_0 \simeq 80 \mu\text{M}$, $[\text{O}_2]_0 = 240 \mu\text{M}$.
only a part of the oxidation products (Chapter 4).

These results provide further evidence that an important pathway for S(−II) sonolysis at pH ≤ 8.5 is thermal decomposition of H₂S within the cavitation bubbles or within the gas–liquid interface. Furthermore, they seem to suggest that elemental sulfur in the main product of that alternative sonolysis pathway.

In conclusion, it has been shown that the sonolysis of S(−II) in the pH range where that species is primarily in the form of HS⁻ and is not expected to undergo thermal decomposition can be modeled with an aqueous free–radical chemical mechanism and a continuous constant release of ∙OH into solution. This simplified approach is not valid at the pH range (≤ 8.5) where a significant part of the total sulfide is in the form of H₂S that can participate in the gas phase high temperature chemistry that takes place inside and near collapsing cavitation bubbles. An extended chemical mechanism that would include both gas and liquid phase chemistry is needed in order to model S(−II) sonolysis in the general case. However, the development of next level model is not feasible at this stage because of the lack of enough information about the number and the size distribution of cavitation bubbles. In addition, little is known about the physical conditions inside the bubble and its surrounding region upon collapse.

It has also been shown that molecular oxygen is important for the sonolysis of S(−II) at alkaline pH because it propagates a free–radical chain reaction that is initiated by ∙OH. Furthermore, the enhancement of oxygen transfer upon sonication with a direct–immersion horn has been shown to be considerable. These results may have important implications for the application of ultrasonic irradiation for the destruction of chemical contaminants in water systems.
References


CHAPTER 6

ULTRASONIC IRRADIATION OF
IODIDE AND PARATHION
IN AQUEOUS SOLUTION
Ultrasonic Irradiation of Iodide

Introduction

The formation of iodine when potassium iodide solutions are subjected to ultrasonic irradiation was one of the first sonochemical observations (1). Various investigators have since studied the chemical effects of ultrasonic waves on potassium iodide solutions in an attempt to elucidate the nature of sonochemistry (e.g., 2–5). Following the discovery that carbon tetrachloride greatly accelerates the formation of iodine (6,4), iodide solutions with traces of carbon tetrachloride (known as "Weissler's solution") were used as chemical dosimeters for sonochemical apparatus (7,8). With the advances in modern spectrophotometry the addition of CCl$_4$, that used to be a source for irreproducibility, seems no longer necessary (9).

It is accepted currently that iodide oxidation upon sonication is due to free–radical reactions initiated by the thermal decomposition of solvent or solute molecules in compressed cavitation bubbles (10). Nevertheless, open questions remain as to the precise chemical mechanisms of KI sonolysis and the importance of additional oxidants (e.g., O$_2$) (4). No direct information exists on the effect of pH on the iodine yield; even the related effect of pH on H$_2$O$_2$ formation upon water sonication has only been studied in the acidic pH region (4). No mention is found in the literature concerning the importance of I$_2$ evaporation from the aqueous solutions, except of the suggestion that care should be taken to minimize it (9). The effect of dissolved gases on I$_2$ yields has not been satisfactory resolved (2, 5, 11).

In this section, experimental results obtained when potassium iodide solutions were exposed to 20 kHz ultrasound are presented. The motivations for
performing these experiments were: a) perform a visual inspection of the ultrasonic field to detect possible inhomogeneities, b) address some of the above stated open questions so as to feel confident in using the KI system as a dosimeter to compare the sonochemical efficiency of different experimental set-ups.

Results and discussion

The formation of the blue color iodine–starch complex when starch is added in the KI–CCl₄ solution was used for visual inspection of the action of ultrasound (§). Figure 6.1 shows the rapid change in the color of a 0.9 M solution of KI with 10% per volume starch and at CCl₄ saturation upon sonication in a glass reaction vessel with the 1/2-in. direct immersion horn at 20 kHz, 75 W/cm². The volume of the sonicated solution was 30 ml. Although sonoluminescence experiments have suggested that the ultrasonic field is more intense in the vicinity of the titanium tip (see Chapter 7), no obvious inhomogeneities were observed. This suggests that even though the cavitation events may not be homogeneously distributed in our experimental setup, rapid mixing induced by the moving bubbles results in macroscopically homogeneous chemistry. The KI–CCl₄–starch solution was used subsequently for qualitative screening of different reactor systems. If a sonication set-up produces a field that is adequate to 'do chemistry', a rapid change in the color of that solution should be observed.

Solutions of 1M KI were sonicated under the same experimental conditions of the p–NP and S(−II) ultrasonic irradiation experiments as discussed in Chapters 3 and 4 (i.e., Branson CD200 sonifier, 75 W/cm², stainless steel cell, 25 ml solution). Figure 6.2 shows the observed linear increase of the absorbance at 350 nm. The absorbance at 350 nm is due to the I₃⁻ ion \( [\epsilon_{350} = 2.6 \cdot 10^4 \text{ M}^{-1}\text{sec}^{-1}, (5)] \). The
Figure 6.1. "Weissler's solution" (0.9 M KI, 10% starch, CCl₄) before (top) and after (bottom) sonication at 20 kHz, and 75 W/cm² for ~10 seconds.
Figure 6.2. Absorption at 350 nm with sonication time; 1 M KI, 20 kHz, 75 W/cm², SS cell, 25 ml, T_b ≈ 28 °C.
increase in the absorbance is proportional to the release of iodine into solution, since the equilibrium reaction E1 (Table 6.1) is shifted substantially to the right for \([I^-] \approx 1\, \text{M}\). The corresponding \(I_2\) yield (\(\approx\) increase in \(I_2\)) is \(\approx 12.9\, \mu\text{M}\cdot\text{min}^{-1}\). It is noted that the reproducibility of \(I_2\) sonolysis yields was very good (\(\pm\) 5%).

The rate of \(I_2\) formation decreased by about 1/3 (Figure 6.1, \(d[I_2]/dt = 8.6\mu\text{M}\cdot\text{min}^{-1}\)) when the ports of the stainless steel cell were open, indicating a considerable iodine degassing. It is possible that the decrease in the iodine yield is partly related to the lower pressure in the headspace. When the ports are closed, iodine that is released into the headspace may increase the total gas pressure. Increased pressure is expected to lead to more intense cavitation and thus higher sonochemical yields (7).

The initial pH of 1M KI solution is \(\approx 6.9\). If no buffer is used, pH increases gradually during sonication and stabilizes at \(\approx 8.8\). This is in agreement with the increase of pH from neutral to about 8.2 reported by Renaud (3) for sonication of 1M KI solutions (and indicated by the stoichiometries of equations E2, E4, and E6 and reactions R6 and R15). Figure 6.3 compares the increase in A_{350} in the absence of buffer with that observed when pH was kept constant at 10 with borate buffer. It can be seen that no change in the iodine yield was observed. Gueguen (4) has reported that \(H_2O_2\) yield in sonicated water (at 960 kHz) increased with increasing pH from pH 0.3 to pH 3.0 and remained constant thereafter (up to 6.5 that was the highest pH value that he studied). Assuming that this trend continues into the alkaline region and \(H_2O_2\) yield does not depend on pH, our result is not surprising. Experimental results of Hart & Henglein (5) have indicated that sonolysis yields of \(H_2O_2\) and \(I_2\) are closely related and follow the same trends.

A series of experiments was conducted with a water-jacketed glass vessel in
Table 6.1
Equilibrium reactions

<table>
<thead>
<tr>
<th>id#</th>
<th>Reaction</th>
<th>$k$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>$I_2 + I^- \rightleftharpoons I_3^-$</td>
<td>770</td>
<td>(12)</td>
</tr>
<tr>
<td>E2</td>
<td>$I_{2(aq)} + H_2O \rightleftharpoons I^- + H^+ + HIO$</td>
<td>$3.0 \cdot 10^{-13}$</td>
<td>(13)</td>
</tr>
<tr>
<td>E3</td>
<td>$I^- + I^- \rightleftharpoons I_2^-$</td>
<td>$1.1 \cdot 10^5$</td>
<td>(14)</td>
</tr>
<tr>
<td>E4</td>
<td>HOI $\rightleftharpoons H^+ + OH^-$</td>
<td>$1.0 \cdot 10^{-11}$</td>
<td>(15)</td>
</tr>
<tr>
<td>E5</td>
<td>$O^- + IO_3^- \rightleftharpoons IO_4^{2-}$</td>
<td>$1.0 \cdot 10^6$</td>
<td>(15)</td>
</tr>
<tr>
<td>E6</td>
<td>HIO$_3$ $\rightleftharpoons H^+ + IO_3^-$</td>
<td>0.17</td>
<td>(24)</td>
</tr>
</tbody>
</table>
Table 6.2
Free radical iodide chemistry

<table>
<thead>
<tr>
<th>id#</th>
<th>Reaction</th>
<th>k</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( M^{-1}s^{-1} )</td>
<td></td>
</tr>
<tr>
<td>R1</td>
<td>\cdot OH + \cdot OH \rightarrow H_2O_2</td>
<td>5.5 \cdot 10^9</td>
<td>(16)</td>
</tr>
<tr>
<td>R2</td>
<td>I^- + \cdot OH \rightarrow I^- + OH^-</td>
<td>1.2 \cdot 10^{10}</td>
<td>(16)</td>
</tr>
<tr>
<td>R3</td>
<td>I^- + I^- \rightarrow I_2</td>
<td>8.0 \cdot 10^9</td>
<td>(17)</td>
</tr>
<tr>
<td>R4</td>
<td>I_2^- + I_2^- \rightarrow I_3^- + I^-</td>
<td>3.0 \cdot 10^9</td>
<td>(17)</td>
</tr>
<tr>
<td>R5</td>
<td>\cdot OH + I_2 \rightarrow HOI + I^-</td>
<td>1.1 \cdot 10^{10}</td>
<td>(16)</td>
</tr>
<tr>
<td>R6</td>
<td>I_2^- + HOI \rightarrow 2 I^- + H^+ + IO</td>
<td>1.0 \cdot 10^5</td>
<td>(17)</td>
</tr>
<tr>
<td>R7</td>
<td>\cdot OH + HOI \rightarrow HOIOH</td>
<td>7.0 \cdot 10^9</td>
<td>(16)++</td>
</tr>
<tr>
<td>R8</td>
<td>HOIOH \rightarrow IO + H_2O</td>
<td>1.3 \cdot 10^6*</td>
<td>(17)</td>
</tr>
<tr>
<td>R9</td>
<td>\cdot OH + IO_3^- \rightarrow HIO_4^-</td>
<td>1.3 \cdot 10^9</td>
<td>(16)</td>
</tr>
<tr>
<td>R10</td>
<td>IO_4^{2-} \rightarrow IO_3 + O^-</td>
<td>3.3 \cdot 10^3*</td>
<td>(17)</td>
</tr>
<tr>
<td>R11</td>
<td>NO_2^- + I^- \rightarrow I^- + NO_2^-</td>
<td>8.8 \cdot 10^9</td>
<td>(17)</td>
</tr>
<tr>
<td>R12</td>
<td>I^- + NO_2 \rightarrow I^- + NO_2^-</td>
<td>1.1 \cdot 10^5</td>
<td>(17)</td>
</tr>
<tr>
<td>R13</td>
<td>I_2 + O_2^- \rightarrow I_2^- + O_2</td>
<td>5.5 \cdot 10^9</td>
<td>(18)</td>
</tr>
<tr>
<td>R14</td>
<td>I_3^- + O_2^- \rightarrow I_2^- + I^- + O_2</td>
<td>8.0 \cdot 10^8</td>
<td>(18)</td>
</tr>
<tr>
<td>R15</td>
<td>NO_2^- + NO_2 \rightarrow NO_2^- + NO_3^- + 2 H^+</td>
<td>1.0 \cdot 10^8</td>
<td>(17)</td>
</tr>
<tr>
<td>R16</td>
<td>NO_2^- + OH \rightarrow NO_2^- + OH^-</td>
<td>1.0 \cdot 10^{10}</td>
<td>(16)</td>
</tr>
<tr>
<td>R17</td>
<td>5IOH \rightarrow HIO_3 + 2 I_2 + 2 H_2O</td>
<td>very fast</td>
<td></td>
</tr>
<tr>
<td>R18</td>
<td>H_2O_2 + 2 I^- + 2 H^+ \rightarrow I_2 + 2 H_2O</td>
<td>moderated, rapid(13) hastened by molybdate</td>
<td>(23)</td>
</tr>
</tbody>
</table>
Figure 6.3. Comparison of I₃ yields in the presence of borate buffer (pH 10) and in the absence of buffer (pHᵢₙ 6.9, pHᵢₙₐ₅ 8.8).
order to study the effect of dissolved gases on the I$_2$ sonolysis yields. The vessel is connected to the nodal point of the horn with a teflon part; the configuration is similar to "Suslick's glass cell" (7). The volume of the sonicated solution was 100 ml. Similarly to the stainless steel cell, two side ports and a bottom port allowed for the dispersion of different gases into the solution before sonication: all ports were closed with rubber septa; the desired gas was bubbled into the bulk of the solution using a syringe through the bottom port, and air was removed from the headspace with the use of a second syringe from one of the side ports (volume of headspace $\approx$ 60 ml). Bubbling times varied between 40 and 90 minutes. Repeated experiments showed that 40 minutes of bubbling gave the same results as extended bubbling for the gases used. Therefore, most of the experiments shown in Figure 6.4 were conducted after 40 minutes of bubbling of the appropriate gas.

The effect of different gases on the iodine yields is shown in Figure 6.4. It can be seen that the highest yield is obtained in sonication under oxygen, but this yield is comparable to that obtained under argon. Table 6.3 presents the absolute and relative yields of I$_2$ for the four gases that were studied, and compares our findings with previous related studies. Given the differences in the experimental conditions, our results are in general agreement with those reported by Hart and Henglein (5) and Gueguen (11). Weissler's results (2) seem to indicate that under his experimental conditions dissolved gases were not critical. Nevertheless, the same investigator found zero I$_2$ yield under helium and carbon dioxide. It has to be noted that he measured iodine by titration with sodium thiosulfate and the concentrations that he reports for the experiments without CCl$_4$ may have been close to his analytical limit of detection.

While the overall effect of ultrasound on KI could be viewed as reaction of
Figure 6.4. Effect of dissolved gas on iodine yield; 1 M KI, 100 ml glass cell, $T_b \approx 28^\circ C$, 20 kHz, 75 W/cm².
Table 6.3
Effect of dissolved gases on KI sonolysis

<table>
<thead>
<tr>
<th>Gas</th>
<th>$k_o$ (\mu M \cdot min^{-1})</th>
<th>Yields relative to that under $O_2$</th>
<th>This work</th>
<th>(2)</th>
<th>(5)</th>
<th>(11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>2.20</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$Ar$</td>
<td>1.88</td>
<td>0.85</td>
<td>–</td>
<td>0.59</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Air</td>
<td>1.21</td>
<td>0.55</td>
<td>1.39</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$N_2$</td>
<td>0.25</td>
<td>0.11</td>
<td>0.91</td>
<td>–</td>
<td>0.25</td>
<td>–</td>
</tr>
</tbody>
</table>

This work: 20 kHz, 80 W; (2) Weissler, 1950: 1000 kHz, 310 W; (5) Hart & Henglein, 1985: 300 kHz; (11) Gueguen et al., 1957: 960 kHz
'OH radical with I' to produce I' and subsequent recombination of two iodine atoms to produce I₂ (R2 and R3 in Table 6.3), the free–radical chemistry of the system could be much more complicated. Table 6.1 and Table 6.2 present some of the equilibrium and free–radical reactions of the iodine system that may be relevant to I' sonication. Based on the equilibrium constant for equation E3, I' will be converted to I₂⁻, and diiodine radical could either recombine to give I₃⁻ and I⁻ (R4) or oxidize HOI with formation of IO⁻ (R6). It must be noted that there are several forms of I(VI) in addition to HIO₄⁻ and IO₄²⁻ (i.e., H₅IO₆⁶, H₄IO₆²⁻, H₂IO₅²⁻, HIO₃⁻) that could be important. Furthermore, reactions with O₂ or oxygen atoms, O, have not been included because of lack of appropriate data. Not enough information was found for high temperature gas phase reactions of I₂ in the gas phase of the cavities. It is expected that iodine atoms will be formed and it may be possible to have a radical chain mechanism involving additional oxidants (e.g., O₂, O, NO₂).

The observed increase of I₂ formation under argon can be explained by increased temperature during collapse. As discussed in Chapter 2, the presence of monoatomic gases in the imploding cavity results in higher T because of their higher ratio of specific heats, \( \gamma (\gamma \approx 1.7 \text{ for Ar, and } \approx 1.4 \text{ for O}_2, \text{N}_2, \text{air}) \). The fact that the thermal conductivity of Ar is about 70% lower than that of the other three gases should also favor higher local temperature upon collapse.

Comparing the effect of the three gases that have approximately the same \( \gamma \) (i.e., O₂, N₂, and air) it becomes clear that oxygen promotes the oxidation rate. The importance of O₂ has been reported before (5) and those researchers actually found that a mixture of 30% oxygen and 70% argon gives the highest I₂ yield. The addition of oxygen results in higher 'OH yields because of its high temperature reaction with hydrogen atoms to give 'OH and O [i.e., H + O₂ → 'OH + O]
In the absence of O₂, about 80% of the ·OH and H· radicals originally formed from thermal dissociation of water are lost due to recombination (20). Oxygen atoms are also formed by direct thermal decomposition of O₂ in the hot regions of the bubble and their reaction with OH₂ yields additional ·OH (O + OH₂ → ·OH + ·OH). On the other hand, increasing concentrations of oxygen in the gas phase lower the γ value of the mixture and result in less intense cavitation.

The lower yields under nitrogen can be explained by scavenging of ·OH and O in the gas phase by N₂ with formation of N₂O, NO initially and then HNO₂, HNO₃ (21). Hart et al. (22) observed that H₂O₂ formation upon sonication of water was ≈ 7.6 times higher under Ar than under N₂ (13 μM·min⁻¹ : ≈ 1.7 μM·min⁻¹). We found that I₂ yield under Ar was ≈ 7.5 times more than under N₂. This confirms that I₂ formation is closely related to the formation of H₂O₂.

It is easy to see that the I₂ yield under air is not simply the superposition of the iodine yields under O₂ and N₂ (i.e., \( \frac{d[I₂]}{dt}_{\text{air}} > \{0.29 \cdot \left[\frac{d[I₂]}{dt}\right]_{O₂} + 0.71 \cdot \left[\frac{d[I₂]}{dt}\right]_{N₂}\}\)). This result could be due to the fact that when both O₂ and N₂ are present in the cavities, N₂ scavenges oxygen atoms to form nitrogen oxides that will eventually result in increased concentrations of nitrogen dioxide radical into solution. This radical can oxidize I⁻ to I⁺ (R12). Therefore, more O or ·OH that would be otherwise 'lost' to H₂O₂ or H₂O₂ through recombination reactions is used to oxidize I⁻ in the presence of nitrogen. It is noted that HO₂ does not oxidize I⁻; but actually it is reducing I₂ or I₃ back to I⁻ (R13, R14). H₂O₂ on the other hand can oxidize I⁻ (R18) but that reaction is fast only in acidic solution and in the presence of catalyst (molybdate + I⁻ in acid solution is the standard method for measuring H₂O₂). Therefore, H₂O₂ is not expected to contribute significantly to I⁻ oxidation; Hart & Henglein's results collaborate that argument (5).
The disproportional enhancement of I\(_2\) formation under air, as compared to that under nitrogen, suggests that gas phase reactions of iodine species with O\(_2\), O or \(\cdot\)OH are not very important. If they were, the additional scavenging of those oxygen species by N\(_2\) should not be that important. It has to be stressed, however, that no effort was made to measure oxidized iodide species other than I\(_2\). It is therefore conceivable that the relative yields of I\(_2\) do not represent relative rates of overall I\(^-\) oxidation. Detailed study of the free-radical-ultrasound-induced chemistry of the iodide system was not within the scope of this work.

Samples taken immediately after bubbling showed no oxidation of I\(^-\) upon aeration or even oxygenation of the solution. This is in agreement with the known slow rate of I\(^-\) oxidation by molecular oxygen (23) and with simple observations made in this lab; the observed iodine in 1M KI solutions left in the dark was \(\leq 3.0 \mu\text{M}\) after 24 hours.

The agreement between control experiments, where KI solutions were sonicated without any prior bubbling, and air experiments, with 40 minutes bubbling of compressed air, shows that bubbling did not affect sonochemical yields. That suggests that under our experimental conditions, we are not limited in the number of available 'cavitation nuclei' or pre-existing gas bubbles. Additional evidence supporting that conclusion is presented in Chapter 7 (effect of fine sand on sonication).

**Conclusions**

The mechanism of KI sonolysis could be more complicated than the simple reaction of I\(^-\) with \(\cdot\)OH. Molecular oxygen clearly plays an important role in this free radical oxidation. High temperature reactions of I\(_2\) in the gas phase were
suspected but the effect of dissolved gases on I₂ yield seems to indicate otherwise.

Potassium iodide can be used as an overall sonochemical dosimeter but a closed system is necessary. Considerable amounts of the I₂ produced can be lost through evaporation (as much as 33% for the commercial Branson CD200 system with the 1/2-in. horn and the 50 ml total volume stainless steel cell). The I₂ yield is independent of pH in the neutral to alkaline region.
Ultrasonic Irradiation of Parathion

Introduction

Parathion (O, O diethyl–O–p–nitrophenyl thiophosphate) is one of the organic pesticides that are used in large quantities all over the world. Organic esters used to be considered as a "safer" alternative to DDT and other chlorinated hydrocarbons. Nevertheless, there has been evidence presented that suggests that organophosphates can be quite persistent under environmental conditions of natural waters (25). For example, at 20 °C and pH 7.4 parathion was reported to have a half-life of 108 days; its most toxic metabolite, paraoxon, had a half-life of 144 days (25).

Ultrasonic irradiation may present an alternative treatment method for the destruction of organics present in water systems (e.g., groundwater or surface waters contaminated by pesticides). In this section, the effect of ultrasonic irradiation on parathion–saturated aqueous solutions is reported.

Experimental

The ultrasonic irradiation of parathion–saturated deionized water was conducted with the experimental setup and under the same conditions that were used for the p–nitrophenol experiments (Chapter 3).

P–nitrophenol concentrations were measured spectrophotometrically as described in Chapter 3. Nitrite, nitrate, sulfate, phosphate, and oxalate ions were determined with a Dionex 2020i ion chromatograph and a Dionex AS4–A column. The eluent consisted of a mixture of 14.7 mM Ethylenediamine, 10 mM NaOH, 10 mM H₃BO₃, and 1 mM Na₂CO₃.
Results and discussion

Sulfate, nitrite, nitrate, p-nitrophenol (p-NP), phosphate, and oxalate were identified as products of parathion sonolysis. Figure 6.5 shows the evolution of these species with sonication time for an initially saturated parathion solution. The solubility of parathion in water is 82 μM (24 μg/ml) at 25 °C (26).

Since the observed [SO$_4^{2-}$] was ≈ 82 μM after two hours of sonication, we can conclude that all of the initial parathion was decomposed in ≤ 2 hours under our experimental conditions. Furthermore, [SO$_4^{2-}$] increased linearly with sonication time with a zero-order rate of ≈ 0.68 μM·min$^{-1}$. Figure 6.5 shows that [NO$_y$] + [p-NP], where [NO$_y$] = [NO$_2^-$] + [NO$_3^-$], were formed at the same rate. PO$_4^{3-}$ and C$_2$O$_4^{2-}$ were formed at a lower rate.

No buffers were used and the pH of the solution changed during sonication. The pH of the initial solution was 6.1. After half hour of sonication the pH dropped at 4.1 and remained close to that value thereafter (3.9 at 1 hr, and 3.7 at 2 hr).

At any pH, p-nitrophenol is found to be the major product of the hydrolysis of parathion (25). When hydrolysis is catalyzed by heavy metal ions, deethylation of parathion can also take place and a secondary ester of phosphoric acid appears as an additional product (27). The equations describing these two pathways of hydrolysis are as follows:

\[
\begin{align*}
(C_2H_5O)_2P-O-\text{NO}_2 & \rightarrow (C_2H_5O)_2P-OH + HO-\text{NO}_2 \\
\end{align*}
\]
Figure 6.5. Products of parathion sonication at 75 W/cm², T₀ ≈ 28 °C, pΗi₀ ≈ 6.0, and initial parathion concentration of ≈ 82 μM.
It is believed that at alkaline pH reaction (6.1) proceeds via nucleophilic substitution of the nitrophenolate group by OH\(^-\), while rupture of the O – C bond apparently occurs in the acidic pH region (28).

Our experimental results suggest that when parathion is subjected to ultrasonic irradiation both the P = S and the P – nitrophenolate bonds break and SO\(^4\)\(^-\) and p-NP are formed. Deethylation of the resulting diethyl phosphate moiety leading to the formation of PO\(^3\)\(^-\) and C\(_2\)O\(^2\)\(^-\) seems to follow at a slower rate. P-NP, which is the only toxic compound among these initial products, will decompose further during sonication (see Chapter 3) to NO\(_y\), benzoquinone, 4-nitrocatechol and organic acids (formate, acetate, oxalate), and eventually to NO\(_y\) and CO\(_2\). The overall effect of sonication on parathion is shown schematically in Figure 6.6.

Parathion has a low vapor pressure (26) and it is not expected to enter the cavities during sonication. It can be argued that the pathways for parathion sonolysis are the same as those accepted for the sonolysis of pNP, i.e., thermal decomposition in the interfacial region and reaction with \(^{\cdot}\)OH radicals (see Chapter 3). Further experimental work could provide enough data to assess the relative importance of those two pathways.
Figure 6.6. Schematic presentation of the effect of ultrasonic irradiation on parathion.
Conclusion

Ultrasonic irradiation of a parathion-saturated aqueous solution at 20 kHz and 75 W/cm² resulted in complete destruction of parathion within 2 hours. The observed products included inorganic species (sulfate, nitrate, phosphate) and simpler organics (mainly pNP and organic acids) that are known to degrade further under the action of ultrasound. Clearly, ultrasonic irradiation (US) has an advantage versus catalyzed hydrolysis of organophosphates; US results in harmless products, while many of the hydrolytic products (e.g., substituted phenols) may be toxic or cause taste and odor problems in water systems.
References


CHAPTER 7

EFFECT OF PHYSICAL AND CHEMICAL PARAMETERS ON SONOLYSIS OF CHEMICAL COMPOUNDS
Introduction

The effects of different parameters on the sonolysis yields of the chemicals studied are presented in this chapter. The observed effects are discussed in view of the sonolysis mechanisms proposed in the previous chapters. The parameters studied included: ionic strength and specific ions, input power, bulk solution temperature, dissolved gases, particles, sonication setup (reaction vessel and sonication unit type), and operation mode (flow through vs batch operation). Sonolysis of S(−II) in wastewater is also compared to that observed in clean water.

Results and discussion

Ionic strength and specific ions

No significant effect of the ionic strength on p–NP sonolysis yields was observed; sonolysis rates were the same in the presence or absence of nitrate or sulfate ions. On the other hand, p–NP sonolysis rates decreased in the presence of nitrite ions (Chapter 3).

Figure 7.1 presents the effect of NaCl and CaCl₂ on the sonolysis of S(−II) at alkaline pH. It can be seen that S(−II) decomposition rate increases with increasing electrolyte concentration. A plot of the logarithm of the observed initial zero–order rate, \( k_0 \), as a function of the square root of the ionic strength of the solution, I, is shown in Figure 7.2. This plot would seem to suggest that there is an effect of the cation too, i.e., that S(−II) sonolysis is enhanced by the presence of Ca\(^{2+}\). Nevertheless, when \( k_0 \) is plotted versus chloride concentration (Figure 7.3) the experimental results obtained with both NaCl and CaCl₂ fall on the same line,
Figure 7.1  Effect of a) NaCl and b) CaCl₂ on the sonolysis of S(−II); 
[S(−II)]₀ ≈ 200 µM, pH 10, SS cell.
Figure 7.2 Plot of $\log k_o$ vs $\sqrt{I}$, using data of Figure 7.1.
Figure 7.3      Plot of $k_0$ vs $[\text{Cl}^-]$, using data of Figure 7.1.
suggesting that the observed increase in $k_0$ is due to the presence of the Cl$^-$ ions and not to a general ionic strength effect.

Further evidence for a specific effect of halogen ions on the sonolysis of S(−II) were obtained when S(−II) was sonicated in the presence of I$^-$. Figure 7.4 shows the enhancement of S(−II) decomposition at pH 10 in the presence of 1M KI. Only trace amounts of iodine (I$_2$) were observed until practically all S(−II) was oxidized. This suggests that the intermediate species of the sonolysis of I$^-$ (Chapter 6) are used for the oxidation of S(−II) instead of forming I$_2$. The $E^0$ for the I$_2^-$/2I$^-$ couple is reported as 1.03 V, i.e., very close to the 1.08 V suggested for the HS/HS$^-$ couple (1). It is therefore plausible that I$_2^-$, which is expected to be the main intermediate of the I$^-$ oxidation to I$_2$ (see Chapter 6), is reduced back to I$^-$ while oxidizing HS$^-$ to HS$. I$^-$ is thus acting as a catalyst that enhances the rate of S(−II) sonolysis.

Comparing Figure 7.1 and Figure 7.4 it becomes clear that I$^-$ has a more significant 'catalytic' effect on S(−II) sonolysis than Cl$^-$. Since Cl$_2^-$ is a much stronger oxidant than I$_2^-$ [$E^0$ for the Cl$_2^-$/2Cl$^-$ couple is 2.09 V (1)], the experimental results suggest that larger amounts of oxidized iodide species are formed. It seems reasonable to assume that this is due to the fact that iodide is a softer and less polar species than chloride and therefore goes preferably in the interfacial region of the bubble. As discussed in Chapter 3, cavitation bubbles are essentially hydrophobic, thus hydrophobic compounds can accumulate in the hot surroundings of the interfacial region where they subsequently undergo high temperature reactions.

Further evidence for the suggested role of halide ions on the sonolysis of chemical compounds was obtained when p-NP was sonicated in the presence of 1M KI. Figure 7.5 shows that I$^-$ acts as an inhibitor in the case of p-NP. That is in
Figure 7.4  Effect of KI on $S(-II)$ sonolysis at pH 10.
Figure 7.5  Effect of KI on p-NP sonolysis.
line with the proposed mechanism for p–NP sonolysis. As discussed in Chapter 3, p–NP is also expected to undergo high temperature reactions in the interfacial region. The presence of the smaller I⁻ ions in the same region inhibits the thermal decomposition of p–NP. Furthermore, ·OH radicals are scavenged by I⁻ at or near the interfacial region thus preventing the secondary mechanism of p–NP sonolysis (i.e., reaction with ·OH).

Phosphate and borate ions had no effect on the sonolysis of S(−II) (see Chapter 4). On the other hand, carbonate and bicarbonate ions were shown to have an inhibitory effect on the sonolysis of S₂O₅²⁻ (Figure 7.6). These results can be explained by the fact that the first-order rate constants for the reaction of carbonate/bicarbonate with ·OH are at least 2 orders of magnitude higher than the corresponding first-order constants for phosphate or borate (see Chapter 4).

**Input power and temperature**

The effect of input power of the sonifier (P) and bulk temperature of the solution (Tₑ) on S(−II) sonolysis yields in alkaline pH are presented in Chapter 4 (Figures 4.11 and 4.12). S(−II) sonolysis in the alkaline pH region is attributed to free–radical oxidation (see Chapters 4, 5), and the negligible effect of Tₑ can be easily explained by the low activation energies of free–radical reactions. The zero–order rate of S(−II) oxidation increased linearly with P, for P up to ≈ 100 W (upper limit of the CD200 sonication unit). It is noted that care was taken to separate the effects of Tₑ and P: the temperature of the cooling system was varied so as to keep Tₑ constant. It is also noted that P values were calculated using calorimetry (Chapter 4). This method has been shown to give similar results to those obtained by measurement of the radiation pressure (2).
Figure 7.6  Effect of CO$_3^{2-}$/HCO$_3^-$ on the sonolysis of S$_2$O$_3^{2-}$. 
Dissolved gases

The two important properties that determine the effect of a particular gas on sonochemical reactions are its ratio of specific heats, \( \gamma \), and its chemical reactivity. The higher \( \gamma \) values of monoatomic gases result in more intense cavitation (i.e., higher T, P upon collapse). On the other hand, a diatomic gas, such as O\(_2\), that can participate in high temperature reactions inside the hot cavity enhances oxidative destruction of solutes by scavenging radical species that would otherwise recombine before reaching the solution phase and/or by providing additional excited species as a result of its thermal decomposition. The investigation of the ultrasonic oxidation of S(−II) has shown that dissolved molecular oxygen in particular can also play an important role by propagating a free–radical chain reaction initiated by \( \cdot \)OH. The production of I\(_2\) upon sonication of a KI solution in the presence of various gases is presented and discussed in Chapter 6.

Vessel type

In addition to the stainless steel cell (Chapters 3, 4, and 6), several glass vessels (total volume \( \simeq 40 \) – \( 200 \) ml) were used for some experiments so as to allow for visual observation of the sonicated solution. All vessels were water–jacketed and temperature of the sonicated solution was controlled using a water recirculation system. Calorimetry showed that the power delivered to the solution from the commercial CD200 sonicator with the 1/2-in. immersion–horn increased with increasing horn immersion, but was practically independent of the volume of the vessel. For example, for immersion depth of 1 cm and power dial set to 9 the input power ranged only from \( \simeq 74 \) W to \( \simeq 78.5 \) W for a small glass cell with 30 ml of
solution to a larger cell with 200 ml of solution. For the latter reaction vessel, the input power increased to \( \approx 89 \) and \( \approx 98.5 \) W for immersion depth 2.4 and 3.9 cm respectively.

Sonoluminescence experiments showed that cavitation intensity (as indicated by the light emitted from a luminol solution sonicated in the dark) is not uniform over the whole volume of the solution. Depending on the reaction vessel, solution volume, and horn immersion depth one or more regions of intense sonoluminescence were observed with the naked eye. The main region was always near the tip of the horn and extended down to the bottom of the reaction vessel when the distance between the tip and the bottom was less than \( \approx 1.5 \) cm. Sonoluminescence patterns were similar with those observed by Reynolds et al. (3) with the use of a high–gain image intensifier system (3, Figure 7.7). Unfortunately, the appropriate experimental set–up for the recording of these patterns was not available in our laboratory (i.e., photomultiplier or image intensifier system).

The cavitation–induced damage of simple commercially available aluminum foil was used as a qualitative probe of the ultrasonic field inside the stainless steel cell. The inside of the stainless steel cell was covered with aluminum foil and 25 ml of deionized water were sonicated for a few seconds. The aluminum foil covering the bottom part of the cell was shredded to pieces practically instantaneously while the aluminum foil covering the wall near the liquid/headsapce interface sustained only minor damage. These observations suggested that the more intense cavitation region is between the tip of the sonicator and the bottom of the reactor cell.

The observed initial S(–II) sonolysis rate at pH 10 and in a small glass cell (total volume \( \approx 40 \) ml) was similar to that obtained in the stainless steel (SS) cell under similar conditions (i.e., solution volume, bulk temperature, solution
Figure 7.7  Sonoluminescence patterns observed by (top) Reynolds et al. (1982), and (bottom) Crum & Reynolds (1985) with a direct immersion horn (reproduced from refs. 3 and 4, respectively).
composition). Nevertheless, the decrease of S(-II) in the glass cell did not remain linear with sonication time (see Figure 7.8). The available headspace was considerably lower in the glass cell as compared to the SS cell and one possible explanation is oxygen depletion that would result in a slower oxidation rate as discussed in Chapter 4.

**Particles**

The effect of two different sizes of silica particles was studied in the 40 ml glass vessel. Large sand particles (500 μm average size OTTAWA 30) were used to determine whether the presence of these particles would have an adverse effect on the sonication rate because of sound attenuation. No such effect was observed even at very high solids concentration (Figure 7.9). Fine particles (7 nm average size AEROSIL 380, Degussa) were used in an attempt to enhance cavitation by providing additional nuclei for bubble formation and thus result in an increased S(-II) oxidation rate. Figure 7.9 shows that these fine particles did not have an effect on the sonochemical rate of S(-II) oxidation in air-saturated water solutions at a concentration of 100 mg·l⁻¹.

The insignificant effect of sand particles at the sizes and concentration studied can be explained by the fact that air-saturated solutions already contain a large number of 'weak spots' that act as nuclei for the formation of cavities. This argument is strengthened by the absence of any observable effect of air bubbling on the sonolysis of iodide (Chapter 6).
Comparison between SS and Glass cell

$[S(- II)]_o = 200 \mu M$, $pH = 10$, $T_b = 39 \, ^oC$

Figure 7.8 Comparison between a glass sonication reactor (30 ml) and the stainless steel (SS) cell (25 ml); $[S(- II)]_o = 200 \mu M$, $pH = 10 \, ^oC$, $T_b = 39 \, ^oC$. 
Figure 7.9  Effect of silica particles on S(−II) sonication. IS: Sand particles (0.5 mm), IFS: fine amorphous silica particles (7 nm).
Continuous flow operation

A continuous flow experimental set-up that involves recycle of the solution to be sonicated (i.e., multiple passes through the sonicator and a holding reservoir where sampling is performed) was designed. S(-II) and KI solutions were sonicated in that set-up in order to compare the efficiency of the ultrasonic apparatus during flow-through operation to that of the batch mode operation. A schematic representation of the system is shown in Figure 7.10. Both the sonication vessel and the reservoir were closed to the atmosphere. The contents of the sonication cell are vigorously mixed due to the action of the ultrasound, and the reservoir is continuously mixed with a mechanical mixer. Therefore, both systems are CSTR's. The mathematical representation of the system is as follows:

Reservoir mass balance: \[ V_r \cdot \frac{dC_r}{dt} = Q \cdot C_s - Q \cdot C_r - k_{1r} C_r V_r \] (7.1)

Sonication cell mass balance: \[ V_s \cdot \frac{dC_s}{dt} = Q \cdot C_r - Q \cdot C_s - k_{os} V_s \] (7.2)

B.C. \[ C_r = C_s = C_0 \quad \text{at } t=0 \] (7.3)

where:

- \( Q \) = flow rate
- \( V_r, V_s \) = reservoir and sonication cell volume respectively
- \( C_r, C_s \) = reservoir and sonication cell S(-II) concentration respectively
- \( k_{1r} \) = first-order rate constant for S(-II) removal while in the reservoir
- \( k_{os} \) = zero-order rate constant for S(-II) removal due to sonication
Continuous Flow Sonication

Figure 7.10  Schematic representation of the continuous system used.
The solution of the system of the two ODE's (7.1) and (7.2) with the initial condition (7.3) is as follows:

\[ C_r = (C_0/b) \cdot A + (C_0/b)(D_r+D_s) \cdot B - [(D_r k_{os})/(D_s k_{1s} b)] \cdot C \]  \hspace{1cm} (7.4)

\[ C_s = (C_0/b) \cdot A + [C_0 c - k_{o2}/b] \cdot B - [(D_r k_{os} + k_{tr} k_{os})/(D_s k_{1s} b)] \cdot C \]  \hspace{1cm} (7.5)

where
\[ A = \lambda_1 e^{\lambda_1 t} - \lambda_2 e^{\lambda_2 t} \]
\[ B = e^{\lambda_1 t} - e^{\lambda_2 t} \]
\[ C = \lambda_2 e^{\lambda_1 t} - \lambda_1 e^{\lambda_2 t} + b \]
\[ b = [(D_r + D_s + k_{tr})^2 - 4D_s k_{tr}]^{0.5} \]
\[ c = D_r + D_s + k_{tr} \]
\[ \lambda_1 = -c/2 + b/2 \]
\[ \lambda_2 = -c/2 - b/2 \]
\[ D_r = Q/V_r = 1/\text{retention time in reservoir} \]
\[ D_s = Q/V_s = 1/\text{retention time in sonication cell} \]

The zero–order rate constant for the decrease of \([S(−II)]\) due to sonication, \(k_{os}\), can be calculated by fitting the experimental \(C_r\) values (\([S(−II)]\) profile with time in the reservoir) to equation (7.4). The other parameters are all known. The rate constant for the removal of \(S(−II)\) in the reservoir, \(k_{tr}\), is found from control experiments where a \(S(−II)\) solution (from the same stock that is used for the sonication experiment) is stirred in an identical reservoir under the same conditions (headspace, lighting etc.).
When $k_{1r} \approx 0$, equation (7.4) is simplified to:

$$C_r = C_0 - \left[\frac{(k_{os}D_r)}{(D_r+D_S)}\right] \cdot t - \left[\frac{(k_{os}D_r)}{(D_r+D_S)^2}\right] (e^{-(D_r+D_S)t} - 1)t$$  \hspace{1cm} (7.6)

and for $t >> 1/(D_r+D_S)$ the concentration in the reservoir is given by:

$$C_r = \left[C_0 + \frac{(k_{os}D_r)}{(D_r+D_S)^2}\right] - \left[\frac{(k_{os}D_r)}{(D_r+D_S)}\right] \cdot t$$  \hspace{1cm} (7.7)

In that case, $k_{os}$ can be easily calculated from the slope or the intercept of $C_r$ vs $t$.

Experimental $k_{1r}$ values were in agreement with the first-order rate constants expected for $S(-II)$ uncatalyzed oxidation by molecular oxygen (see Appendix A). Although these $k_{1s}$ values are low ($k_{1r} \leq 5 \cdot 10^{-4}$ min$^{-1}$), the use of (7.7) instead of (7.4) would involve an error of $\sim 8\%$ for the particular experimental setup ($V_s = 40$ ml, $V_r = 200$–1000 ml, $C_0 = [S(-II)]_0 = 200 \mu$M).

Figure 7.11 shows the fraction of $S(-II)$ remaining in the reservoir vs time for typical experiments where the sonication unit is the same as the one used for most of the experiments, i.e., CD200 sonifier, output power = 80 W (intensity at the tip 75 W$\cdot$cm$^{-2}$, 1/2-in. horn, SS cell. The sonicated volume was $V_s = 40$ ml (determined by the flow-through capacity of the cell). The flow rate was 165 ml/min and $[S(-II)]_0$ was 200 $\mu$M for all three experiments but $V_r$ was 200, 280 and 1000 ml respectively. The solid lines in Figure 7.11 are the best fit of the experimental data with equation (7.4). All three experiments were in agreement and gave $k_{os} = 5 \mu$M$\cdot$min$^{-1}$. Control experiments gave a first-order rate constant for $S(-II)$ removal in the reservoir $k_{1r} = 5 \cdot 10^{-4}$ min$^{-1}$. As expected, $k_{os}$ values do not change when the flow changes (not shown). The flow rate only affects the rate
Figure 7.11  Fraction of S(−II) remaining in the holding reservoir; Q=165 ml/min, 1/2-in. horn, 80 W, \([S(−II)]_0 = 200 \mu M\), pH=10, SS cell \((V_s=40 \text{ ml})\), \(V_f = 200, 280, \text{ and } 1000 \text{ ml}\).
of sulfide decrease in the reservoir, not the rate at which it is destroyed at the sonication unit. This rate of \( S(-II) \) oxidation in the sonication cell is 37% lower than the corresponding rate for batch sonication of a 25 ml solution. Continuous flow experiments where 1 M solutions of KI were sonicated with the same system at \( Q = 860 \text{ ml/min} \) and \( V_r = 280 \text{ ml} \) gave \( k_{os} = 8 \mu\text{M/min} \), i.e., a reduction of 38% as compared to the batch experiments (again, performed with a 25 ml solution). This is in perfect agreement with the \( S(-II) \) results. It can be therefore concluded that operation of this type of sonifiers in the flow-through mode does not greatly change the efficiency of the unit (in terms of the total amount of the chemical of interest destroyed per unit of total energy input). It must be noted that during batch operation filling the SS cell near maximum capacity with 40 ml of solution results in decrease of the observed reaction rate (about 17% decrease as compared to sonication of 25 ml; see Figure 4.10). Therefore, the \( \approx 37\% \) decrease mentioned above corresponds to an actual \( \approx 24\% \) \( = (0.63/0.83) \times 100 \) decrease in the efficiency of the unit under flow-through operation.

**Sonication unit**

A larger sonifier (VC1500) was tested with a power supply of up to 1500 W, and with a horn of 3/4-in. diameter. A special stainless steel flow-through chamber (FTC) was also acquired for continuous flow operation with VC1500. Initial experiments showed that continuous sonication of \( S(-II) \) using the new chamber and the larger unit was only \( \sim 60\% \) faster than the smaller unit with the 1/2-in. horn and the stainless steel cell. Figure 7.12 shows this difference; for \( [S(-II)]_0 = 200 \mu\text{M} \) and \( V_r = 280 \text{ ml} \) the \( k_{os} \) in the FTC/VC1500 system is 8 \( \mu\text{M} \cdot \text{min}^{-1} \) as compared to 5 \( \mu\text{M} \cdot \text{min}^{-1} \) in the SS/CD200. It must be noted that \( V_s \)
Figure 7.12  Continuous flow sonication; comparison of the effect of two different sonication units on the fraction of $S(\text{-II})$ remaining in the reservoir; $V_r = 280 \text{ ml}$, $[S(\text{-II})]_o = 200 \mu\text{M}$, pH 10.
for FTC was 36 ml which is close to the 40 ml capacity of the stainless steel cell.

Experiments with the VC1500 but the 1/2-in. horn and the stainless steel cell gave identical results as the smaller unit (CD200) for both S(II) and KI. Figure 7.13 shows the increase in the absorbance at 350 nm (directly proportional to the concentration of iodine) for the two power supply units CD200 and VC1500 both with the SS cell. The actual input power, as calculated from temperature data, was not much different and it seems that there is a limit to the energy that can be taken by a liquid from the 'direct immersion horn' type of sonicators. In that case the sonochemical efficiency is not affected by the use of a larger power supply since the 1/2-in. horn is not drawing more power even though it is available to it. Figure 7.14 shows again the results of the batch sonication of 1 M KI solution in the SS cell with the CD200 unit and the VC1500 unit now operating under three different nominal power outputs. It can be seen that increasing the nominal power output (i.e., turning the power dial of the unit at 60%, 40% and 20% of the maximum available power of 1500 W) does not increase the rate of KI formation even though the temperature data (see Figure 7.15) show that the energy transferred to the solution increases with increasing power. This latter result can be due to increased mechanical stress on the titanium horn/tip resulting in overheating of the horn and subsequent heating of the sonicated liquid.

In an attempt to achieve full benefit from the larger power unit, a 'cup-horn' type sonicator was used. Figure 7.16 shows a schematic diagram of that ultrasonic apparatus; it is connected to the power supply in a similar way as the direct immersion horn used previously. The main difference is that there is a much larger radiating surface (of 7.5 cm diameter) instead of the 1/2-in. or 3/4-in. titanium tip and there need be no coupling of a transducer with a tip (which was suspected to be
Figure 7.13  Sonication of 1 M KI solution. Continuous flow (C) and batch (b) operation using two different power supplies with the same SS cell and 1/2-in. horn.
Figure 7.14  Sonication of 1 M KI using SS/VC1500 at different nominal output powers.
Water heating during sonication

VC1500, SS cell, V=25ml, no cooling

Figure 7.15
Rise in temperature of 25 ml water with sonication time; SS/VC1500, different nominal power (e.g., power output = 20 means that maximum nominal power is 20% of 1500 W). Sonication stopped at t=120 sec.
Figure 7.16   Schematic diagram of cup–horn sonication reactor configuration.
the problem with the direct immersion horn). An important point is that because of the larger surface area of the radiating surface of the cup–horn (44.2 cm² as compared to \( \approx 1.2 \) cm² for the 1/2-in. titanium tip) the intensity of the sound field delivered to the solution is much lower (intensity = power/vibrating area). If the solution to be irradiated is placed in a reaction vessel inside the water that is in contact with the radiating surface (as shown in Figure 7.16) the ultrasonic intensity inside the reaction vessel is even lower because of sound attenuation due to the bottom of the vessel. The height of the liquid above the radiating surface (\( h \)) is also very important; \( h \) must be an integer multiple of the wavelength of the sound waves (\( \lambda \)) in order for a stable sound field to be established.

Preliminary experiments with the configuration shown in Figure 7.16 were successful in establishing a sound field that would result in observable sonochemical effects. Figure 7.17 illustrates the change in color of an initially clear KI – CCl₄ – starch solution sonicated in a 50 ml flask inside the cup horn. Figure 7.18 compares the sonochemical yield of iodine in the flask/cup horn system to that observed with the direct immersion horn and different reaction vessels. It can be seen that sonochemical yields in the former system were rather low and results were not always reproducible. Therefore, that type of experimental set–up was not used further. A series of experiments were performed in the cup horn using the membrane surface for direct sonication of the solution of interest. This practice can result in damage of the radiating surface in the long–run but did not have any obvious short–term effects. Of course, the cup horn was washed repeatedly after each experiment and it was 'self–cleaned' by sonicating deionized water for a prolonged time.
Figure 7.17  KI – CCl\textsubscript{4} – starch solution sonicated inside a flask in the cup horn.
Figure 7.18  Comparison of the $I_3^-$ release during sonication of a 1M KI solution with the direct immersion horn (and different reaction vessels) and the cup horn with a 50 ml flask.
Figure 7.19 shows the results of continuous flow sonication experiments for S(−II) and KI respectively with the VC1500 power supply unit connected to the cup–horn and operating at 50% nominal power. The solution to be sonicated was introduced through the coolant inlet and left the system via the coolant overflow port (shown in Figure 7.16). The height of the irradiated solution was 5.8 cm (irradiated volume = V_s = 270 ml) and Q = 320 ml/min, V_r = 1500 ml for both experiments. From temperature data the input power was calculated to be 330 W giving an ultrasonic intensity at the radiating surface of 7.5 W·cm⁻² and an energy input of 3.2 J·ml⁻¹·s⁻¹. The zero–order sonolysis rate constants, k(0s), calculated from the experimental data were 10 and 16 μM/min for S(−II) and KI, respectively. These rates are twofold faster than the continuous flow experiments performed with the unit connected to the 1/2-in. 'direct immersion horn' [for both S(−II) and KI]. In the latter case, the power input was ≈ 3.2 W·ml⁻¹ and the ultrasonic intensity at the horn tip was 75 W·cm⁻². The total amount of S(−II) or I⁻ oxidized per unit of input energy during direct sonication in the cup–horn is 5.2 [= 2 × (3.2/1.2)] times higher than in the case of the direct immersion horn. Therefore, a reactor configuration in which the solution is directly sonicated by relatively large surface area membranes seems to be more efficient as compared to the direct immersion horn configuration. It must be noted that those experiments gave increased k(1r) values, especially for iodide [6·10⁻³ and 7.5·10⁻² min⁻¹ for S(−II) and KI respectively] which accounts for the loss of linearity of the concentration vs time profiles (Figure 7.19). For KI this could mean that part of the iodine that is formed upon sonication escapes from the solution (larger open surface in the sonication vessel in this configuration).
Figure 7.19 Continuous flow sonication with Cup–Horn/VC1500, $Q=300$ ml/l, $V_s=270$ml, $V_r=1500$ml. (a, top) $[S(-II)]_0=200$ μM, pH=10; solid line for $k_{os}=10$μM/min, $k_{tr}=0.006$min.$^{-1}$ (b, bottom) 1M KI; solid line for $k_{os}=16$μM/min, $k_{tr}=0.075$min.$^{-1}$.
Wastewater

Wastewater collected from the inlet of San Jose Creek Water Reclamation Plant was used for a series of batch sonication experiments. The raw wastewater was spiked with S(–II) and was diluted with borate buffer (20% of buffer per volume in the final solution) to raise the pH at a value of \( \approx 10 \). Under the same experiments conditions that were used for the deionized water sulfide experiments described in Chapter 4 (i.e., CD200 sonication unit at 20 kHz, 75 W · cm\(^{-2}\), 25 ml solution in stainless steel cell) the initial rates of S(–II) oxidation were similar to those observed in deionized water.

Figure 7.20 shows the profile of \([S(–II)]\) with sonication time for a typical experiment at pH 10 (20% borate buffer). The straight line represents the linear S(–II) decrease observed in deionized water under the same experimental conditions. It can be seen that in the case of wastewater there is a divergence from this line at longer sonication times. This is most likely due to oxygen depletion (see Chapter 5). It is also possible that other oxidizable species present in wastewater interfere with S(–II) sonolysis at low sulfide concentrations by competing for the available oxidants (mainly \( \cdot \)OH, \( O_2 \), \( O_2^- \)).

Repeated experiments confirmed that the depletion of S(–II) during sonication in alkaline pH was best described by a first order reaction. The effect of initial sulfide concentration, \([S(–II)]_o\), on the first-order reaction constant, \( k_1 \), is shown in Figure 7.21. It can be seen that the rate of S(–II) oxidation increases with increasing \([S(–II)]_o\). The following experimental expression was obtained:

\[
k_1 = 9.1 \cdot 10^{-4} \cdot [S(–II)]_o^{0.535}, \ r^2 = 0.9
\] (7.8)

where \( k_1 \) is in min\(^{-1}\) and \([S(–II)]\) in M.
Comparison between water and wastewater

$pH=9.5, [S(-II)]_0=130\mu M$

Figure 7.20  
S(-II) sonication in wastewater (20% borate buffer); $pH=9.5$, $T_b = 39$ °C.
Figure 7.21   S(−II) sonication in wastewater; Effect of $[S(−II)]_o$ on first-order reaction rate constant.
Conclusions

The observed effects of bulk solution temperature and dissolved gases on the sonolysis of the chemicals studied are in agreement with the sonolytic mechanisms proposed for these chemicals and the existing acoustic cavitation theory. General ionic strength effects do not appear to be important for the sonolysis of chemicals, but specific ions (e.g. halogens) can have significant catalytic or inhibitory effects. These ions can react with \('\mathrm{OH}\) radicals or can be involved in high temperature reactions at or near the interfacial region of cavitating bubbles. In either case, they can either interfere with the reactions of the chemical of interest, or provide additional oxidants for its destruction.

Sonication of \(\mathrm{S}(-\mathrm{II})\) in wastewater produces similar results as sonication of aqueous \(\mathrm{S}(-\mathrm{II})\) solutions. The experimental results obtained for the \(\mathrm{S}(-\mathrm{II})\) system suggest that the free–radical oxidation reactions were not affected significantly by the complex wastewater matrix. This result is an encouraging sign for the potential of ultrasound as an alternative method of wastewater treatment.

Experimental results obtained with the use of two different power supply units and three different reactor configurations showed that \(i\) the nominal power output of a sonication unit is not a good indication of its sonochemical efficiency, \(ii\) sonication units with larger radiating surfaces are a better choice than localized application of high intensity ultrasound; there is a limit to the 'acoustical energy' that can be delivered to a solution with the direct–immersion–horn type of sonicators, and \(iii\) commercial sonicators of the direct–immersion–horn type have similar sonochemical efficiency for both batch and flow–through operation. Scale–up of the sonication process is not evident and more work in this area is needed.
References


CHAPTER 8

CONCLUSIONS
Conclusions

- Oxidizable inorganic and organic chemical compounds decompose rapidly when exposed to ultrasonic irradiation. Sonodegradation time scales range from minutes to hours with the ultrasonic devices used in this study. For example, $\tau_{1/2}$ for 100 $\mu$M H$_2$S at neutral pH sonicated with an immersion horn at 20 kHz and 75 W·cm$^{-2}$ is $\approx$ 2 minutes. In the same ultrasonic apparatus, $\tau_{1/2}$ for p–nitrophenol (p–NP) and parathion degradation is about 30 minutes and 1 hour, respectively.

- Sonolytic decomposition mechanisms are similar to those observed in radiolysis and combustion chemistry. The ultrasonic degradation of H$_2$S, p–NP and parathion can be explained, in part, by reaction with ·OH radicals generated from dissociation of water upon sonication and by thermal decomposition. The relative importance of those two degradation pathways depends mainly on the ability of the chemical of interest to enter into the gas phase of the cavitating bubbles or to accumulate in the interfacial region of the cavities.

The observed reaction kinetics and product distributions suggest that reaction with ·OH is the principal pathway for the sonolysis of H$_2$S at pH $\geq$ 10 (where H$_2$S is mainly present in the form of HS$^-$) but thermal decomposition of H$_2$S within or near collapsing cavitation bubbles is the predominant pathway at pH $\leq$ 8.5.

The sonochemical degradation of p–nitrophenol appears to proceed via high-temperature pyrolytic reactions in the hot surroundings of the cavitation bubbles. The main reaction pathway appears to be carbon–nitrogen bond cleavage. Reaction with ·OH appears to be a secondary reaction pathway. Thus, we have
shown that thermal decomposition can be the dominant sonodegradation pathway even for non-volatile organic compounds. These chemicals were previously thought to degrade primarily via reaction with 'OH. Based on the reaction products and the kinetic observations during p-nitrophenol sonolysis and with the use of chemical thermometry, the average effective temperature of the interfacial region surrounding the cavitation bubbles has been estimated to be ≈ 800 K (direct immersion probe, at 20 kHz and 75 W·cm⁻²).

- The sonolytic oxidation of H₂S at pH ≥ 10 was successfully modeled with an aqueous-phase free-radical chemistry mechanism. This model development assumed a continuous and uniform 'OH input into solution from the imploding cavitation bubbles. This result suggests that the use of simplified approaches for modeling the liquid-phase sonochemistry of a well-mixed solution may be justified when 'OH radical reactions predominate. For the immersion probe at 20 kHz and 75 W·cm⁻², the effective 'OH uniform release into the bulk solution was estimated to be 3.5 μM·min⁻¹ with a corresponding steady-state 'OH concentration of ≤ 0.1 μM.

- Sonolytic reaction yields and overall reaction rates depend on various physical and chemical parameters. The observed effects of the parameters studied in this work are in qualitative agreement with the sonolysis mechanisms proposed for the chemicals of interest and the existing hydrodynamic theories of acoustic cavitation.

We have shown that the presence of other chemical constituents can influence significantly the outcome of the sonolysis of the chemicals of interest. For
instance, halogen ions promote the sonolytic degradation of S(−II) at alkaline pH while the same ions inhibit the sonolysis of p-nitrophenol. However, the ionic strength of the solution does not appear to have a direct effect on sonochemical reactions (i.e., the presence of 'sonochemically inert' ions such as sulfate or nitrate did not affect sonolytic yields).

A direct linear relationship between the applied power at 20 kHz and the observed rate of S(−II) sonodegradation has been found. However, bulk solution temperature did not have a pronounced effect on the oxidative destruction of that chemical.

Sonication of a KI solution in the presence of different gases showed that the nature of the dissolved gases plays an important role in aqueous sonochemistry. The relative iodine yields are 1.00 : 0.85 : 0.55 : 0.11 in the presence of O₂, Ar, air, and N₂, respectively.

The study of S(−II) sonolysis showed that oxygen can also play an important role by propagating a free-radical chain reaction initiated by 'OH. Furthermore, sonication seems to enhance the oxygen transfer to solution from the atmosphere.

The ultrasonic degradation of p-NP and S(−II) were shown to depend on the pH of the solution; in both cases oxidation rates increased with decreasing pH. However, iodide sonolysis was not affected by pH. It appears that pH does not affect the primary sonochemistry of water (i.e., intensity of cavitation, formation of excited species), but can have a significant effect on the sonochemistry of the solute especially if it has a pH-dependent speciation.

Addition of fine particles in the sonicated solution or air bubbling prior to sonication did not affect sonochemical yields. That suggests that the efficiency of sonolysis with an immersion probe in deionized water is not limited in the number
of available 'cavitation nuclei' or pre-existing bubbles.

Sonication of \( S(-II) \) in wastewater indicates that sonochemical free-radical reactions are not significantly affected by the complex wastewater matrix.

- Sonication with an ultrasonic device with a larger radiating surface (cup-horn type) resulted in faster and more efficient oxidation than localized application of high intensity ultrasound (direct-immersion-horn type). The operation of the direct-immersion-horn type sonicator with the commercial stainless steel cell in the flow-through mode resulted in only a modest decrease in the sonochemical efficiency of the unit (\( \approx 24\% \) decrease in the amount of chemical oxidized per unit energy supplied to the system). Results obtained from batch experiments with that configuration can therefore be extrapolated to continuous flow operation.

- Sonolysis is relatively inefficient with respect to utilization of the gross input energy. Less than 1\% of of the total energy supplied to the system is used in the actual production of free-radical reactions with the ultrasonic setups used in this work. Even so, the relative efficiency of ultrasound in terms of the total power consumed per mole of \( \text{p-nitrophenol degraded per liter of water} \) is superior to photolysis.

- Ultrasound has the potential to become a viable alternative for the destruction of chemical contaminants in water and wastewater. Its low energy utilization efficiency would currently limit its potential use to relatively low-flow specific applications such as groundwater remediation, or pretreatment of industrial
wastes where, despite the high cost, this method could still compete with alternative technologies for the treatment of hazardous and persistent chemicals mainly because of its high effectiveness and its relatively easy and flexible operation. There is room for improvement of sonochemical efficiency by optimizing reactor design and physical/chemical operation conditions.

**Recommendations for future research**

- A model that includes both gas and liquid-phase chemistry and incorporates the physics of bubble collapse and bubble clouds dynamics would offer a more realistic and comprehensive mathematical representation of sonochemistry.

  However, the development of such a model is not feasible at this stage because of lack of enough information about the number and size distribution of cavitation bubbles under intense sonication, about the dynamics of bubble clouds and about the physical conditions inside the bubble and its surrounding region upon collapse. Research in the above areas is necessary before mathematical models coupling the chemistry and physics involved in sonochemistry can be developed.

- The overall mechanisms involved in the ultrasonic decomposition of chemical compounds are now relatively well understood. However, more research is needed in order to gain an insight into the chemical and physical phenomena occurring in microscopic scale. Minimal information exists concerning the physical and chemical conditions inside and in the vicinity of imploding bubbles and the temporal and spatial concentration profiles of excited species and solute molecules.
Ultrasound has the potential to become a competitive technology for water and wastewater treatment. However, more research is needed to address issues such as optimal reactor design and ultrasound-induced mixing, degassing, and cavitation damage before large-scale applications can be considered. The effects of temperature, ionic strength, and ultrasonic intensity should be studied further with different substrates. The effects of frequency and pressure should also be addressed.

It is recommended that a high intensity flow-through sonication system that uses sound reverberation between two flat plates (Near-field Acoustical Processor) be tested. This system is expected to have a higher efficiency and it should be relatively easy to scale-up.
APPENDIX A

Catalytic Autoxidation of Hydrogen Sulfide in Wastewater

(Environmental Science & Technology, 1991, 25, 1153)
ABSTRACT

The catalytic effectiveness of cobalt(II)–4,4',4'',4'''-tetrasmephtalocyamine [Co(II)TSP] for the autooxidation of hydrogen sulfide, S(–II), in wastewater was investigated. At pH 7 and 25°C the rate of S(–II) oxidation is first-order with respect to [S(–II)]. A fractional order on the catalyst was observed. At oxygen concentrations 15 to 200 µM the oxygen dependence can be described by simple Michaelis–Menten kinetics with $K = 63$ µM. The uncatalyzed oxidation of sulfide by molecular oxygen was found to be faster in wastewater than in clean water. This difference was attributed to microbial oxidation of S(–II) and to catalytic action of transition metals present in wastewater.
INTRODUCTION

Corrosion of concrete structures by sulfuric acid generated due to the presence of hydrogen sulfide is a problem often encountered in wastewater collection systems (1–3). Domestic sewage contains sulfates and other sulfur compounds, which under anaerobic conditions can be reduced to sulfides. Various industries may also discharge sulfur in the form of sulfides (e.g. tanneries, abattoirs, fell morgering works, coal–gas works, oil refineries, sulfur dye works). In partially filled sewers, hydrogen sulfide may be transferred from the liquid phase to the gas phase and finally to the crown of the sewer where it is oxidized in the presence of thiobacilli to H₂SO₄. The generation of acidity on the crown results in the corrosion of the concrete (1).

The problem of corrosion of concrete pipes due to the presence of hydrogen sulfide has been a focus of attention for many years (1–3). Aeration of wastewater, by compressed air or pure oxygen, is one of the control measures commonly employed in sewers to oxidize sulfides while still in the liquid phase (1–2).

In general, the oxidation of reductants such as H₂S by O₂ proceeds slowly in the absence of catalysts (4–13) because of unfavorable spin state symmetries that result from the differences in the electronic configurations of the reactants. Transition metal ions and complexes are usually effective catalysts because they are able to alter the electronic structure of either H₂S or O₂ in order to surmount the activation energy barrier imposed on the reaction by spin–state symmetry restrictions.

The oxidation of S(–II) {i.e., H₂S, HS⁻, S²⁻} by oxygen has a complicated stoichiometry because of the wide array of products and metastable intermediates
produced during the course of the reaction. Products and intermediates which have been identified (4–13) include: \( S_n \) (colloidal sulfur), \( S_8 \) (elemental sulfur - orthorombic), \( S_2O_3^{2-} \) (thiosulfate), \( SO_3^{2-} \) (sulfite), \( S_4^{2-} \) and \( S_8^{2-} \) (polysulfide ions), \( S_4O_6^{2-} \) (tetrathionate) and \( SO_4^{2-} \) (sulfate). The major products and intermediates, \( S_8, SO_3^{2-}, S_2O_3^{2-} \), and \( SO_4^{2-} \) are formed according to the following stoichiometries:

\[
8 \text{H}_2\text{S} + 4 \text{O}_2 \rightarrow S_8 + 8 \text{H}_2\text{O} \quad (1)
\]

\[
\text{H}_2\text{S} + \frac{3}{2} \text{O}_2 \rightarrow 2 \text{H}^+ + SO_3^{2-} \quad (2)
\]

\[
SO_3^{2-} + \frac{1}{8} S_8 \rightarrow S_2O_3^{2-} \quad (3)
\]

\[
\text{H}_2\text{S} + 2 \text{O}_2 \rightarrow 2 \text{H}^+ + SO_4^{2-} \quad (4)
\]

The actual time-dependent distribution of products and intermediates depends on pH and the concentrations of the catalyst, \( S(-II) \) and oxygen employed (4, 6).

Previous studies (5, 9–10) have shown that cobalt(II) and nickel(II) are the most effective catalysts for oxidation of \( \text{H}_2\text{S} \). Cobalt(II) \( 4,4',4'',4'''\)-tetrasulfophthalocyanine has also been reported to be an effective catalyst for the homogeneous and heterogeneous autoxidation of reduced sulfur compounds (4, 14–16). However, its effectiveness in complicated matrices such as wastewater had not been established.

The catalytic effectiveness of cobalt(II) \( 4,4',4'',4'''\)-tetrasulfophthalocyanine [Co(II)TSP] for \( \text{H}_2\text{S} \) oxidation was studied in wastewater obtained from a tertiary wastewater treatment plant in Los Angeles County. The kinetics of \( S(-II) \)
oxidation in the influent were investigated and empirical rate laws were determined.

EXPERIMENTAL SECTION

Preparation of Cobalt(II)–tetradsodium–tetrasulfophthalocyanine

Cobalt(II) 4,4',4'',4'''–tetrasulfophthalocyanine, Co(II)TSP, is a square–planar complex in which the metal center is bonded to the four pyrrole nitrogens of the ligand. The tetradsodium salt CoNa₄C₃₂H₁₂N₈O₁₂S₄·6H₂O was prepared based on the procedure described originally by Weber (17–18) and subsequently modified by Boyce et al. (14). In our preparation the following modifications to the original procedure were made: The monosodium salt of 4–sulfophtalic acid was prepared from 4–sulfophthalic acid and an equimolar concentration of sodium hydroxide. Sulfophthalic acid is usually a 50% water mixture; most of the water was evaporated to give a yellow/brown oil. Addition of excess ethanol and then equimolar sodium hydroxide as a solid with stirring to prevent overheating results in the precipitation of an almost white solid of the 4–sulfophthalate. The salt was washed with ethanol and dried in a desiccator overnight. Cobalt(II) in the form of cobalt(II) chloride hexahydrate was added and carefully mixed but not ground (grinding leads to a purple hygroscopic solid) to the prescribed mixture of 4–sulfophthalate, ammonium chloride, urea and ammonium molybdate. After the prescribed treatment with nitrobenzene and methanol excess Co(II) was extracted from the product by dissolving the solvent–free product in a solution of 1N HCl/75% ethanol, saturated with NaCl at 4 °C. Heating to 60 –
80°C accelerates the process and cooling in the refrigerator overnight precipitates most of the solid as a very fine powder (slimy), which was separated by filtration. The resulting precipitate was dissolved in 150 ml solution of 50% ethanol/0.1N NaOH, saturated with NaCl at 4 °C, and heated for 1 hour at 80 °C. After cooling the solution in the refrigerator overnight, the almost clean dark blue product was filtered. Excess chloride was washed out by heating the solid with 100 ml 70% ethanol for 1 hour to 60 °C, followed by filtration of the hot mixture. This process was repeated (3–6 times) until no Cl\(^-\) could be detected in the solution (no white AgCl precipitate upon addition of AgNO\(_3\)). Organic impurities were extracted by refluxing the pure product 3 times with absolute ethanol for 1 hour, followed by filtration of the hot mixture. The blue pure product was dried overnight in a desiccator. The elemental analysis (theoretical values in given brackets) for the final product was as follows: C: 35.52% (35.34%); H: 2.59% (2.23%); N: 9.93% (10.30%); S: 11.79% (11.43%); Na 7.76% (8.45%); Co 5.09% (5.42%). UV/VIS spectra were identical to those described in a previous report (4).

Reagents

All reagents were of analytical grade. Doubly-distilled (18 MΩ–cm) deionized water was used for the preparation of all solutions. S(II) stock solutions were prepared from Na\(_2\)S·9H\(_2\)O crystals (Aldrich) that had been washed with deionized water and dried. The actual concentrations were determined by potentiometric titration with Pb(ClO\(_4\))\(_2\) (Orion). Stock solutions were stored in a refrigerator and no significant decrease in sulfide concentration was detected during a period of approximately 10 days. Mixtures of mono and disodium phosphate salts (Mallinckrodt) were used as buffers. Sodium perchlorate (EM Science) was used to
adjust the ionic strength of the reaction solutions.

**Experimental Apparatus**

Experimental techniques and apparatus used in this study were similar to those described previously (4, 6–8). Experiments were conducted in sealed water-jacketed, glass reaction vessels with a total volume of 1.5 to 2.0 l. The design and operation of the batch reactor system have been described previously (4, 15). An aluminum cover was used to protect the reaction solution against light. To minimize the potential catalytic effect of trace-metal contaminants, all glassware was washed with phosphate free detergent (Alconox), soaked in dilute HNO₃, and then rinsed several times with deionized water.

Two types of Dissolved Oxygen (DO) probes were used in order to measure oxygen concentrations. Concentrations above 0.4 mM were measured with an INGOLD type 531 oxygen electrode with coupled amplifier, linked to a RADIOMETER ion 83 ionmeter, while for concentrations below 0.4 mM an ORION 97–08–00 oxygen electrode was used. Sulfide concentrations were measured with a sulfide ion electrode (ORION 94–16 Ag/Ag₂S with double junction reference electrode) coupled to an ORION 801–A ion analyzer. pH measurements were performed with a RADIOMETER pH electrode and a PHM84 pH meter. An automatic titration system (autoburette ABU12 and titrator TTT60) was utilized to control pH in the absence of a buffer. The temperature was maintained constant at 25°C with the use of a HAAKE A80 water circulation and temperature controlling system. Spectrophotometric measurements were performed on an HP 8450A UV/VIS spectrophotometer. An AMSCO 2022 autoclaving apparatus was used to autoclave wastewater at temperature 120 °C and pressure
20 psi. All instruments were interfaced to an IBM-AT computer for data collection. During an experiment, data from all but the sulfide electrodes were taken continuously (every 10 seconds) and stored for later analysis.

All electrodes were calibrated at regular time intervals and showed no significant drift with time. The sulfide ion specific electrode (ISE) was calibrated both for clean water and wastewater. The EMF versus concentration response of the electrode was found to follow the Nernst equation with similar slopes in both systems.

**Kinetic Data**

Control experiments in Milli-Q water were conducted in buffered solutions (mono/disodium phosphate buffer, pH=6.6, I=0.4M), at constant temperature (T=25°C), under oxygen saturation, and in the presence of various catalysts [Co(II)TSP, NiCl₂, CuCl₂]. The buffer/catalyst mixture was purged with pure oxygen gas (PO₂ = 1 atm) until oxygen saturation was established (initial oxygen concentration 1.2 mM). Reactions were initiated by adding a known volume of sulfide stock solution. Initial experiments with the sulfide electrodes immersed in the reaction medium gave inconsistent results. Intermediates such as polysulfides and elemental sulfur were found to interfere with the Ag₂S electrode measurements. These interferences were overcome by taking samples periodically from the reaction vessel, using a syringe through a septum in one of the reaction vessel openings, and analyzing for sulfide after dilution 1:1 with SAOB (sulfide antioxidant buffer: a mixture of 67g Na₂EDTA, 35g ascorbic acid, 80g NaOH in 1000 ml). In selected experiments, UV/VIS spectra of samples were also taken during the course of the reaction.
Wastewater experiments were performed at pH 7 and T = 25°C in the presence or absence of Co(II)TSP and at various initial oxygen concentrations. Oxygen concentrations were established by dispersing oxygen gas, compressed air, or a mixture of oxygen and nitrogen gas into the wastewater. At the end of aeration, pH was adjusted to 7.0 using perchloric acid and the appropriate amount of sulfide stock was added. Even though no buffer was added the pH of the medium remained constant during the experiment. Sampling and measurement techniques were the same as those used in the control water experiments.

For a reaction that is first order with respect to total sulfide (i.e. pseudo–first–order conditions of constant pH, T, and ionic strength with \([O_2] \gg [S(-II)]\) or \([O_2]\) held constant, \(d[S(-II)]/dt = -k_{obs}[S(-II)]\)), a plot of the sulfide–specific electrode potential, \(E_h\), versus time should yield a straight line with a positive slope equal to \(\frac{RT}{nF} \cdot k_{obs}\) (7). In that case the pseudo–first–order constant \(k_{obs}\) can be readily obtained from

\[
k_{obs} = \frac{2F}{RT} \frac{dE_h}{dt}
\]

where \(\frac{2F}{RT} = 7.785 \times 10^{-2} \text{ mV}^{-1}\) at 25°C.

The empirical rate law was deduced from data sets accumulated for the observed pseudo–first–order rate constants under a variety of initial conditions, using the principle of the initial rates method (19). It is noted that the order obtained by this method deals with initial slopes (in this case initial \(k_{obs}'s\)) and the change in concentrations of reactants is small in the initial stage of the reaction. Therefore, the validity of the method does not change materially even if the concentrations of the reactants that are assumed to remain constant are not in
excess, as long as these initial concentrations are kept the same for all experiments of a particular data set (10, 23).

RESULTS AND DISCUSSION

Kinetic results in water

Kinetic measurements of the sulfide autoxidation in the control experiments with clean water were performed in near neutral oxygen saturated water (pH 6.7, \([O_2]_o=1.2\) mM) at \(T = 25\) °C, using Co(II)TSP, Cu(II) and Ni(II) as catalysts. The catalyst concentrations ranged from 0.01 to 100 \(\mu\)M. Initial sulfide concentrations varied between \(6.25 \cdot 10^{-5}\) and \(2.0 \cdot 10^{-3}\) M (2 to 64 mg/l).

The plots of \(E_h\) versus time remained linear for more than 95% of the reaction (i.e. 95% depletion of the initial \([S(-II)]\)). The corresponding \([O_2]\) decrease was consistent with the decrease of \([S(-II)]\) and showed a 1:1 relation (\([O_2]_{utilized}: [S(-II)]_{oxidized}\)) at the completion of the reaction in cases where initial concentrations of sulfide and oxygen were practically the same, and a 2:1 ratio in cases where \([O_2]_o>>[S(-II)]\). The observed stoichiometry indicates that sulfate is the final product when oxygen is in excess (eq. 4), while elemental sulfur is one of the final products when sulfide is present in excess (eq. 1). In the latter case, formation of elemental sulfur was also observed visually as an increase in turbidity during the course of the reaction and isolated as a yellowish white precipitate at completion of the experiment. The linearity of the \(E_h\) versus \(t\) confirmed previous observations that the reaction was first order with respect to \([S(-II)]\) (4). The pseudo–first–order rate constants, \(k_{obs}\), were calculated for each kinetic run from the slope of the potential curve (eq. 5); they are summarized in Table A.1.
Table A.1

Pseudo-first-order rate constants ($k_{obs}$) for the catalytic oxidation of sulfide in oxygen saturated deionized water

<table>
<thead>
<tr>
<th>Catalyst (M)</th>
<th>[S(−II)] (M)</th>
<th>electrode slope mV/min</th>
<th>$k_{obs}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 $\cdot$ 10$^{-4}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>1.33 $\cdot$ 10$^{-1}$</td>
<td>1.01 $\cdot$ 10$^{-2}$</td>
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<tr>
<td>1.0 $\cdot$ 10$^{-5}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>9.20 $\cdot$ 10$^{-2}$</td>
<td>7.16 $\cdot$ 10$^{-3}$</td>
</tr>
<tr>
<td>1.0 $\cdot$ 10$^{-6}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>–</td>
<td>&lt; 1 $\cdot$ 10$^{-3}$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0 $\cdot$ 10$^{-5}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>2.28 $\cdot$ 10$^{-1}$</td>
<td>1.78 $\cdot$ 10$^{-2}$</td>
</tr>
<tr>
<td>3.0 $\cdot$ 10$^{-5}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>1.12 $\cdot$ 10$^{-1}$</td>
<td>8.71 $\cdot$ 10$^{-3}$</td>
</tr>
<tr>
<td>1.0 $\cdot$ 10$^{-5}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>6.00 $\cdot$ 10$^{-2}$</td>
<td>4.67 $\cdot$ 10$^{-3}$</td>
</tr>
<tr>
<td>Co(II)TSP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 $\cdot$ 10$^{-8}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>3.50 $\cdot$ 10$^{-2}$</td>
<td>2.78 $\cdot$ 10$^{-3}$</td>
</tr>
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<td>5.0 $\cdot$ 10$^{-8}$</td>
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<td>1.82 $\cdot$ 10$^{-1}$</td>
<td>1.42 $\cdot$ 10$^{-2}$</td>
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<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>3.30 $\cdot$ 10$^{-1}$</td>
<td>2.55 $\cdot$ 10$^{-2}$</td>
</tr>
<tr>
<td>1.0 $\cdot$ 10$^{-7}$</td>
<td>1.0 $\cdot$ 10$^{-3}$</td>
<td>2.47 $\cdot$ 10$^{-1}$</td>
<td>1.93 $\cdot$ 10$^{-2}$ **</td>
</tr>
<tr>
<td>3.0 $\cdot$ 10$^{-7}$</td>
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<td>4.34 $\cdot$ 10$^{-1}$</td>
<td>3.38 $\cdot$ 10$^{-2}$</td>
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<tr>
<td>5.0 $\cdot$ 10$^{-7}$</td>
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<td>6.02 $\cdot$ 10$^{-1}$</td>
<td>4.68 $\cdot$ 10$^{-2}$</td>
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<td>2.0 $\cdot$ 10$^{-3}$</td>
<td>2.20 $\cdot$ 10$^{-1}$</td>
<td>1.71 $\cdot$ 10$^{-2}$</td>
</tr>
</tbody>
</table>

* From absorbance data
** hv experiment
Figure A.1 shows the non-linear dependence of $k_{\text{obs}}$ on [Co(II)TSP]. At low concentrations $k_{\text{obs}}$ has a stronger dependence on the catalyst concentration than at higher concentrations. This behavior can be attributed in part to the monomer/dimer equilibrium of Co(II)TSP, where the dimeric species (i.e., [Co(II)TSP]$_2$) is catalytically less active (4, 15). At pH 6.7 an observed fractional-order dependence of 0.498 was determined for [Co(II)TSP] $\geq$ 5$\cdot$10$^{-8}$ M (i.e., $k_{\text{obs}} = 62.934\cdot$[Co(II)TSP]$^{0.498}$ with $r^2 = 0.929$). This value is close to the 0.5 order that is predicted theoretically (15) when the dimeric form of the catalyst predominates.

In one experiment the reaction solution was irradiated with low-intensity light during the entire kinetic run. The resulting rate constant is slightly lower but similar to those of the thermal reactions. Thus activation of the catalyst by light as reported earlier (14) for the case of S(IV) oxidation does not appear to be important.

The dependence of $k_{\text{obs}}$ on [S(−II)] is shown in Figure A.2 (pH = 6.7, phosphate buffer, T = 25°C, oxygen saturation, [Co(II)TSP] = 0.1 $\mu$M). Varying the initial [S(−II)] from 6.25 $\times$ 10$^{-5}$ M to 2.0 $\times$ 10$^{-3}$ M does not change the observed rate constant ($k_{\text{obs}} \approx 0.02 \text{ min}^{-1}$). This observation reconfirms the first-order dependence of the reaction on [S(−II)] and shows that our analysis based on the initial rate constant $k_{\text{obs}}$ is valid even when [$O_2$]$_0$ is of the same order as [S(−II)]$_0$.

Experiments performed with Cu$^{2+}$ or Ni$^{2+}$ as catalysts showed a dramatic decrease in catalytic activity compared to the activity of Co(II)TSP. At 1.0 $\mu$M Cu$^{2+}$ $k_{\text{obs}} < 10^{-4}$ min$^{-1}$, while at [Cu$^{2+}$] = 100 $\mu$M $k_{\text{obs}}$ was 0.01 min$^{-1}$. In the latter case however the actual [Cu$^{2+}$] in solution was probably lower than the calculated value due to the formation of a dark brown precipitate (CuS, pK$_{so}$=37) after the
Figure A.1  $k_{obs}$ dependence on [Co(II)TSP] for Co(II)TSP–catalyzed sulfide oxidation in water; T=25°C, pH=6.7 (phosphate buffer), oxygen saturation ($[O_2]=1.2 \cdot 10^{-3}$ M)
Figure A.2  \( k_{\text{obs}} \) dependence on \([S(-II)]\) for Co(II)TSP catalyzed sulfide oxidation in water; \( T=25^\circ\text{C}, \text{pH}=6.7 \) (phosphate buffer), oxygen saturation, \([\text{Co(II)TSP}]=10^{-7} \text{ M}\)
addition of sulfide. This effect was not observed at lower [Cu$^{2+}$]. At these lower concentrations Cu$^{2+}$ may form soluble complexes with polysulfides. These initial intermediate oxidation products of sulfide autoxidation are expected to be excellent complexing ligands with the ability to form water soluble metal–polysulfide species (10–11). Polysulfides are formed during all control clean water experiments where [S(–II)]$_0$ $\geq$ 1 mM (*vide infra*). In all cases ([S(–II)] $\simeq$ 1.0 mM) the concentrations of total S$^{2-}_n$ exceeds $10^{-6}$ M and can be as high as 100 $\mu$M.

The Ni(II)–catalyzed autoxidation of sulfide leads to higher $k_{obs}$ values than for Cu(II) catalysis. For example, at 1 $\mu$M catalyst, $k_{obs}(Ni^{2+}) = 5 \times 10^{-3}$ min$^{-1}$ as compared to $k_{obs}(Cu^{2+}) \leq 1 \times 10^{-4}$ min$^{-1}$. The superior catalytic effect of Ni$^{2+}$ has been reported previously (6, 12). A comparison of the observed rate constants for the catalytic oxidation of S(–II) is given in Figure A.3. The graphic relationships show that Co(II)TSP is a significantly better catalyst than either Cu$^{2+}$ or Ni$^{2+}$ with a pronounced catalytic activity even at concentrations as low as 0.01 $\mu$M ($k_{obs} = 2.8 \times 10^{-3}$ min$^{-1}$). The much higher $k_{obs}$ values, reported for even much lower concentrations (e.g. at [Co(II)TSP]= $2.5 \times 10^{-9}$ M, $k_{obs} = 0.36$ min$^{-1}$ (1)) are believed to be artifacts due to the electrode interferences (*vide supra*).

Because of the strong absorbance of hydrogen sulfide and its oxidation products (e.g. polysulfides) in the UV range, spectrophotometric measurements are a convenient way to follow their concentration changes during the reaction. Thus spectra of the ongoing reaction were taken at different time intervals. Typical spectra are shown in Figure A.4 for Ni$^{2+}$–catalyzed oxidation. The sequential spectra show a continuous decrease of [HS] at $\lambda = 230$ nm and an initial increase in absorption at $\lambda > 260$ nm for the first 20 – 30 min reaction time due to the production of polysulfides (peaks) and elemental sulfur (turbidity with broad
Figure A.3  $k_{obs}$ values for different catalysts; T=25°C, pH=6.7, oxygen saturation
Figure A.4  UV/VIS spectra during a kinetic run in water; \([\text{Ni}^{2+}]=3 \cdot 10^{-5}\text{M}, \ [\text{S(-II)}]=10^{-3}\text{M}, \ [\text{O}_2]=1.2 \cdot 10^{-3}\text{M} \) (oxygen saturation), pH=6.7, T=25 °C; \(t_0\) = time corresponding to the first curve, \(Dt\) = time increment, arrows indicate direction of reaction.
absorbance into the visible region, no characteristic maxima). During the reaction, this latter absorption decreases suggesting the dissolution (i.e. further oxidation) of the colloidal elemental sulfur.

The decrease in the HS\(^{-}\) absorbance can be correlated to the change in \([S(-\text{II})]\), using the acid/base sulfide equilibria:

\[
\begin{align*}
\text{H}_2\text{S} & \rightleftharpoons \text{HS}^{-} \rightleftharpoons \text{S}^{2-} \\
& \overset{pK_{a1}}{\rightleftharpoons} \overset{pK_{a2}}{\rightleftharpoons}
\end{align*}
\]

\[
[S(-\text{II})] = \alpha_1 \text{[HS}^{-}\text{]} \tag{6}
\]

where

\[
\alpha_1 = \frac{K_{a1}[H^{+}]}{([H^{+}]^2 + K_{a1}[H^{+}] + K_{a1}K_{a2})} \tag{7}
\]

and \(K_{a1}, K_{a2}\) are the first \((pK_{a1} = 7.00)\) and second \((pK_{a2} \geq 14.00)\) acid–dissociation constants for \(\text{H}_2\text{S}\), respectively. The value of \(pK_{a2}\) was previously accepted to be about 14.00 \((20)\) but a later spectrophotometric study \((21)\) reports it as 17.00. In any case, \(K_{a2} \ll K_{a1}\) and equation (7) can be simplified to:

\[
\alpha_1 = \frac{K_{a1}}{[H^{+}] + K_{a1}} \tag{7a}
\]

Under the experimental conditions used in this study, pseudo–first–order rate constants can be calculated from linear plots of \(\ln (A_{\text{HS}^{-}} - A_{\infty})\) versus time. These rates (included in Table 1) agree well with those found from the \(\text{Ag}_2\text{S}\) electrode measurements, indicating that both methods respond linearly to the same species (i.e. \(\text{HS}^{-}\) or \(\text{S}^{2-}\)). However, the spectrophotometric analysis at \(\lambda = 230\) nm leads to slightly lower \(k_{\text{obs}}\) values, which could be due to interferences by polysulfide ions.
These unstable intermediates have well defined spectra at $\lambda \geq 300$ nm (22–23), but no information about their exact absorbance at $\lambda < 300$ nm is available (22).

Polysulfides are in equilibrium with elemental sulfur (a stable oxidation product in neutral to acidic solutions) and sulfide. They form as intermediates during the autoxidation of sulfide, mainly at neutral pH and high [S(−II)] concentrations (4, 7). The maximum yield of polysulfides at pH 7 with [O$_2$] = 1.2 mM and [S(−II)] = 1.0 mM has been reported to be 14% (23). The most stable species in neutral solutions saturated with S$^0$ have been reported to be the tetra- and pentasulfides, S$_4^{2−}$ and S$_5^{2−}$, respectively. The ratio of S$_4^{2−}$: S$_5^{2−}$ was calculated to be 1:5 (23) or 1:1 (22). Lowering the [S$_8$]/[S(−II)] ratio leads to the formation of tri- or disulfides (22). This behavior is reflected in the spectra shown in Figure 4. Our calculations suggest a conversion of less than 16% of the initial [S(−II)] to tetra- and pentasulfides after 30 minutes of reaction time.

From the experimental results reported by Hong et al. (14), an initial rate constant $k_{obs} \simeq 1.5 \cdot 10^{-2}$ min$^{-1}$ can be calculated for the Co(II)TSP catalyzed sulfide autoxidation at pH=9.2, [S(−II)]$_0$=1 mM, [O$_2$]$_0$=0.25 mM, $T=25^\circ C$, $I=0.4$ M, [Co(II)TSP]=0.17 $\mu$M. This value is of the same order of magnitude with our results, but lower, as could be expected from the fact that they were working at a higher pH. Experimental results of Hoffmann and Lim (4) indicated that the rate of the reaction is maximum around neutral pH.

Snavely and Blount (5) have studied sulfide autoxidation catalyzed by metal ions in sour water (3.5% NaCl), [S(−II)]$_0$=6.25 mM, [O$_2$]$_0$=0.19 mM, and at various pH values. A direct comparison of experimental rates is not easy, since they worked at higher sulfide concentrations and [S(−II)]$>>$[O$_2$], and they also reported the rate in terms of the zero order decrease in oxygen concentration. Nevertheless,
the rate constants that can be calculated from their data are within the same order of magnitude with ours in the case of Ni\(^{2+}\) (about 4 \(\times\) 10\(^{-2}\) min\(^{-1}\) for [Ni\(^{2+}\)] = 18 \(\mu\)M, pH = 6.8, as compared to 1.8 \(\times\) 10\(^{-2}\) min\(^{-1}\) for [Ni\(^{2+}\)] = 30 \(\mu\)M, pH = 6.7), while being one order of magnitude lower for Cu\(^{2+}\) (about 10\(^{-3}\) min\(^{-1}\) for [Cu\(^{2+}\)] = 172 \(\mu\)M, pH = 6.4, as compared to 10\(^{-2}\) min\(^{-1}\) for [Cu\(^{2+}\)] = 100 \(\mu\)M, pH = 6.7).

**Kinetic results in wastewater**

Initial experiments were conducted at 25 °C, pH = 7.0, at two different O\(_2\) concentrations 1.2 \(\times\) 10\(^{-3}\) M (PO\(_2\) = 1 atm) and 2.5 \(\times\) 10\(^{-4}\) M (PO\(_2\) = 0.21 atm) and initial sulfide concentrations 10\(^{-4}\) M and 1.5 \(\times\) 10\(^{-4}\) M (3.2 and 5 mg/l). Several experiments were performed with autoclaved wastewater to determine the importance of biological sulfide oxidation in situ by microorganisms. Autoclaving was selected as sterilization procedure after comparing the oxidation rates in autoclaved and 0.45\(\mu\) filtered primary sewage (the latter was faster).

Samples were taken periodically, by syringe, and the [S(−II)]'s were determined with the sulfide ISE (measurements were performed in SAOB). The plots of potential vs time were linear for more than 90% of the reaction. The decrease in [O\(_2\)] was directly proportional to the decrease of [S(−II)] in a 2:1 ratio ([O\(_2\) used]:[S(−II) oxidized]) at the completion of the reaction. This indicates that the final oxidation product was sulfate (as expected, since O\(_2\) was in excess).

The pseudo–first–order rate constants (\(k_{obs}\)) for different experiments, under oxygen and air saturation are given in Table A.2. The uncatalyzed sulfide oxidation was faster in wastewater than in clean water. The enhanced oxidation rate can be attributed to the activity of the microorganisms and to the catalytic activity of transition metals present in wastewater. The uncatalyzed oxidation
Table A.2
Pseudo first-order rate constants ($k_{obs}$) for Co(II)TSP catalyzed sulfide oxidation in sewage, under air and oxygen saturation

<table>
<thead>
<tr>
<th>Co(II)TSP ($\mu$M)</th>
<th>S(–II) (mM)</th>
<th>pH</th>
<th>$k_{obs}$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Oxygen saturation ([O$_2$]=1.2 mM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>primary effluent</td>
<td>0.00</td>
<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.00</td>
<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.00</td>
<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
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<td>0.10</td>
<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.10</td>
<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
<td>raw sewage</td>
<td>0.00</td>
<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
<td>&quot;</td>
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<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
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<td>0.1</td>
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</tr>
<tr>
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<td>0.1</td>
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<td>0.50</td>
<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.75</td>
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<td>7.00</td>
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<tr>
<td>&quot;</td>
<td>1.00</td>
<td>0.1</td>
<td>7.00</td>
</tr>
<tr>
<td>b) Air saturation ([O$_2$]=0.25 mM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>raw sewage</td>
<td>0.00</td>
<td>0.15</td>
<td>7.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.10</td>
<td>0.15</td>
<td>7.00</td>
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<tr>
<td>&quot;</td>
<td>1.00</td>
<td>0.15</td>
<td>7.00</td>
</tr>
</tbody>
</table>

a) filtered sewage, diluted 1:3
b) autoclaved, diluted 1:3
c) diluted 1:3
d) autoclaved
rates are in good agreement with the rates reported by Wilmot et al. (24) for Australian wastewaters (typical \( k_{\text{obs}}' \)'s \( \approx 0.02 \text{ min}^{-1} \)). They also reported a 12 – 56% reduction in oxidation rate after sterilization, which also agrees with our results.

Co(II)TSP was seen to catalyze S(–II) autoxidation in wastewater and \( k_{\text{obs}} \) values were similar to those in clean water, as shown in Figure A.5. However, the biological contribution to the net oxidation had to be taken into consideration. Figure A.6 shows that the rate constants for fresh and autoclaved wastewater differ by a constant amount. This difference, \( 0.0132 \text{ min}^{-1} \), was attributed to the biological component and the fact that it remains constant indicated that the presence of the catalyst does not affect the sulfide–oxidizing microorganisms. When this component is subtracted from the overall rate, a slight loss of catalytic activity of Co(II)TSP compared to clean systems is noted (Figure 5). This is in agreement with findings of Hong et al. (14) that Co(II)TSP is a less efficient catalyst for the oxidation of HS\(^-\) in heterogeneous systems than in homogeneous solutions. The dependence of the corrected Co(II)TSP–catalyzed oxidation rate, \( k_{\text{obs}}' = k_{\text{obs}} - 0.0132 \), on [Co(II)TSP] was found to be non-linear. Double logarithmic plots of \( k_{\text{obs}}' \) versus [Co(II)TSP] show an apparent reaction order, \( \beta \),

\[
k_{\text{obs}}' = k_i \cdot [\text{Co(II)TSP}]^\beta.
\] (8)

of 0.60 (\( r^2 = 0.982 \)) and 0.55 (\( r^2 = 0.991 \)) in wastewater at oxygen and air saturation respectively. The order was 0.53 (\( r^2 = 0.965 \)) for air–saturated autoclaved wastewater. All these values are quite close to the expected value of 0.5 for clean water.

In the case of filtered primary effluent, the sulfide concentration was followed spectrophotometrically and pseudo–first–order rate constants were obtained from linear plots of \( \ln(A_{\text{HS}} - A_\infty) \) versus time and were found to be in agreement with
Figure A.5  Co(II)TSP-catalyzed sulfide oxidation; comparison between water and wastewater; open circles, dashed line: water data, closed circles: wastewater raw data, open triangles, solid line: wastewater data corrected for biological component. T=25°C, neutral pH, oxygen saturation, [S(−II)]₀ = 100 μM.
Figure A.6  Co(II)TSP–catalyzed sulfide oxidation; comparison between raw and autoclaved wastewater. T=25°C, neutral pH, air saturation, \([S(-II)]_o = 150 \mu M\).
those obtained from the ISE measurements. However, the spectrophotometric analysis was not possible in the case of fresh or autoclaved sewage due to the high turbidity of the solution.

A series of experiments was conducted at lower oxygen concentrations (below air saturation). Figure A.7 shows the dependence of $k_{\text{obs}}$ on the oxygen concentration at $T = 25 \, ^{\circ}\text{C}$, $\text{pH} = 7.0$, $[\text{S(III)}]_0 = 1.5 \cdot 10^{-4} \, \text{M}$, $[\text{Co(II)TSP}] = 1 \, \mu\text{M}$ (0.059 mg/l as Co$^{2+}$). In the few experiments where S(II) was not in excess care was taken to determine $k_{\text{obs}}$ within the initial stage of the reaction so as to minimize the error inherent in assuming constant [S(II)]. As expected, the oxidation of sulfide was faster in fresh wastewater as compared to autoclaved wastewater. For the catalyzed oxidation, the oxidation rate increased with increasing initial oxygen concentration for $[\text{O}_2] < 3 \, \text{ppm}$ but was essentially constant at higher $[\text{O}_2]$. A similar trend was also observed for the uncatalyzed reaction.

If a dependence of the form

$$k_{\text{obs}} = k_m [\text{O}_2]^\gamma$$  \hspace{1cm} (9)

is assumed, $\gamma$ can be found from a double-logarithmic plot of $k_{\text{obs}}$ against initial $[\text{O}_2]$. Using this approach a fractional reaction order ($\gamma$) of 0.55 ($r^2 = 0.97$) and 0.58 ($r^2 = 0.90$) was found for the uncatalyzed and catalyzed sulfide oxidation, respectively. These values are consistent with the value of 0.56 reported by Chen and Morris (6) for sulfide oxidation in buffered water.

Alternatively, a bisubstrate Michaelis–Menton rate law can be used (4, 24) and then,

$$k_{\text{obs}} = \frac{k \cdot [\text{O}_2]}{K + [\text{O}_2]}$$ \hspace{1cm} (10)
Figure A.7  Dependence of $k_{\text{obs}}$ on $[O_2]$ for sulfide oxidation in wastewater; $T=25^\circ$C, neutral pH, $[S(-II)]_o = 150 \, \mu$M
k and K can be calculated by plotting $k_{\text{obs}}$ vs $-k_{\text{obs}}/[O_2]$. Such a plot should give a straight line of slope K and intercept k. Using this approach, the following values were calculated:

uncatalyzed sulfide oxidation : $k = 0.0458 \text{ min}^{-1}$, $K = 74 \mu\text{M} \ (2.64 \text{ ppm})$

catalyzed (1$\mu\text{M}$ CoTSP) " : $k = 0.126 \text{ min}^{-1}$, $K = 65 \mu\text{M} \ (2.07 \text{ ppm})$

The values for the uncatalyzed S(−II) oxidation are in general agreement with the values reported by Wilmot et al. (24) (k ranging from 0.024 to 0.087, K = 94 $\mu$M) for various Australian wastewaters. The curves shown in Figure A.7 have been calculated using the above constants (k and K). Table A.3 summarizes the pseudo-first-order rate constants for different oxygen concentrations.

Figure A.8 shows spectra of Co(II)TSP (10$\mu$M) in deionized water and in wastewater (after filtration with a 0.2 $\mu$ filter). The visible spectrum of Co(II)TSP has a characteristic double hump. The absorption bands at 625 nm and 670 nm have been attributed to the dimer and the summation of monomeric species (16, 25–26). The spectra of Fig. A.8 show that the catalyst adsorbs partially onto particles in wastewater (both peaks are lower for the latter case) but not to a great extent. Using $\epsilon_{625} = 1.9 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ and $\epsilon_{663} = 1.03 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ for the dimer \{[Co(II)TSP]$_2$\} and the monomer \{Co(II)TSP\}, respectively (26), it can be calculated that approximately 80% of the total catalyst remains in solution.

Spectra taken at different times after the addition of sulfide in oxygenated, Co(II)TSP containing, deionized water solution showed an absorption shift from 636 nm to 670 nm. That can be explained by a shift in the monomer/dimer equilibrium, upon coordination of HS$^-$ and O$_2$ at the Co(II) center. The monomer appears to be the catalytically active species as it is also indicated by the approximately half order dependence of the oxidation reaction on Co(II)TSP (15).
Table A.3

Pseudo first-order rate constants ($k_{\text{obs}}$) for Co(II)TSP catalyzed sulfide oxidation in raw sewage, and low oxygen concentrations

<table>
<thead>
<tr>
<th>O$_2$ (ppm)</th>
<th>Co(II)TSP (µM)</th>
<th>$k_{\text{obs}}$ (min$^{-1}$)</th>
<th>Comments</th>
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<tbody>
<tr>
<td>0.1</td>
<td>0.0</td>
<td>&lt; 0.001</td>
<td>A *</td>
</tr>
<tr>
<td>0.1</td>
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<td>&lt; 0.001</td>
<td>C</td>
</tr>
<tr>
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<td>1.0</td>
<td>&lt; 0.001</td>
<td>A</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0</td>
<td>&lt; 0.001</td>
<td>A a</td>
</tr>
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<td>&lt; 0.001</td>
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<td>A</td>
</tr>
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</table>

* A, B, C represent different batches of raw sewage

a autoclaved

All experiments at $[\text{S(II)}]_0 = 150$ µM
Figure A.8  UV/VIS spectra of Co(II)TSP in water and wastewater; 
\[ [\text{Co(II)TSP}] = 10^{-5}\text{M} \]
Spectra taken during the experiments with wastewater at low oxygen concentrations indicate that there is no loss of the catalyst during the reaction.

The reproducibility of the experiments with wastewater was reasonable. Samples were collected from the inlet at the San Jose Creek Water Reclamation Plant and were kept refrigerated (at temperature near 0 °C) in sealed containers until they were used for experiments. The pH and DO remained constant for a period of 1 – 2 weeks. Most experiments were conducted within a week from the collection of the samples. Experimental rate constants exhibited some variability for different samples (i.e. samples collected on different occasions) but were consistent for all the experiments conducted with the same batch of wastewater. Furthermore, the general trends were the same even for samples from different batches of raw wastewater.

Mechanism

The mechanism of the Co(II)TSP-catalyzed oxidation of reduced sulfur compounds by dioxygen has been discussed previously (4, 14–16). The catalyzed autoxidation of S(–II) appears to proceed via the following ternary complex mechanism:

\[
\frac{K_d}{2} \quad \frac{K_1}{K_2} \quad \frac{K_3}{K_4} \quad \frac{K_5}{K_6}
\]

\[
\text{(Co(II)TSP)}^{4-} \xrightarrow{K_d} 2 \text{Co(II)TSP}^{2-} \quad \text{(11)}
\]

\[
\text{Co(II)TSP}^{2-} + \text{HS}^- \xrightarrow{K_1} \text{(HS)Co(II)TSP}^{3-} \quad \text{(12)}
\]

\[
\text{(HS)Co(II)TSP}^{3-} + \text{O}_2 \xrightarrow{k_2} \text{(HS)Co(III)TSP(O}_2^\cdot)^{3-} \quad \text{(13)}
\]
(HS)Co(III)TSP(O_2^\cdot)^{3-} + HS^{-} \xrightarrow{k_3 \ \text{slow}} (HS)Co(III)TSP(O_2^\cdot)(HS)^{4-} \quad (14)

(HS)Co(III)TSP(O_2^\cdot)(HS)^{4-} \xrightarrow{k_4 \ \text{fast}} (HS)Co(II)TSP(O_2^\cdot)^{5-} + S^{0} + H^{+} \quad (15)

(HS)Co(II)TSP(O_2^\cdot)^{5-} + 2 H^{+} \xrightarrow{k_5 \ \text{fast}} (HS)Co(II)TSP^{3-} + H_{2}O_{2} \quad (16)

HS^{-} + H_{2}O_{2} + H^{+} \longrightarrow \frac{1}{8} S_{8} + 2 H_{2}O \quad (17)

HS^{-} + 4 H_{2}O_{2} \longrightarrow SO_{4}^{2-} + 4 H_{2}O + H^{+} \quad (18)

The catalytic activity of Co(II)TSP toward S(-II) autoxidation involves 1) the dissociation of the dimeric form of the catalyst into the monomeric form (eq. 11), 2) the complexation of the bisulfide ion (HS^{-}) in an open axial coordination site on the central metal atom (eq. 12), 3) the binding of dioxygen in a position trans to the bound HS^{-}, and the simultaneous electron delocalization from the cobalt center to the bound dioxygen (superoxide formation, eq. 13), 4) the formation of a ternary adduct with another HS^{-} molecule (eq. 14), 5) the oxidative transfer of two electrons from HS^{-} to the Co(III)-O_2^{2-} moiety resulting in the formation of elemental sulfur as S^{0} and the release of a proton (eq. 15), and 6) the protonation of the bound O_2^{3-} to form hydrogen peroxide (eq. 16). Elemental sulfur can be further oxidized to thiosulfate and sulfate. Hydrogen peroxide, which is generated as an intermediate in the above reaction sequence, reacts with S(-II) according to the
stoichiometries reported previously (7) (eqs. 17–18).

The mechanism given in eqs. 11–16 leads to the following theoretical rate expression (15):

$$- \frac{d[S(-II)]}{dt} = \frac{k'K' \left[ (Co(II)_TSP) \frac{1}{2} \right][O_2][HS^-]}{K_A + K_B [O_2] + K_C [HS^-] + [O_2][HS^-]}$$  \hspace{1cm} (19)

where

$$k' = \frac{k_4k_5}{k_4 + k_5}$$

$$K' = K_1K_d \frac{1}{2}[HS^-]$$

$$K_A = \frac{k_5(k_2k_4 + k_2k_3)}{k_2k_3(k_4 + k_5)}$$

$$K_B = \frac{k_5(k_4 + k_4)}{k_3(k_4 + k_5)}$$

$$K_C = \frac{k_4k_5}{k_2(k_4 + k_5)}$$

The theoretical rate expression can be simplified for pseudo-first-order conditions, and it is consistent with our empirical observation of eq. 10.

Two possible mechanisms have been suggested for the catalysis of S(-II) autoxidation by transition metal ions (10) (1) electron transfer leading to free
radical formation, or 2) formation of metal–sulfide complexes leading to sulfur precipitation. We believe that catalysis of S(−II) autoxidation by Cu(H₂O)⁶⁺ and presumably by Ni(H₂O)⁶⁺ is initiated by an outer–sphere electron transfer from HS⁻ to the hexaaquo metal ion to form HS⁻ radical. The HS⁻ radical is oxidized further by a free radical chain sequence involving oxygen as shown below:

\[ \text{Cu}^{2+} + \text{HS}^- \rightarrow \text{Cu}^+ + \text{HS}^- \]  \hspace{1cm} (20)

\[ \text{HS}^- + \text{O}_2 \rightarrow \text{HS}^- + \text{O}_2^- \]  \hspace{1cm} (21)

\[ \text{HS}^- + \text{O}_2 \rightarrow \text{HSO}_2^- \]  \hspace{1cm} (22)

\[ \text{HSO}_2^- + \text{O}_2 \rightarrow \text{HSO}_4^- \]  \hspace{1cm} (23)

\[ \text{HSO}_4^- + \text{O}_2 \rightarrow \text{HSO}_4^- + \text{O}_2 \]  \hspace{1cm} (24)

\[ 2 \text{HS}^- \rightarrow \text{H}_2\text{S}_2 \]  \hspace{1cm} (25)

\[ \text{H}_2\text{S}_2 \rightarrow 2 \text{H}^+ + \text{S}_2^{2-} \]  \hspace{1cm} (26)

\[ \text{HS}^- + \text{HS}^- \rightarrow \text{H}_2\text{S}_2^{-} \]  \hspace{1cm} (27)

\[ \text{H}_2\text{S}_2^{-} + \text{O}_2 \rightarrow \text{H}_2\text{S}_2 + \text{O}_2^{-} \]  \hspace{1cm} (28)

\[ \text{H}_2\text{S}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 + \text{S}_2 \]  \hspace{1cm} (29)
A similar free radical pathway has been proposed by Chen and Morris (6).

**CONCLUSIONS**

Co(II)TSP is a substantially more effective catalyst for the autoxidation of sulfide than Ni$^{2+}$ and Cu$^{2+}$ ions. Spectrophotometric measurements provide evidence for the production of intermediates such as elemental sulfur (S$_8$) and polysulfides (S$_2^{2-}$, S$_3^{2-}$, S$_4^{2-}$, S$_6^{2-}$). When [O$_2$] $>>$ [S(−II)] the stoichiometry of the reaction is 2:1 ([O$_2$ used]:[S(−II) oxidized]) with SO$_4^{2-}$ formed as the product. When [O$_2$] $\simeq$ [S(−II)] the reaction stoichiometry is 1:1 and elemental sulfur is formed as one of the products.

The uncatalyzed oxidation of sulfide by molecular oxygen was found to be faster in wastewater than in clean water. This difference was attributed to microbial oxidation of S(−II) and to catalytic action of transition metals present in wastewater. Co(II)TSP has been shown to catalyze the autoxidation of sulfide in wastewater. The reaction rate is first order with respect to total sulfide and has a fractional (0.55) dependency on the catalyst.

Our results suggest that Co(II)TSP can be used for H$_2$S control in sewers in conjunction with oxygen or compressed air injection. Because of the relatively high value of the Michaelis–Menten rate constant K, maximum advantage of the catalyst is taken when dissolved oxygen levels are about 4 ppm or higher. On the other hand, even at the low oxygen concentrations typically encountered in sewers ($\leq$ 1 ppm) sulfide oxidation rates more than double in the presence of 1μM of Co(II)TSP.
Acknowledgments

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References


APPENDIX B

Peroxymonosulfate: An alternative to hydrogen peroxide for the control of hydrogen sulfide

(Research Journal of Water Pollution Control Federation, in print)
ABSTRACT

The oxidation of total dissolved sulfide, where $S(-II) = H_2S + HS^- + S^{2-}$, by peroxymonosulfate, $HSO_5^-$, has been studied in wastewater. Peroxymonosulfate was found a more rapid and efficient oxidant of $S(-II)$ than either $H_2O_2$ or $Fe(II)$. The combination of peroxymonosulfate and hydrogen peroxide was additive in terms of $S(-II)$ oxidation, while the combination of peroxymonosulfate and $Fe(II)$ resulted in a decrease in the effectiveness of $Fe(II)$ as an oxidant. Peroxymonosulfate has been shown to be a viable alternative to $H_2O_2$ for the control of sulfide–induced corrosion in concrete sewers.

KEYWORDS

corrosion, hydrogen sulfide, oxidation, peroxymonosulfate, sewers, wastewater.
INTRODUCTION

Hydrogen sulfide ($H_2S$) gas generation in sewers, the subsequent production of sulfuric acid ($H_2SO_4$) on concrete sewer crowns and the resultant corrosion of the structural components are problems often encountered in wastewater collection systems (ASCE, 1989; Thistlethwayte, 1972; Pomeroy and Bowlus, 1949). Current strategies for the control of hydrogen sulfide gas in sewers involve chemical, biochemical, and physical treatment schemes that are designed to suppress $H_2S$ generation, to retard or prevent $H_2S$ oxidation to $H_2SO_4$ on sewer crowns, to trap $H_2S$ in the flowing wastewater, or to oxidize $H_2S$ in the liquid phase in order to prevent its transfer into the gas phase.

Aeration of wastewater, by compressed air or pure oxygen, is one of the control measures commonly employed in sewers to oxidize sulfides while still in the liquid phase (ASCE, 1989). Nevertheless, the oxidation of reductants such as $H_2S$ by $O_2$ proceeds slowly in the absence of catalysts (Chen and Morris, 1972a,b; Snavely and Blount, 1969; Weres et al., 1985) because of unfavorable spin state symmetries that result from the differences in the electronic configurations of the reactants (Hoffmann and Lim, 1979). More powerful (i.e. $E^o > 1.29$ V) oxidants than $O_2$ can be used to achieve a faster rate of oxidation of $H_2S$ (Hoffmann, 1977; Dohnalek and FitzPatrick, 1983). The oxidant that is most commonly used for the control of sulfides in wastewater collection systems is hydrogen peroxide. The effectiveness of $H_2O_2$ depends on the degree of sulfide control required and the concentration of compounds, other than sulfide, that are present in the wastewater in a reduced state and will compete for $H_2O_2$. Large scale applications of $H_2O_2$ for $S(\text{-II})$ control in sewers have shown that stoichiometric ratios of $\geq 6:1$
([H$_2$O$_2$]:[S(−II)]) are required to keep [S(−II)] ≤ 0.2 ppm (ASCE, 1989).

Peroxymonosulfate ion, a monosubstituted derivative of hydrogen peroxide (HOOSO$_5^-$) is often more reactive kinetically than HOOH, even though it is only slightly more powerful as an oxidant [E$_{HSO_5/HSO_4^-}^{\circ}$ = + 1.82 V; E$_{H_2O_2/H_2O}^{\circ}$ = + 1.776 V (Balej, 1984; Steele, 1982; Spiro, 1979)]. In addition to its enhanced reactivity, HSO$_5^-$ appears to be more stable than H$_2$O$_2$ with respect to spontaneous decomposition in water. Peroxymonosulfate is commercially available as a free-flowing powder known by the trade names Oxone (DuPont) or Curox (Interox). These products are triple salts with the composition 2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$. Simple peroxymonosulfate salts (i.e. KHSO$_5$) are difficult to prepare.

Betterton and Hoffmann (1990) have recently studied the kinetics of S(−II) oxidation by peroxymonosulfate, HSO$_5^-$, in pure water over the pH range of 2.0 to 6.3. They reported that the reaction of HSO$_5^-$ with S(−II) is 3–4 orders of magnitude faster than the corresponding reaction with H$_2$O$_2$. Peroxymonosulfate could thus be a viable alternative to H$_2$O$_2$ for the control of sulfide-induced corrosion in concrete sanitary sewers and wastewater treatment facilities but its effectiveness and its specificity for oxidation of S(−II) in actual wastewater had not been studied before.

The effectiveness of HSO$_5^-$ for H$_2$S oxidation was studied in wastewater obtained from the influent of a tertiary wastewater treatment plant in Los Angeles County and compared to that of H$_2$O$_2$. The effective molar stoichiometry of oxidant used to total sulfide oxidized, i.e., [HSO$_5$]$_{used}$:[S(−II)]$_{oxidized}$, as a function of the ratio of the initial concentrations of HSO$_5^-$ and S(−II), [HSO$_5$]$_0$:[S(−II)]$_0$, was also examined. Combined reagent additions, where peroxymonosulfate was used
together with another chemical reagent (H₂O₂, FeCl₂, or S₂O₅²⁻), were investigated in water and wastewater in order to determine optimal conditions for HSO₅⁻ application. Control kinetic experiments following the oxidation of S(−II) in the presence of H₂O₂ and FeCl₂ were conducted in both clean water and wastewater.

**EXPERIMENTAL**

**Reagents**

All reagents were of analytical grade. Doubly–distilled (18 MΩ·cm) deionized water was used for the preparation of buffer solutions and for clean water experiments. S(−II) stock solutions were prepared from Na₂S·9H₂O crystals (Aldrich) that had been cleaned with deionized water and lightly dried with absorbent paper. The actual concentrations were determined by potentiometric titration with Pb(ClO₄)₂ (Orion) or AgNO₃. Stock solutions were stored in a refrigerator and no significant decrease in sulfide concentration was detected during a period of approximately 10 days. Mono and disodium phosphate salts, acid phthalate salts (Mallinckrodt), borate (Spectrum), sodium hydroxide and hydrochloric acid (Baker) were used for the preparation of the buffers. A triple salt commercially available by the name of Oxone (Aldrich) was used as source of peroxymonosulfate (2 KHSO₅·KHSO₄·K₂SO₄). Peroxymonosulfate solutions were prepared by dissolving Oxone in a portion of the appropriate buffer and adjusting the pH (if necessary) with NaOH before making up to the mark in a volumetric flask. Ferric and ferrous chloride and sodium persulfate were purchased from Baker, and hydrogen peroxide stocks were prepared from a 30% solution (Mallinckrodt).
Apparatus

Experimental techniques and apparatus used in this study were similar to those described previously (e.g., Chen and Morris, 1972; Hoffmann, 1977). Experiments were conducted in sealed water-jacketed, glass reaction vessels with total volumes ranging from 50 to 1600 ml. The design and operation of the batch reactor system have been described previously (Hoffmann and Lim, 1979; Kotronarou and Hoffmann, 1991).

Oxygen concentrations were measured with an ORION 97-08-00 oxygen electrode. Sulfide concentrations were measured with a sulfide ion electrode (ORION 94-16 Ag/Ag2S with double junction reference electrode) coupled to an ORION 801-A ion analyzer. pH measurements were performed with a RADIOMETER pH electrode and a PHM84 pH meter. The temperature was maintained constant with the use of a HAAKE A80 water circulation and temperature controlling system. Hydrogen peroxide concentrations in stock solutions were determined iodometrically (Allen, 1952). Spectrophotometric measurements were performed on an HP 8450A UV/VIS spectrophotometer.

All instruments were interfaced to an IBM-AT computer for data collection. Oxygen concentration and pH were monitored continuously during the kinetic experiments. Samples from the reaction vessel were taken periodically (syringes, septa) and analyzed for sulfide after a 1:1 dilution with sulfide antioxidant buffer (SAOB; a mixture of 67 g of Na2EDTA, 35 g ascorbic acid, and 80 g of NaOH in 1 L).

All electrodes were calibrated at regular time intervals and showed no significant drift with time. The sulfide ion specific electrode (ISE) was calibrated both for clean water and wastewater. The EMF versus concentration response of
the electrode was found to follow the Nernst equation with similar slopes in both systems.

RESULTS AND DISCUSSION

Sulfide oxidation in raw wastewater

Wastewater samples were collected from the inlet at the San Jose Creek Water Reclamation Plant. Raw wastewater was kept refrigerated (at temperatures near 0 °C) in sealed containers until it was used for experiments. The pH and DO remained constant for a period of 1 – 2 weeks and were around 7.5 and less than 1.5 ppm respectively. Most experiments were conducted within a week from the collection of the samples.

As we have reported previously (Kotronarou and Hoffmann, 1991), the oxidation of S(−II) in raw wastewater with no added catalyst or oxidant had an apparent first order rate with respect to S(−II) (i.e., \( \frac{d[S(−II)]}{dt} = −k_{obs}[S(−II)] \)) and was faster than in clean water. Table B.1 presents typical observed first-order reaction constants calculated from kinetic experiments where the disappearance of S(−II) in sulfide-spiked wastewater was followed with time. These constants are consistent with the oxidation rates observed in our previous work where wastewater from the same treatment plant was used (Kotronarou and Hoffmann, 1991). They are also in good agreement with the rates reported by Wilmot et al. (1988) for various Australian wastewaters (e.g., \( k_{obs} ≈ 0.02 \) min⁻¹).

Experimental rate constants exhibited a certain variability especially for different batches (i.e. samples collected on different occasions) but the general trends were the same and the oxidation rates for the same batch differed by less
Table B.1
Pseudo–first–order rate constants ($k_{obs}$) for the oxidation of sulfide in wastewater

<table>
<thead>
<tr>
<th>Sample #</th>
<th>pH</th>
<th>[S(−II)]₀ (μM)</th>
<th>$k_{obs}$ (min⁻¹)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.8</td>
<td>100</td>
<td>$2.76 \cdot 10^{-2}$</td>
<td>same day collection</td>
</tr>
<tr>
<td>2</td>
<td>9.8</td>
<td>100</td>
<td>$3.40 \cdot 10^{-3}$</td>
<td>sample #1 stored overnight at pH = 9.8</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>200</td>
<td>$7.14 \cdot 10^{-4}$ *</td>
<td>sample #1 four days after collection</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>200</td>
<td>$3.04 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>200</td>
<td>$2.20 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>200</td>
<td>$2.70 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9.4</td>
<td>200</td>
<td>$2.30 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9.4</td>
<td>200</td>
<td>$2.40 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9.4</td>
<td>400</td>
<td>$2.27 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9.5</td>
<td>100</td>
<td>$2.04 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9.5</td>
<td>100</td>
<td>$1.80 \cdot 10^{-2}$</td>
<td>sample #4 stored overnight</td>
</tr>
<tr>
<td>5</td>
<td>9.3</td>
<td>100</td>
<td>$1.53 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9.3</td>
<td>100</td>
<td>$1.58 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.3</td>
<td>100</td>
<td>$2.42 \cdot 10^{-2}$</td>
<td>sample #5 stored overnight; supernatant</td>
</tr>
<tr>
<td>7</td>
<td>9.3</td>
<td>100</td>
<td>$2.86 \cdot 10^{-2}$</td>
<td>sample #5 stored overnight; contents mixed</td>
</tr>
<tr>
<td>8</td>
<td>9.3</td>
<td>100</td>
<td>$5.10 \cdot 10^{-2}$</td>
<td>sample #4 two days after collection</td>
</tr>
<tr>
<td>8</td>
<td>9.6</td>
<td>800</td>
<td>$6.40 \cdot 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>9.3</td>
<td>100</td>
<td>$4.40 \cdot 10^{-2}$</td>
<td>sample #4 three days after collection</td>
</tr>
<tr>
<td>10</td>
<td>9.4</td>
<td>200</td>
<td>$4.90 \cdot 10^{-2}$</td>
<td>sample #9 stored for 5 days</td>
</tr>
<tr>
<td>11</td>
<td>7.3</td>
<td>100</td>
<td>$3.40 \cdot 10^{-2}$</td>
<td>same day collection</td>
</tr>
<tr>
<td>12</td>
<td>7.2</td>
<td>100</td>
<td>$3.10 \cdot 10^{-2}$</td>
<td>sample #11 stored overnight</td>
</tr>
<tr>
<td>13</td>
<td>7.1</td>
<td>100</td>
<td>$2.30 \cdot 10^{-2}$</td>
<td>sample #11 stored for 7 days</td>
</tr>
</tbody>
</table>

* reaction at T = 4 °C in dark

Samples were stored in dark, at T < 4 °C and unless it is stated otherwise no buffer was added during storage (typical pH of raw wastewater samples ≃ 7.5). To achieve pH ≃ 9.5 borate buffer was added (20% per solution volume for pH ≃ 9.4, 30% for pH ≃ 9.8) before the kinetic experiment. All kinetic experiments were performed at T = 25 °C.
than 20%. The observed uncatalyzed oxidation rates generally increased with time, even when wastewater was stored near \( T = 0 \, ^\circ C \). A slow generation of S(−II) during storage was also noticed (less than 100 \( \mu M = 3.2 \) ppm in about 1 month). Uncatalyzed oxidation rates were lower for samples stored at pH 10 (30% borate buffer pH 10). Furthermore, the observed rate decreased with initial sulfide concentration, \([S(−II)]_0\). This can be explained by the fact that the biological component of the oxidation (i.e., oxidation of sulfide by microorganisms present in the wastewater) is not expected to increase continuously with increasing \([S(−II)]\).

**Peroxymonosulfate experiments**

- **Kinetics**

The total sulfide, S(−II), is present in the form of \( H_2S, HS^- \) or \( S^{2-} \). The relative amounts of these three species depend on the pH of the solution based on the acid/base sulfide equilibria:

\[
H_2S \overset{pK_{a1}}{\rightleftharpoons} HS^- \overset{pK_{a2}}{\rightleftharpoons} S^{2-}
\]  

(1)

where \( K_{a1}, K_{a2} \) are the first (\( pK_{a1} = 7.00 \)) and second (\( pK_{a2} = 17.00 \)) acid–dissociation constants for \( H_2S \), respectively. The value of \( pK_{a2} \) was previously accepted to be ~ 14 (Smith and Martell, 1976), but an earlier spectrophotometric study (Giggenbach, 1971) reported it to be 17.00. It now seems clear that \( pK_{a2} \) is much higher than 14 and that \( S^{2-} \) is not present at appreciable concentrations even in basic solutions (Myers, 1986). Therefore, the species \( S^{2-} \) can be neglected for all practical purposes, and the concentrations of \( H_2S \) and \( HS^- \) are given by:

\[
[H_2S] = \alpha_0[S(−II)]
\]  

(2)
\[ [\text{HS}^-] = \alpha_1[S(-\text{II})] \] 

(3)

where

\[ \alpha_0 = \frac{[\text{H}^+]^2}{([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2})} \propto \frac{[\text{H}^+]}{[\text{H}^+] + K_{a1}} \] 

(4)

\[ \alpha_1 = \frac{K_{a1}[\text{H}^+]}{([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2})} \propto \frac{K_{a1}}{[\text{H}^+] + K_{a1}} \] 

(5)

Therefore, the fraction of the total sulfide, [S(-II)], that is in the form of HS\(^-\) increases with increasing pH. At pH around neutral, 50% of the total S(-II) is present in the form of HS\(^-\); and at pH 10 practically all S(-II) is present as HS\(^-\).

A two-term rate law of the following form has been reported for the oxidation of S(-II) by HSO\(_5\) in water (Betterton and Hoffmann, 1990):

\[-d[S(-\text{II})]/dt = k_1[H_2S][\text{HSO}_5] + k_2[\text{HS}^-][\text{HSO}_5] \] 

(6)

where \( k_1 = 19.8 \text{ M}^{-1}\text{s}^{-1} \) and \( k_2 = 1.22 \cdot 10^4 \text{ M}^{-1}\text{s}^{-1} \) at 4.9 °C and \( \mu = 0.2 \text{ M} \). Based on the activation parameters reported by Betterton and Hoffmann (1990) \( \Delta H_{k1}^\ddagger = 2.8 \text{ kJ mol}^{-1}, \Delta H_{k2}^\ddagger = 38.7 \text{ kJ mol}^{-1} \) the reaction rate constants at 25 °C can be calculated to be: \( k_1 = 21.5 \text{ M}^{-1}\text{s}^{-1} = 1.29 \cdot 10^3 \text{ M}^{-1}\text{min}^{-1} \) and \( k_2 = 3.78 \cdot 10^4 \text{ M}^{-1}\text{s}^{-1} = 2.27 \cdot 10^6 \text{ M}^{-1}\text{min}^{-1} \). The fact that \( k_2 \) is more than 3 orders of magnitude higher than \( k_1 \) explains the observed steep increase in the overall reaction rate with increasing pH. At neutral pH the half life for the oxidation of aqueous S(-II) by 100 \( \mu \text{M} \) HSO\(_5\) can be calculated to be 0.4 second. Peroxymonosulfate is the only significant oxidant at neutral pH since its acidity constants are \( pK_{a1} < 0 \) and \( pK_{a2} = 9.88 \) (Spiro, 1979).
The oxidation of aqueous H_2S by H_2O_2 follows the same rate law (Hoffmann, 1977) with k_1 = 8 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1} and k_2 = 4.8 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1} at 25 ^\circ\text{C} and \mu = 0.4 \text{ M}. Millero et al. (1989) report a value for k_2 of 5.1 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1} at 25 ^\circ\text{C}; they did not observe a two-term rate law and thus do not report a value for k_1.

A series of experiments was conducted where known amounts of HSO_5^- were added to sulfide-spiked wastewater. The pH of the solution was 7.0 – 7.5 and the temperature was kept constant at 25 ± 1 ^\circ\text{C}. Total sulfide concentrations were determined before and after the addition of the oxidant. Upon addition of HSO_5^- a sudden drop in the total sulfide concentration was observed followed by a slower oxidation of the same magnitude as in plain wastewater. The initial oxidation was completed in less than 2 minutes; that was the time required for mixing of the reactants and sampling for total sulfide. Figure B.1 shows the percentage of S(−II) oxidized after 2 min for different molar ratios of initial concentrations of peroxymonosulfate and sulfide, [HSO_5^-]_0/[S(−II)]_0. For molar ratios ≥ 2 complete S(−II) oxidation was observed in less than 2 minutes.

Upon H_2O_2 addition in sulfide-containing wastewater an initial exponential decrease in [S(−II)] was observed. This initial decrease was the same for molar ratios [H_2O_2]_0/[S(−II)]_0 between 1 and 6 and [S(−II)]_0 = 200 \mu\text{M} (6.4 \text{ ppm}). The corresponding first-order rate was k_{obs} = 0.18 \text{ min}^{-1}. At the later stage of the reaction, after the depletion of H_2O_2, the rate of sulfide oxidation was similar to that observed in plain wastewater. A molar ratio [H_2O_2]_0/[S(−II)]_0 = 6:1 was necessary in order to achieve complete oxidation of 200 \mu\text{M} S(−II) in 30 min.

It is noted that our kinetic observations for sulfide oxidation by H_2O_2 in wastewater are similar with those reported by Cadena & Peters (1988) for wastewater collected at a wastewater treatment plant in Albuquerque. These
Figure B.1  S(−II) oxidation by HSO₅⁻ in wastewater. Percentage of \([S(-II)]_o\) oxidized after 2 minutes of HSO₅⁻ addition; pH ≈ 7.5, \([O_2]_o \leq 1.5\) ppm, \([S(-II)]_o = 200 \mu M (6.4 \, \text{ppm})\), T = 25 °C.
researchers reported a value of 0.12 min\(^{-1}\) for the observed initial first–order rate. They also observed a 99% S(−II) oxidation after 30 min for \([H_2O_2]_o:[S(−II)]_o = 3:1\). In our experiments, although we observed \(\approx 96\%\) oxidation for molar ratio of 3:1 we had to double the dosage (i.e., use \([H_2O_2]_o:[S(−II)]_o = 6:1\)) in order to achieve complete oxidation after 30 min of reaction time. This result is consistent with the results reported for large–scale field applications of \(H_2O_2\) for the control of \(H_2S\) in sewers, where a dose close to 6:1 is usually necessary in order to remove sulfides completely (ASCE, 1989).

- **Stoichiometry**

As reported earlier for clean water (Betterton and Hoffmann, 1990), the stoichiometry of the reaction of \(HSO_5^-\) with S(−II) depends on the pH of the solution and the initial molar ratio of the reactants. It was suggested that if there is a large excess of oxidant, especially at high pH, then sulfate and \(H^+\) are produced,

\[
HS^- + 4 HSO_5^- \rightarrow 5 H^+ + 5 SO_4^{2-}
\]  

whereas if the oxidant and the reductant are present in approximately equimolar proportions (especially at low pH) then the products are elemental sulfur, sulfate and water.

\[
HS^- + HSO_5^- \rightarrow \tfrac{1}{8} S_8 + SO_4^{2-} + H_2O
\]

High pH appears to favor sulfate formation, while low pH appears to favor \(S^0\) formation (at high \([HSO_5^-]\)). This behavior parallels that found for the oxidation of
H$_2$S by H$_2$O$_2$ (Hoffmann, 1977). It should be noted that reaction (7) results in the release of proton acidity whereas reaction (8) does not. This may have important implications for the application of HSO$_5^-$ in the control of hydrogen sulfide.

For wastewater applications it is the 'effective stoichiometry' (i.e. the ratio of [HSO$_5^-$]$_{used}$ to [S(−II)]$_{oxidized}$) that is important. Figure B.2 presents the effective stoichiometry observed in experiments conducted in wastewater at different pH values and initial molar ratios of [HSO$_5^-$]$_o$:[S(−II)]$_o$. It was observed that at neutral pH and concentrations of interest ([S(−II)] around 5 ppm) the ratio of [HSO$_5^-$]$_{used}$ (assumed to be the initial concentration of oxidant added to the solution, [HSO$_5^-$]$_o$) to [S(−II)]$_{oxidized}$ increases linearly with the initial molar ratio from [HSO$_5^-$]$_o$:[S(−II)]$_o$ ≈ 0.5 up to [HSO$_5^-$]$_o$:[S(−II)]$_o$ ≈ 3. From linear regression of the experimental data for wastewater at neutral pH the following relationship was found to hold for $1 \leq [\text{HSO}_5^-]_o:[\text{S(−II)}]_o \leq 3$:

$$[\text{HSO}_5^-]_o:[\text{S(−II)}]_{oxidized} = 1.27 \cdot ([\text{HSO}_5^-]_o:[\text{S(−II)}]_o), \quad r^2 = 0.956 \quad (9)$$

For [HSO$_5^-$]$_o$:[S(−II)]$_o$ = 3 the effective stoichiometry was [HSO$_5^-$]$_o$:[S(−II)]$_{oxidized}$ = 4:1, which is the maximum theoretically expected (from eq. 7) assuming that all of the HSO$_5^-$ added is used for the oxidation of S(−II). For [HSO$_5^-$]$_o$:[S(−II)]$_o$ > 3 complete S(−II) oxidation was observed, and since no analysis was done to determine residual HSO$_5^-$, it was not possible to confirm that the actual stoichiometry [HSO$_5^-$]$_{used}$:[S(−II)]$_{oxidized}$ was 4:1 as expected.

It is interesting to note that the effective stoichiometry in wastewater is similar to that observed in clean water experiments (see Figure B.2). The fact that the efficiency of HSO$_5^-$ for sulfide oxidation is not reduced in wastewater indicates
Figure B.2  S(−II) oxidation by HSO₅⁻ in wastewater. Effect of $[\text{HSO}_5^-]_o:[\text{S(−II)}]_o$ on effective reaction stoichiometry $[\text{HSO}_5^-]_o:[\text{S(−II)}]_{\text{oxidized}}$. 
that HSO$_5^-$ reacts preferentially with sulfide and not with other oxidizable substrates present in this complex matrix.

Our experimental results in wastewater indicate that a molar dosage of [HSO$_5^-$]$_o$:[S(−II)]$_o = 2:1$ would lead to $\geq 95\%$ instantaneous S(−II) oxidation, while a molar dosage of 1:1 would lead to an instantaneous oxidation of the order of 85%. Obviously, the appropriate dosage for a particular application would depend on the level of sulfide control desired. It must be noted that if HSO$_5^-$ is added in the form of a salt (in our experiments the triple salt of Oxone that contains 2 molecules of HSO$_5^-$ and has a molecular weight 614.78 gr/mole) the molecular weight of the salt must be used to calculate the corresponding weight ratio from the molar ratio. For the triple salt of Oxone, a molar dosage of [HSO$_5^-$]$_o$:[S(−II)]$_o = 1:1$ corresponds to a weight dosage of 9.6:1.

Control experiments with iron salts

Iron salts are occasionally used in wastewater collection systems and anaerobic digesters to control hydrogen sulfide (ASCE, 1989; Pomeroy and Bowlus, 1949). We decided to investigate the effect of combined addition of ferrous chloride (FeCl$_2$) and peroxymonosulfate. Therefore, control experiments were conducted where a known amount of FeCl$_2$ was added to sulfide–spiked solutions and the disappearance of total dissolved sulfide, S(−II), was followed with time.

Initial experiments were conducted in water, at neutral pH, $T = 25 \, ^\circ\text{C}$ and air saturation ($[O_2] = 2.4 \cdot 10^{-4} \, M = 7.7 \, \text{ppm}$). The oxidation of S(−II) in the presence of FeCl$_2$ initially followed first–order kinetics, and typical observed first–order rates, $k_1$, can be seen in Table B.2. From linear regression of the data, the following expression was derived: $k_1 = 89.73 \cdot [\text{FeCl}_2]^{0.75}$, $r^2 = 0.986$; where $k_1$ in
Table B.2

Sulfide oxidation in the presence of FeCl$_2$

<table>
<thead>
<tr>
<th>[FeCl$_2$] (M)</th>
<th>[S(−II)]$_0$ (μM)</th>
<th>$k_1$ min$^{-1}$</th>
<th>% S(−II) oxidized in 30 minutes</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, pH = 7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.0 \cdot 10^{-5}$</td>
<td>100</td>
<td>$1.5 \cdot 10^{-2}$</td>
<td>36 [O$_2$]$_0 = 240$ μM</td>
<td></td>
</tr>
<tr>
<td>$5.0 \cdot 10^{-5}$</td>
<td>100</td>
<td>$6.4 \cdot 10^{-2}$</td>
<td>68</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1.0 \cdot 10^{-4}$</td>
<td>100</td>
<td>$8.4 \cdot 10^{-2}$</td>
<td>60</td>
<td>&quot;</td>
</tr>
<tr>
<td>$5.0 \cdot 10^{-4}$</td>
<td>100</td>
<td>0.37</td>
<td>69</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1.0 \cdot 10^{-3}$</td>
<td>100</td>
<td>0.43</td>
<td>73</td>
<td>&quot;</td>
</tr>
<tr>
<td>Wastewater, pH = 7.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.0 \cdot 10^{-3}$</td>
<td>125</td>
<td>1.00</td>
<td>87</td>
<td>3.4 $\cdot$ 10$^{-5}$ M FeCl$_3$ present</td>
</tr>
<tr>
<td>$1.0 \cdot 10^{-4}$</td>
<td>125</td>
<td>0.23</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>$2.0 \cdot 10^{-5}$</td>
<td>61</td>
<td>$6.63 \cdot 10^{-2}$</td>
<td>86</td>
<td></td>
</tr>
</tbody>
</table>

All rates at T = 25°C
min\textsuperscript{-1} and [FeCl\textsubscript{2}] in M. It must be noted that due to the low solubility of FeS (FeS\textsubscript{(s)} + H\textsubscript{2}O \rightleftharpoons Fe\textsuperscript{2+} + HS\textsuperscript{-} + OH\textsuperscript{-}, \(K_{sp} = 6 \cdot 10^{-19}\), Myers, 1986) the concentration of free Fe\textsuperscript{2+} in solution is expected to be much lower than the concentration of total FeCl\textsubscript{2} that was used in the above experimental expression. For example, at neutral pH and total sulfide concentration 100 \(\mu\)M, the equilibrium [Fe\textsuperscript{2+}] calculated using the above \(K_{sp}\) is \(\approx 0.12 \ \mu\)M.

The fast initial oxidation of S(-II) was followed by a slower oxidation rate and tapered off at some point after which no further decrease in S(-II) was observed. This could not always be explained by oxygen depletion. It seems plausible that the fast initial S(-II) removal is associated with formation of iron–sulfide complexes and subsequent precipitation and physical S(-II) removal from the solution, while the later slower S(-II) removal is the result of chemical reactions due to the presence of Fe\textsuperscript{2+}. The percentage of initial [S(-II)] oxidized after 30 minutes is also given in Table B.2.

Experiments were subsequently conducted in wastewater. No oxygen was added, and the initial oxygen concentration was that of the wastewater, that was less than 1.5 ppm. Even after subtracting the observed first–order oxidation rate constant for S(-II) oxidation in plain wastewater the initial oxidation rate of S(-II) in the presence of FeCl\textsubscript{2} was about twofold higher in wastewater than the corresponding one for clean water. Nevertheless, the final percentage of S(-II) oxidized was the same for [FeCl\textsubscript{2}] ranging between 50 \(\mu\)M and 1 mM and it was about 85%.

In one experiment, a combination of FeCl\textsubscript{2} and FeCl\textsubscript{3} was used, but no enhancement of the initial oxidation rate or the final S(-II) removal was observed. It must be noted that Fe\textsuperscript{2+} gets oxidized to Fe\textsuperscript{3+} rather readily in the presence of
oxygen. The following experimental rate law is known for pH ≥ 4.5 (Stumm and Morgan, 1981):

\[
\frac{d[\text{Fe}^{2+}]}{dt} = k[\text{OH}^-]^2[\text{Fe}^{2+}][\text{O}_2]
\]  
(10)

where \( k = 8 \cdot 10^{13} \text{ M}^{-2}\text{atm}^{-1}\text{min}^{-1} \). From the above expression and at neutral pH the half-life of \( \text{Fe}^{2+} \) can be calculated to be 4 minutes under air saturation and 22 minutes at \([\text{O}_2] = 1.5 \text{ ppm} \). Therefore, it is possible that at least some of the iron present in the solution is effectively in the form of \( \text{Fe}^{3+} \) and not \( \text{Fe}^{2+} \) and our experimental results present the effect of mixtures of \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \).

**Combined additions of HSO₅⁻ and other chemicals**

Several experiments were conducted in water where peroxymonosulfate and hydrogen peroxide were added together in solutions containing S(−II), at neutral pH and \( T = 25^\circ \text{C} \). An initial sudden drop in \([\text{S(−II)}] \) was observed, followed by a slower decrease afterwards (see Figure B.3). The initial \([\text{S(−II)}] \) oxidation was attributed to peroxymonosulfate while the later slower reaction was assigned to hydrogen peroxide. The ratio of \([\text{HSO}_5^-]_0 \) to \([\text{S(−II)}]_0 \) initially oxidized was practically the same as that observed when only \([\text{HSO}_5^-] \) was present except at low \([\text{S(−II)}]_0 \) values where it was somewhat higher. The first-order rates observed after the initial steep sulfide decrease were in agreement with the rates obtained when only hydrogen peroxide was present. These results indicate that when peroxymonosulfate is used in conjunction with hydrogen peroxide for the oxidation of sulfide the effects of those reagents are simply added together.

Combined additions of \( \text{FeCl}_2 \) and peroxymonosulfate in S(−II) containing
Figure B.3  Combined addition of HSO$_5^-$ and H$_2$O$_2$ in water; [S(−II)]$_o$ = 68 μM, pH = 6.3; arrows indicate additions of HSO$_5^-$; [HSO$_5^-$] = 25 μM after each addition; [H$_2$O$_2$] = 200 μM added at t = 10 min; first-order S(−II) decrease between HSO$_5^-$ additions same as for control experiment when only H$_2$O$_2$ was present.
wastewater at pH around neutral and $T = 25$ °C gave similar results as described above for $\text{H}_2\text{O}_2$ and $\text{HSO}_5^-$. The stoichiometry for the initial reaction was not really affected, but the later reaction rate was much lower than that observed in wastewater experiments when only $\text{FeCl}_2$ was present. These experiments showed that the combined application of peroxymonosulfate and $\text{FeCl}_2$ in wastewater does not affect much the oxidation by peroxymonosulfate but decreases considerably the effect of $\text{FeCl}_2$ on $\text{S}(-\text{II})$ oxidation.

Persulfate ($\text{S}_2\text{O}_8^{2-}$) was added to sulfide–containing deionized water at neutral pH and $T = 25$ °C. No change in $[\text{S}(-\text{II})]$ was observed over a period of about half an hour for $[\text{S}_2\text{O}_8^{2-}]$ up to about 1 mM. A few experiments showed that the addition of $\text{S}_2\text{O}_8^{2-}$ together with peroxymonosulfate at neutral pH and $T = 25$ °C had no effect on the oxidation of $\text{S}(-\text{II})$ by peroxymonosulfate. Work on $\text{S}_2\text{O}_8^{2-}$ was not pursued further.

CONCLUSIONS

Peroxymonosulfate is an efficient oxidant for $\text{S}(-\text{II})$ control in wastewater. At neutral pH $\text{HSO}_5^-$ reacts with $\text{S}(-\text{II})$ in less than 2 minutes contact time and complete oxidation is achieved at molar dosages $[\text{HSO}_5^-]:[\text{S}(-\text{II})] \geq 2:1$. Hydrogen peroxide on the other hand, requires higher molar ratios $([\text{H}_2\text{O}_2]:[\text{S}(-\text{II})] \approx 6)$ and longer times ($\approx 30$ minutes) to achieve complete oxidation. Peroxymonosulfate is not only more efficient than hydrogen peroxide but also presents advantages with respect to storage and handling since it is available in the form of a powder.

It has to be noted, however, that if peroxymonosulfate is added in the form of a triple salt the weight ratio, $[\text{total weight of oxidant}]:[\text{weight of total sulfide}]$, ...
required is higher than the molar ratio. For example, for the commercially available Curox or Oxone (2·KHSO₅·KHSO₄·K₂SO₄, FW = 614.78 gr) a molar ratio of [HSO₅⁻]₀/[S(−II)]₀ = 1:1 corresponds to a weight ratio of Oxone:sulfide = 9.6:1. The cost of Oxone or Curox per weight is currently similar to that of H₂O₂ (there is no wide market for Oxone/Curox at present). Therefore, the use of HSO₅⁻ as an alternative to H₂O₂ does not present an economic advantage at the moment. Combined addition of peroxymonosulfate and hydrogen peroxide can reduce the required cost for sulfide control and could be advantageous in cases where an instantaneous partial control of sulfide is desired while a slower rate for subsequent complete oxidation can be tolerated.

Another point that has to be stressed is that the use of a triple salt like Oxone or Curox results in sulfate concentrations that are higher than those corresponding to the oxidation of the sulfide present in the system; one additional mole of SO₄²⁻ is added per mole of HSO₅⁻. This fact precludes the use of these salts in cases where sulfate is the limiting factor for sulfide generation. Nevertheless, oxidized sulfur is usually not limiting with respect to sulfide production in sewers (ASCE, 1989) and this factor is not expected to be critical for applications in sewers.

Full-scale testing of peroxymonosulfate in sewers is recommended. Recommended molar ratios of [HSO₅⁻] to [S(−II)] for initial testing is between 1:1 and 2:1. Use of excess HSO₅⁻ should be avoided and operation at low pH are preferable.

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REFERENCES


APPENDIX C

USMODEL AND EPIS
COMPUTER CODES
USMODEL
program hmodel

character*30 optitle
character*1 op
character*20 inputs, outputs
dimension x(22), dxdt(22), rk(47), rr(47)
real NO2min

common for EPIS

common/epcom/ymin,hmax
common/int1/rele,ho
common/int2/kto1,mfepi

common/rxn/rn,rk
common/rxns/dxdt,rr
common/vdata/Sm02,O2o,S2O3o
common/flags/flag1
common/ohin/Ohin,Ohminus,Oho,H2O2in,O2k1,Hplus,N02min
common/alpha/a102,a112,a118,a128

Set up parameters for EPIS

neg=22
nr=47
rele=1.0e-2
kto1=5
mfepi=22
tout=0.
flag1=0.

continue

input names of input and output files
not active at the moment for output files
Results are written in pre-specified files

write(*,100)
100 format(’input the name of the data file’)
read(*,110) inputs
110 format(a20)
open(1, file=inputs, status=’old’)
open(11, file=’error.res’, status=’unknown’)
write(*,120)
120 format(’input the name of the output file’)
read(*,110) outputs

pH is treated as a fixed parameter.
[OH-], [H+], and alphas are calculated here

write(*,*) ’input pH’
read(*,*) pH
Hplus=10.**(-pH)
a102=Hplus/(Hplus+10.**(-7.02))
OHminus=10.**(-14.)/10.**(-pH)
a112=10.**(-7.02)/(Hplus+10.**(-7.02))
a118=Hplus/(Hplus+10.**(-7.18))
a128=10.**(-7.18)/(Hplus+10.**(-7.18))

Input of OH, H2O2, NO2- into the aqueous phase
is treated as a constant and is read here

write(*,*) ' input OH (uM/min)',
read(*,*) OHin
write(*,*) ' input OHo (uM)',
read(*,*) OHo
write(*,*) ' input H2O2in (uM/min)',
read(*,*) H2O2in
write(*,*) ' input NO2min (uM/min)',
read(*,*) NO2min

Read rate constants from input file

call input(neq,x,nr,rk)

Specify names of output files

open(2,file='gen.res',status='new')
open(3,file='sulf.res',status='new',rec=250)
open(4,file='rad.res',status='new',rec=250)
open(5,file='ox.res',status='new',rec=250)

write titles in result files

write(2,401) pH, OHin,OHo,H2O2in
+,'NO2min,neq,nr,Sm2o,O2o,O2kl,S2O3o
401 format(5x,'S(-II) + OH in aqueous phase'
 +'/5x,'temperate = 25 C, pH = ',f5.2/
 +'/5x,'OHinput = ',f7.2,' uM/min'/
 +'/5x,'OHo = ',f7.2,' uM'/
 +'/5x,'H2O2input = ',f7.2/5x,'NO2-input = ',f7.2/
 +'/5x,'# of species = ',i3
 +'/5x,'# of reactions = ',i3/5x
 +,'[S(-II)]o = ',f7.2/5x,[O2]o = ',f7.2/5x,
 +,'K1[O2] = ',e10.4/5x,'[S2O3--]o = ',f7.2)
write('***)' ' H+ = ', Hplus,' OH- = ', OHminus
write(2,411) a102,a112,a118,a128
411 format(1x,'S(-II)a0 = ',e10.4, ' S(-II)a1 = ',e10.4/+	x,'S(IV)a0 = ',e10.4,' S(IV)a2 = ',e10.4)

convert uM/min to M/s (units used in DIFFUN)

OHin=Oin*1.e-6/60.
NO2min=NO2min*1.e-6/60.
H2O2in=H2O2in*1.e-6/60.
write(3,402)
402 format(1x,'t (min)',3x,'S(-II)',5x,'S04',5x,'S03'
 +,5x,'S2O3',5x,'NOy',5x,'H2O2')
write(4,403)
403 format(1x,'t (min)',5x,'HS',5x,'H2S2-',5x,'HSOH-',
 +5x,'SO2-',5x,'S2O3H2-',5x,'S4O63-',5x,'SO3-',5x,'SO4-')
write(5,404)
404 format(1x,'O2',5x,'OH',5x,'H2O2',5x,'O2-',5x,'NO2-',5x,'NO3-
 +,5x,'NO2')

tout=0.
Call subroutine OUT to write initial values

call out(neq,x,tout,dxtt,rr)

input time step and total # of steps
calculate parameters needed for EPIS

write(*,140)
140 format(' input time increment in secs')
read(*,*) tdelt
ho=1.0e-4*tdelt
ymin=1.0e-12
hmax=0.1*tdelt
write(*,150)
150 format(' input # of time steps')
read(*,*) iter
write(*,*) ' input tprint (in secs)'
read(*,*) tprint

last chance to change ho, ymin, hmax
(parameters used in EPIS)

write(*,*) ' do you want to change ho/ymin/hmax?'
read(*,56) op
if(op.ne.'y') go to 777
write(*,*)'ho=’,ho
write(*,55)
55 format(' do you want to change it? (Y/N)'
read(*,56) op
if(op.eq.'y') read(*,*) ho
write(*,*)'ymin=’,ymin
write(*,55)
read(*,56) op

if(op.eq.'y') read(*,*) ymin
write(*,*)'hmax=’,hmax
write(*,55)
read(*,56) op
if(op.eq.'y') read(*,*) hmax

777 continue

Last chance to change rate constants

write(*,*) ' do you want to change a rate constant? (y/n)'
read(*,56) op
if(op.ne.'y') go to 77

800 continue
write(*,*) ' input # of the k (1-47) or 0 to terminate'
read(*,*) idk
if(idk.gt.47) go to 800
if(idk.eq.0) go to 77
write(*,*) ' old value: ',rk(idk)
write(*,*) ' input new value'
read(*,*) rk(idk)
go to 800

77 tin=tout
index=1

Loop for EPIS starts here

do 200 i=1,iter
```
tout=tn+i*tdelt
write(*,*) 'starts Loop ',i
call drive(neq,t,ho,x,tout,rele,ktol,mfep1,index)
if index is not 0, results cannot be trusted!
if(index.ne.0)then
write(*,*),t',t','tout','tout','ho','ho','index',index
end if
write(*,*),end Loop ',i
write(*,*)(x(k),k=1,neq)

At the specified time intervals, write concentrations
in result files
tindex=tout/tprint
itindex=tindex
dif=tindex-float(itindex)
if(dif.eq.0.) then
call out(neq,x,tout,dxdtt,rr)
write(*,*),completed:',tout,'secs,Loop:',i
endif

use Warren's option for calculation of derivatives in EPIS
after each step
index=7
200 continue
end of Loop
close(1)
close(2)
close(3)
close(4)
close(5)
close(11)
write(*,*) do you want to start a new run? (Y/N)'
read(*,56)op
if(op.ne.'y') go to 88
flag1=1.
goto 1.
88 continue
stop
end

END OF MAIN PROGRAM

******************************************************************************

SUBROUTINE INPUT

initialize vector x and read rate constants

subroutine input(neq,x,nr,rk)
character*1 op
dimension x(neq),rk(nr)
real NO2min
common parameters
```
common/flags/flag1
common/vdata/Sm2o, O2o, S203o
common/intl/rele,ho
common/int2/ktol,mfepi
common/ohinp/OHin, OHminus, OHo, H2O2in, O2kl, Hplus, NO2min

give a chance to change data related to EPIS

write('*,*) 'do you want to check/change data?'
read('*,99) op
if(op.ne.'y') go to 98
99 format(a1)
write('*,*)'rele=', rele,'do you want to change it? (Y/N)'
read('*,99) op
if(op.eq.'y') read('*,*) rele
write('*,*)'ktol=', ktol,'do you want to change it? (Y/N)'
read('*,99) op
if(op.eq.'y') read('*,*) ktol
write('*,*)'mfepi=', mfepi,'do you want to change it? (Y/N)'
read('*,99) op
if(op.eq.'y') read('*,*) mfepi
continue

initialize vector x

X(1) : OH
X(2) : S(-II) = H2S + HS-
X(3) : HS
X(4) : O2
X(5) : H2S2-
X(6) : HSOH-
X(7) : H2S2t = H2S2 + HS2- + S2--
X(8) : S(IV) = HSO3- + SO3--
X(9) : SO2-
X(10) : S2O3--
X(11) : S2O3OH--
X(12) : S4O6----
X(13) : O2-
X(14) : SO3-
X(15) : SO4-
X(16) : H2O2
X(17) : SO4--
X(18) : NO2-
X(19) : NO3-
X(20) : NO2
X(21) : HS2
X(22) : H2S2O

write('*,*) ' reading input'
do 1 i=1, neq
  1 x(i)=0.

Read initial concentrations of selected species
and oxygen transfer coefficient, O2kl
((O2) addition is O2kl*(O2)s-[O2])

write('*,*) ' input initial [S(-II)] (uM)'
read('*,*) Sm2o
write('*,*) ' input initial [O2] (uM)'
read('*,*) O2o
write('*,*) ' input O2 tranfer coef (1/s)'
read(*,*) O2kl
write(*,*) 'input initial [S2O3] (uM)'
read(*,*) S2O3o
write(*,*) 'input initial [NO2-] (uM)'
read(*,*) NO2o
write(*,*) 'input initial [NO3-] (uM)'
read(*,*) NO3o
write(*,*) Sm2o,o2o,oho,NO2o,NO3o

convert concentrations to M
x(1)=OHo*1.e-6
x(2)=Sm2o*1.e-6
x(4)=O2o*1.e-6
x(10)=S2O3o*1.e-6
x(18)=NO2o*1.e-6
x(19)=NO3o*1.e-6

read rate constants (unless this is not the first run)
if(flagl.eq.0.) then
  do 2 i=1,nr
    read(1,*) rk(i)
  2 continue
endif
write(*,*) 'finished reading data'
return
end

SUBROUTINE OUTPUT (writes results in output files)
subroutine out(neq,x,tout,dxdt,rr)
dimension x(22),xs(22),rr(47),dxdt(22)

  ttt=tout/60.
do 555 j=1,neq
    xs(j)=x(j)*1.e6
    xNOy=xs(18)+xs(19)
    write(3,161) ttt,xs(2),xs(17),xs(8),xs(10),xNOy+
      ,xs(16)
  161 format(1x,f6.2,6(1x,e9.3))
    write(4,162) ttt,xs(3),xs(5),xs(6),xs(9),xs(11),xs(12),+
      ,xs(14),xs(15)
  162 format(1x,f6.2,8(1x,e9.3))
    write(5,163) ttt,xs(4),xs(1),xs(16),xs(13)+
      ,xs(18),xs(19),xs(20)
  163 format(1x,f6.2,7(1x,e9.3))
do 999 kk=1,neq
    write(*,*) 'species#',kk,' is ',xs(kk),' his rate is ',dxdt(kk)
  999 continue
  do 888 kk=1,47
    write(*,*) 'rate of rxn#',kk,' is ',rr(kk)
  888 continue
return
end

SUBROUTINE DIFFUN
the derivatives of the ODE's solved by EPIS are defined here

subroutine diffun(neq,t,xxx,dxdt)
dimension x(22),dxdt(22),xxx(22)
dimension rk(47),rr(47),dxdt(22)
real NO2min

common for EPIS

common/epcomy/ymin,hmax
common/epco99/ncstep,ncfe,ncje

common for input, etc

common/rxnr/nr,rk
common/rxns/dxdt,rr
common/ohinp/Ohin,OHminus,OHo,H2O2in,02k1,Hplus,NO2min
common/alpha/a102,a112,a118,a128

This DO LOOP can be used to set negative values to zero (not recommended for normal runs!)
do 55 kk=1,neq
x(kk)=xxx(kk)
dxdt(kk)=dxdt(kk)
if(x(kk).lt.0.) x(kk)=0.
continue

55
calculate the rates of the reactions X(1:22) are species as defined in INPUT

rr(1)=rk(1)*x(1)*x(1)
rr(2)=rk(2)*x(1)*x(2)*a102
rr(3)=rk(3)*x(1)*x(2)*a12
rr(4)=rk(4)*x(3)*x(3)
rr(5)=rk(5)*x(3)*x(2)*a102
rr(6)=rk(6)*x(3)*x(2)*a12
rr(7)=rk(7)*x(3)*x(4)
rr(8)=rk(8)*x(3)*x(5)
rr(9)=rk(9)*x(6)*x(2)*a112
rr(10)=rk(10)*x(6)*x(2)*a12
rr(11)=rk(11)*x(6)*x(4)
rr(12)=rk(12)*x(5)*x(5)
rr(13)=rk(13)*x(5)*x(4)
rr(14)=rk(14)*x(7)*x(8)*a128
rr(15)=rk(15)*x(7)*x(4)
rr(16)=rk(16)*x(9)*x(4)
rr(17)=rk(17)*x(1)*x(8)*a128
rr(18)=rk(18)*x(1)*x(8)*a118
rr(19)=rk(19)*x(1)*x(10)
rr(20)=rk(20)*x(11)*x(10)
rr(21)=rk(21)*x(12)
rr(22)=rk(22)*x(1)*x(13)
rr(23)=rk(23)*x(4)*x(14)
rr(24)=rk(24)*x(15)*x(8)*a118
rr(25)=rk(25)*x(15)*x(8)*a128
rr(26)=rk(26)*x(15)*x(13)
rr(27)=rk(27)*x(15)*OHminus
rr(28)=rk(28)*x(15)*x(16)
rr(29)=rk(29)*x(8)*x(13)
rr(30)=rk(30)*x(8)*x(16)*a128+
\[ +7.45e7 \times \text{H}_{\text{plus}} \times x(16) \times x(8) \times a118 \]
\[ r(31) = r(31) \times x(2) \times x(16) \]
\[ r(32) = r(32) \times x(10) \times x(16) \]
\[ r(33) = r(33) \times x(2) \times x(13) \]
\[ r(34) = r(34) \times x(14) \times x(14) \]
\[ r(35) = r(35) \times x(1) \times x(16) \]
\[ r(36) = r(36) \times x(1) \times x(18) \]
\[ r(37) = r(37) \times x(1) \times x(20) \]
\[ r(38) = r(38) \times x(20) \times x(8) \]
\[ r(39) = r(39) \times x(2) \times x(15) \]
\[ r(40) = r(40) \times x(5) \]
\[ r(41) = r(41) \times x(2) \times a112 \times x(9) \]
\[ r(42) = r(42) \times x(14) \times x(2) \times a112 \]
\[ r(43) = r(43) \times x(13) \times x(10) \]
\[ r(44) = r(44) \times x(7) \times x(1) \]
\[ r(45) = r(45) \times x(21) \times x(1) \]
\[ r(46) = r(46) \times x(21) \times x(6) \]
\[ r(47) = r(47) \times x(22) \times x(1) \]

calculate the derivatives for EPIS

dxdt(1) = \text{Ohin} - 2.2 \times r(1) + r(2) - r(3) - r(17) - r(18) - r(19) - r(22)

+rr(27) - rr(29) - rr(35) - rr(36) - rr(37) - rr(44) - rr(45) - 4 \times rr(47)

dxdt(2) = -rr(2) - rr(3) - rr(5) + rr(6) + rr(8) + 2 \times rr(12) + rr(14)

++rr(15) - rr(9) - rr(10) - rr(31) + rr(33) - rr(39)

++rr(40) - rr(41) - rr(42)

dxdt(3) = rr(2) - 2 \times rr(4) - rr(5) - rr(6) - rr(7) - rr(8) + rr(39)

++rr(40) + rr(41) + rr(42) + rr(46)

dxdt(4) = rr(7) - rr(11) - rr(13) - rr(15) + rr(22) + rr(26)

+0.2 \times (2.4e-4 \times x(4) - rr(41)

dxdt(5) = +rr(5) + rr(6) - rr(8) + rr(9) + rr(10) - 2 \times rr(12) - rr(13)

+-rr(40)

dxdt(6) = rr(3) - rr(9) - rr(10) - rr(11) - rr(46)

ndxdt(7) = rr(4) + rr(8) + rr(12) + rr(13) - rr(14) - rr(15) - rr(44)

ndxdt(8) = -rr(14) + rr(16) - rr(17) - rr(18) - rr(24) + rr(25) - rr(29)

++rr(30) + 0.5 \times (21 - rr(34) - rr(30) + rr(42) + rr(43)

ndxdt(9) = rr(7) + rr(11) + rr(15) - rr(16) - rr(41)

ndxdt(10) = rr(14) - rr(19) - rr(20) + (7.4 \times rr(21) - rr(32) - rr(43)

++rr(47)

dxdt(11) = rr(19) - rr(20)

ndxdt(12) = rr(20) - 2 \times rr(21)

ndxdt(13) = rr(13) + rr(16) - rr(22) - rr(26) + rr(28) - rr(29) - 3 \times rr(33)

++rr(35) - 2 \times rr(43)

ndxdt(14) = rr(17) + rr(18) - rr(23) + rr(24) + rr(25) - 2 \times rr(34) - rr(42)

dxdt(15) = 0.5 \times rr(23) - rr(24) - rr(25) - rr(26) - rr(27) - rr(28) - rr(39)

ndxdt(16) = H2O2in + rr(1) - rr(28) - rr(30) - 4 \times rr(31) - 4 \times rr(32)

+-rr(35)

dxdt(17) = 0.5 \times rr(23) + rr(24) + rr(25) + rr(26) + rr(27) + rr(39)

++rr(28) + rr(29) + rr(30) + rr(31) + 2 \times rr(32) + rr(33) + rr(34) + rr(38)

++rr(41) + rr(43)

dxdt(18) = NO2min - rr(36) + 2 \times rr(38)

ndxdt(19) = rr(37)

ndxdt(20) = rr(36) - rr(37) - 2 \times rr(38)

ndxdt(21) = rr(44) - rr(45) - rr(46)

ndxdt(22) = rr(46) - rr(47)

c

return

de
SUBROUTINE DRIVE (N, T0, H0, Y0, TOUT, EPS, IERROR, MF, INDEX)

C*******************************************************************************
C
C PURPOSE:
C To Solve a System of Stiff ODEs, with custom modifications to
C handle a non-negativity constraint and to keep error limited
C where neither simple relative nor absolute error bounds
C are appropriate.
C
C ON ENTRY:
C See original documentation below.
C
C ON RETURN:
C See original documentation below.
C
C COMMENTS:
C This is the November 1982 Modification (called EPIS)
C by Dale Warren (Caltech) of the EPISODE program.
C Adapted in February 1986 for the IBM AT running
C MICROSOFT FORTRAN-77 v3.20.
C The ability to convert to DOUBLE PRECISION has been
C removed (for conciseness and readability).
C*******************************************************************************

THE JUNE 24, 1975 VERSION OF
EPISODE.. EXPERIMENTAL PACKAGE FOR INTEGRATION OF
SYSTEMS OF ORDINARY DIFFERENTIAL EQUATIONS,
DY/DT = F(Y,T), Y = (Y(1),Y(2),...,Y(N)) TRANSPOSE,
GIVEN THE INITIAL VALUE OF Y.
THIS CODE IS FOR THE IBM 370/195 AT ARGONNE NATIONAL LABORATORY
AND IS A MODIFICATION OF EARLIER VERSIONS BY G.D.BYRNE
AND A.C.HINDMARSH.

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LIVERMORE, CA 94550, APRIL 1974. ALSO IN ACM TRANSACTIONS
ON MATHEMATICAL SOFTWARE, 1 (1975), PP. 71-96.

2. A. C. HINDMARSH AND G. D. BYRNE, EPISODE.. AN EXPERIMENTAL
PACKAG FOR THE INTEGRATION OF SYSTEMS OF ORDINARY
DIFFERENTIAL EQUATIONS, UCID-30112, L.L.L., MAY, 1975.

3. A. C. HINDMARSH, GEAR.. ORDINARY DIFFERENTIAL EQUATION

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DRIVE IS A DRIVER SUBROUTINE FOR THE EPISODE PACKAGE.
DRIVE IS TO BE CALLED ONCE FOR EACH OUTPUT VALUE OF T.
IT THEN MAKES REPEATED CALLS TO THE CORE INTEGRATOR
SUBROUTINE, TSTEP.

THE INPUT PARAMETERS ARE AS FOLLOWS.
N = THE NUMBER OF DIFFERENTIAL EQUATIONS (USED ONLY ON
FIRST CALL, UNLESS INDEX = -1). N MUST NEVER BE
T0 = THE INITIAL VALUE OF T, THE INDEPENDENT VARIABLE
(USED FOR INPUT ONLY ON FIRST CALL).

H0 = THE STEP SIZE IN T (USED FOR INPUT ONLY ON THE
FIRST CALL, UNLESS INDEX = 3 ON INPUT). WHEN
INDEX = 3, H0 IS THE MAXIMUM ABSOLUTE VALUE OF
THE STEP SIZE TO BE USED.

Y0 = A VECTOR OF LENGTH N CONTAINING THE INITIAL VALUES OF
Y (USED FOR INPUT ONLY ON FIRST CALL).

TOUT = THE VALUE OF T AT WHICH OUTPUT IS DESIRED NEXT.
INTEGRATION WILL NORMALLY GO BEYOND TOUT AND
INTERPOLATE TO T = TOUT. (USED ONLY FOR INPUT.)

EPS = THE RELATIVE ERROR BOUND (USED ONLY ON FIRST CALL,
UNLESS INDEX = -1). THIS BOUND IS USED AS FOLLOWS.
LET R(I) DENOTE THE ESTIMATED RELATIVE LOCAL ERROR
IN Y(I), I.E. THE ERROR RELATIVE TO YMAX(I), AS
MEASURED PER STEP (OF SIZE H) OR PER SS UNITS OF T.
THEN EPS IS A BOUND ON THE ROOT-MEAN-SQUARE NORM
OF THE VECTOR R, I.E.

N
SQRT ( SUM ( R(I)**2 )/N ) .LT. EPS.
I=1

THE VECTOR YMAX IS COMPUTED IN DRIVE AS DESCRIBED
UNDER IERROR BELOW.
IF ERROR CONTROL PER SS UNITS OF T IS DESIRED, SET SS
TO A POSITIVE NUMBER AFTER STATEMENT 10 (WHERE IT IS
NOW SET TO ZERO) AND UPDATE IT AFTER STATEMENT 60.
SEE ALSO THE COMMENTS ON SS AND YMAX BELOW.

IERROR = THE ERROR FLAG WITH VALUES AND MEANINGS AS FOLLOW.

1  ABSOLUTE ERROR IS CONTROLLED. YMAX(I) = 1.0.
2  ERROR RELATIVE TO ABS(Y) IS CONTROLLED. IF Y(I) = 0.0
A DIVIDE ERROR WILL NOT OCCUR. YMAX(I) = ABS(Y(I)).
3  ERROR RELATIVE TO THE LARGEST VALUE OF ABS(Y(I)) SEEN
SO FAR IS CONTROLLED. IF THE INITIAL VALUE OF Y(I) IS
0.0, THEN YMAX(I) IS SET TO 1.0 INITIALLY AND REMAINS
AT LEAST 1.0.
4  SAME AS 2 EXCEPT IF Y(I) INITIALLY <YMIN, YMAX(I)=YMIN
5  SAME AS 3 EXCEPT IF Y(I) CURRENTLY <YMIN, YMAX(I)=YMIN
6  SAME AS 4 EXCEPT IF Y(I) < 0., Error Criteria Not Met
7  SAME AS 5 EXCEPT IF Y(I) < 0., Error Criteria Not Met
8  SAME AS 4 EXCEPT IF Y(I) < -YMIN, Error Criteria Not Met
9  SAME AS 5 EXCEPT IF Y(I) < -YMIN, Error Criteria Not Met

Note: For 6-9, Special Modification so Y(N)<0. rejected

4 & 5 were added for problems when
IERROR=2 fails because of divide by zero and
IERROR=3 scales poorly to ONE -DRW

Note 4 & 5 require user to set YMIN reasonably in DRIVES

MF = THE METHOD FLAG (USED ONLY ON FIRST CALL, UNLESS
INDEX = -1). ALLOWED VALUES ARE 10, 11, 12, 13,
20, 21, 22, 23. MF IS AN INTEGER WITH TWO DECIMAL
DIGITS, METH AND MITER (MF = 10*METH + MITER). (MF
CAN BE THOUGHT OF AS THE ORDERED PAIR (METH,MITER).)
METH IS THE BASIC METHOD INDICATOR.

METH = 1 INDICATES VARIABLE-STEP SIZE, VARIABLE-
ORDER ADAMS METHOD, SUITABLE FOR NON-
STIFF PROBLEMS.

METH = 2 INDICATES VARIABLE-STEP SIZE, VARIABLE-
ORDER BACKWARD DIFFERENTIATION METHOD,
SUITABLE FOR STIFF PROBLEMS.

MITER INDICATES THE METHOD OF ITERATIVE CORRECTION
(NONLINEAR SYSTEM SOLUTION).

MITER = 0 INDICATES FUNCTIONAL ITERATION (NO
PARTIAL DERIVATIVES NEEDED).

MITER = 1 INDICATES A CHORD OR SEMI-STATIONARY
NEWTON METHOD WITH CLOSED FORM (EXACT)
JACOBIAN, WHICH IS COMPUTED IN THE
USER SUPPLIED SUBROUTINE
PEDERV(N,T,Y,PD,NO) DESCRIBED BELOW.

MITER = 2 INDICATES A CHORD OR SEMI-STATIONARY
NEWTON METHOD WITH AN INTERNALLY
COMPUTED FINITE DIFFERENCE APPROXIMATION
TO THE JACOBIAN.

MITER = 3 INDICATES A CHORD OR SEMI-STATIONARY
NEWTON METHOD WITH AN INTERNALLY
COMPUTED DIAGONAL MATRIX APPROXIMATION
TO THE JACOBIAN, BASED ON A DIRECTIONAL
DERIVATIVE.

INDEX = INTEGER USED ON INPUT TO INDICATE TYPE OF CALL,
WITH THE FOLLOWING VALUES AND MEANINGS:

1 THIS IS THE FIRST CALL FOR THIS PROBLEM.
0 THIS IS NOT THE FIRST CALL FOR THIS PROBLEM,
AND INTEGRATION IS TO CONTINUE.
-1 THIS IS NOT THE FIRST CALL FOR THE PROBLEM,
AND THE USER HAS RESET N, EPS, AND/OR MF.
2 SAME AS 0 EXCEPT THAT TOUT IS TO BE HIT
EXACTLY (NO INTERPOLATION IS DONE).
ASSUMES TOUT .GE. THE CURRENT T.
3 SAME AS 0 EXCEPT CONTROL RETURNS TO CALLING
PROGRAM AFTER ONE STEP. TOUT IS IGNORED.
7 THIS IS NOT THE FIRST CALL, BUT THE Y ARRAY
HAS CHANGED SLIGHTLY, SO THE DERIVATIVES
MUST BE RECOMPUTED (NEW BY DRW)
SINCE THE NORMAL OUTPUT VALUE OF INDEX IS 0,
IT NEED NOT BE RESET FOR NORMAL CONTINUATION.
SINCE THE NORMAL OUTPUT VALUE OF INDEX IS 0,
IT NEED NOT BE RESET FOR NORMAL CONTINUATION.

AFTER THE INITIAL CALL, IF A NORMAL RETURN OCCURRED AND A NORMAL
CONTINUATION IS DESIRED, SIMPLY RESET TOUT AND CALL AGAIN.
ALL OTHER PARAMETERS WILL BE READY FOR THE NEXT CALL.
A CHANGE OF PARAMETERS WITH INDEX = -1 CAN BE MADE AFTER
THEM SUCCESSFUL OR AN UNSUCCESSFUL RETURN.

THE OUTPUT PARAMETERS ARE AS FOLLOWS.

T0 = THE OUTPUT VALUE OF T. IF INTEGRATION WAS SUCCESSFUL,
T0 = TOUT. OTHERWISE, T0 IS THE LAST VALUE OF T
REACHED SUCCESSFULLY.

H0 = THE STEP SIZE H USED LAST, WHETHER SUCCESSFULLY OR NOT.

Y0 = THE COMPUTED VALUES OF Y AT T = T0.

INDEX = INTEGER USED ON OUTPUT TO INDICATE RESULTS,
WITH THE FOLLOWING VALUES AND MEANINGS:

0 INTEGRATION WAS COMPLETED TO TOUT OR BEYOND.
-1 THE INTEGRATION WAS HALTED AFTER FAILING TO PASS THE
ERROR TEST EVEN AFTER REDUCING H BY A FACTOR OF
1.E10 FROM ITS INITIAL VALUE.
-2 AFTER SOME INITIAL SUCCESS, THE INTEGRATION WAS
HALTED EITHER BY REPEATED ERROR TEST FAILURES OR
BY A TEST ON EPS. POSSIBLY TOO MUCH ACCURACY HAS
BEEN REQUESTED, OR A BAD CHOICE OF MF WAS MADE.
-3 THE INTEGRATION WAS HALTED AFTER FAILING TO ACHIEVE
CORRECTOR CONVERGENCE EVEN AFTER REDUCING H BY A
FACTOR OF 1.E10 FROM ITS INITIAL VALUE.
-4 IMMEDIATE HALT BECAUSE OF ILLEGAL VALUES OF INPUT
PARAMETERS. SEE PRINTED MESSAGE.
-5 INDEX WAS -1 ON INPUT, BUT THE DESIRED CHANGES OF
PARAMETERS WERE NOT IMPLEMENTED BECAUSE TOUT
WAS NOT BEYOND T. INTERPOLATION TO T = TOUT WAS
PERFORMED AS ON A NORMAL RETURN. TO CONTINUE,
SIMPLY CALL AGAIN WITH INDEX = -1 AND A NEW TOUT.
-6 INDEX WAS 2 ON INPUT, BUT TOUT WAS NOT BEYOND T.
NO ACTION WAS TAKEN.
-7 INTEGRATION SUSPENDED BECAUSE A Y(I)<0 FOUND,
WITH NRMN<=I<=NRMAX, AND IERROR OF 6 OR 7
HAD PROSCRIBED AGAINST NEGATIVE VALUES --DRW

IN ADDITION TO DRIVE, THE FOLLOWING SUBROUTINES ARE USED BY AND
PROVIDED IN THIS PACKAGE:
INTERP(TOUT,Y,N0,Y0) INTERPOLATES TO GIVE OUTPUT VALUES AT
T = TOUT BY USING DATA IN THE Y ARRAY.
TSTEP(Y,N0) IS THE CORE INTEGRATION SUBROUTINE, WHICH INTEGRATES
OVER A SINGLE STEP AND DOES ASSOCIATED ERROR
CONTROL.
COSSET SETS COEFFICIENTS FOR USE IN TSTEP.
ADJUST(Y,N0) ADJUSTS THE HISTORY ARRAY Y ON REDUCTION OF ORDER.
PSET(Y,N0,CON,MITER,IER) COMPUTES AND PROCESSES THE JACOBIAN
MATRIX, J = DF/DY.
DEC(N,N0,A,IP,IER) PERFORMS THE LU DECOMPOSITION OF A MATRIX.
SOL(N,N0,A,B,IP) SOLVES A LINEAR SYSTEM A*X = B, AFTER DEC
HAS BEEN CALLED FOR THE MATRIX A.
NOTE: PSET, DEC, AND SOL ARE CALLED IF AND ONLY IF MITER = 1
OR MITER = 2.

THE USER MUST FURNISH THE FOLLOWING SUBROUTINES:
DIFFUN(N,T,Y,YDOT) COMPUTES THE FUNCTION YDOT = F(Y,T),
THE RIGHT HAND SIDE OF THE ORDINARY
DIFFERENTIAL EQUATION SYSTEM, WHERE Y
AND YDOT ARE VECTORS OF LENGTH N.
PEDERV(N,T,Y,PD,N0) COMPUTES THE N BY N JACOBIAN MATRIX
OF PARTIAL DERIVATIVES AND STORES IT IN PD AS
AN N0 BY N0 ARRAY. PD(I,J) IS TO BE SET
TO THE PARTIAL DERIVATIVE OF YDOT(I) WITH RESPECT TO Y(J). PEDERV IS CALLED IF AND
ONLY IF MITER = 1. FOR OTHER VALUES OF
MITER, PEDERV CAN BE A DUMMY SUBROUTINE.

CAUTION:
AT THE PRESENT TIME THE MAXIMUM NUMBER OF DIFFERENTIAL
EQUATIONS, WHICH CAN BE SOLVED BY EPISODE, IS 20. TO
CHANGE THIS NUMBER TO A NEW VALUE, SAY NMAX, CHANGE
Y(20,13) TO Y(NMAX,13), YMAX(20) TO YMAX(NMAX),
ERROR(20) TO ERROR(NMAX), SAVE1(20) TO SAVE1(NMAX),
SAVE2(20) TO SAVE2(NMAX), PW(400) TO PW(NMAX*NMAX),
AND IPIV(20) TO IPIV(NMAX) IN THE COMMON AND DIMENSION
STATEMENTS BELOW. ALSO CHANGE THE ARGUMENT IN THE
IF...GO TO 440 STATEMENT (AFTER THE COMMON STATEMENTS)
FROM 20 TO NMAX. NO OTHER CHANGES NEED TO BE MADE TO
ANY OTHER SUBROUTINE IN THIS PACKAGE WHEN THE MAXIMUM
NUMBER OF EQUATIONS IS CHANGED. ELSEWHERE, THE COLUMN
LENGTH OF THE Y ARRAY IS N0 INSTEAD OF 20. THE ROW
LENGTH OF Y CAN BE REDUCED FROM 13 TO 6 IF METH = 2.
THE ARRAY IPIV IS USED IF AND ONLY IF MITER = 1 OR
C MITER = 2. THE SIZE OF THE PW ARRAY CAN BE REDUCED
C TO 1 IF MITER = 0 OR TO N IF MITER = 3.
C C THE COMMON BLOCK EPCOM9 CAN BE ACCESSED EXTERNALLY BY THE USER,
C IF HE DESIRES. IT CONTAINS THE STEP SIZE LAST USED SUCCESSFULLY
C (HUSED), THE ORDER LAST USED SUCCESSFULLY (NQUSED), THE
C NUMBER OF STEPS TAKEN SO FAR (NSTEP), THE NUMBER OF FUNCTION
C EVALUATIONS (DIFFFUN CALLS) SO FAR (NFE), AND THE NUMBER OF
C JACOBIAN EVALUATIONS SO FAR (NJIE).
C C IN A DATA STATEMENT BELOW, LOUT IS SET TO THE LOGICAL UNIT NUMBER
C FOR THE OUTPUT OF MESSAGES DURING INTEGRATION. CURRENTLY, LOUT
C = 3.
C---------------------------------------------------------------
C$ THIS IS THE SINGLE PRECISION VERSION OF SUBROUTINE DRIVE.
C C Set Maximum number of dif. eqs.
PARAMETER ( NMAX =120 )
PARAMETER ( NMAXSQ = NMAX*NMAX )
C* C All the Explicit Variable Type Definitions are Unnecessary
C Simply insert the following card in the each module
C IMPLICIT REAL*(A-H,O-Z) , INTEGER(I-N)
C Where # is 8 for Double Precision and 4 for Single Precision
C*
INTEGER IERROR, INDEX, MP, N
INTEGER IPIV, JSTART, KFLAG, MFC, NC, NFE, NJE,
1 NQUSED, NSQ, NSTEP
INTEGER I, KGO, NHCU, N0
INTEGER LOUT
INTEGER NFLAG
REAL EPS, H0, TOUT, T0, Y0
REAL EPSC, EPSJ, ERROR, HMAX, H, HMIN, HUSED,
1 PW, SAVE1, SAVE2, SS, T, UROUND, YMAX
REAL AYI, D, T0P, Y
REAL HCU, Y
REAL FOUR, HUNDRD, ONE, TEN, ZERO
REAL*4 YMIN, YCUT
DIMENSION Y(NMAX,13)
DIMENSION Y0(N)
C COMMON /EPCOM1/T,H,HMIN,HMAX,EPSC,SS,UROUND,NC,MFC,KFLAG,JSTART
COMMON /EPCOM2/ YMAX(NMAX)
COMMON /EPCOM3/ ERROR(NMAX)
COMMON /EPCOM4/ SAVE1(NMAX)
COMMON /EPCOM5/ SAVE2(NMAX)
COMMON /EPCOM6/ PW(NMAXSQ)
COMMON /EPCOM7/ IPIV(NMAX)
COMMON /EPCOM8/ EPSJ,NSQ
COMMON /EPCOM9/ HUSED,NQUSED,NSTEP,NFE,NJE
C For # of Evaluations
COMMON /EPCO99/ NCSTEP,NCFE,NCJE
C Set by calling prog - DRW
COMMON /EPCOMR/ NRMIN,NRMAX
C Set by calling prog - DRW
COMMON /EPCOMY/ YMIN,HMAXMX
C C Messages to Unit # 3, or FOR003.DAT
DATA LOUT /11/
DATA Hicut /0.1E0/
DATA Four /4.0E0/, Hundrd /1.0E2/, One /1.0E0/,
1 TEN /1.0E1/, Zero /0.0E0/
C Convenient for Nucleation Tests - DRW
C DATA YMIN /1.0E-17/
C Normal Continuation
IF (INDEX .EQ. 0) GOTO 20
C Continue & Hit Exactly
IF (INDEX .EQ. 2) GOTO 25
C Integration Mode Reset
IF (INDEX .EQ. -1) GOTO 30
C Single Step Integration
IF (INDEX .EQ. 3) GOTO 40
C NEW -- Continue with Y modified
IF (INDEX .EQ. 7) GOTO 27
C Bad Input; 1 is First Call
IF (INDEX .NE. 1) GOTO 430
C
IF (EPS .LE. ZERO) GOTO 400
IF (N .LE. 0) GOTO 410
IF (N .GT. NMAX) GOTO 440
IF (|(T0-TOUT)*H0 .GE. ZERO) GOTO 420
WRITE(OUTL,999) T0,H0,TOUT
999 FORMAT(1H ,2X, 'T0=',E12.5,2X, 'H0=',E12.5,2X, 'TOUT=',E12.5)
C---------------------------------------------
C IF INITIAL VALUES FOR YMAX OTHER THAN THOSE BELOW ARE DESIRED,
C THEY SHOULD BE SET HERE. ALL YMAX(I) MUST BE POSITIVE. IF
C VALUES FOR HMINT OR HMAX, THE BOUNDS ON THE ABSOLUTE VALUE OF H,
C OTHER THAN THOSE BELOW, ARE DESIRED, THEY ALSO SHOULD BE SET HERE.
C IF ERROR PER SS UNITS OF T IS TO BE CONTROLLED, SS SHOULD BE SET
C TO A POSITIVE VALUE BELOW. ERROR PER UNIT STEP IS CONTROLLED
C WHEN SS = 1. THE DEFAULT VALUE FOR SS IS 0 AND YIELDS CONTROL
C OF ERROR PER STEP.
C---------------------------------------------
C SET UROUND, THE MACHINE ROUNDOFF CONSTANT, HERE.
C USE STATEMENT BELOW FOR SHORT PRECISION ON IBM 360 OR 370.
C UROUND = 9.53674E-7
C USE STATEMENT BELOW FOR SINGLE PRECISION ON CDC 7600 OR 6600.
C UROUND = 7.105427406E-15
C USE STATEMENT BELOW FOR LONG PRECISION ON IBM 360 OR 370.
C---------------------------------------------
C
C Set for VAX Single Precision
UROUND = 5.960E-8
IF (ERROR.LE.5) GOTO 3
C Default check for negative Y(I)
IF (NRMIN.LE.0) NRMIN=1
C or, for all values of I
C IF (NRMAX.LE.0) NRMAX=N
C Special for MAEROS with Vapor
IF (NRMAX.LE.0) NRMAX=N-1
C
3 DO 10 I = 1,N
C
GOTO (5, 6, 7, 8, 8, 8, 8, 8, 8), IERROR
C IERROR = 1, 2, 3, 4, 5, 6, 7, 8, 9 ------Six Extra by DRW------
C  For ABSOLUTE Error
  5  YMAX(I) = ONE
     GOTO 10
  6  YMAX(I) = ABS(Y0(I))
C  To Avoid Automatic /0
  7  IF (YMAX(I).EQ.ZERO) YMAX(I)=YMIN
     GOTO 10
  8  YMAX(I) = ABS(Y0(I))
C  For SEMI-RELATIVE to I.
  9  IF (YMAX(I).EQ.ZERO) YMAX(I) = ONE
     GOTO 10
C  For RELATIVE Error
 10  WRITE(LOUT,998) I,YMAX(I),ABS(Y0(I)),YMIN
C  998 FORMAT(1H,2X,'I=',I2,2X,'YMAX=',E12.5,2X,'ARY=',E12.5,2X,
           S,'YMIN=',E12.5)
      IF (YMAX(I).LT. YMIN) YMAX(I) = YMIN
 11  Y(I,1) = Y0(I)
      NC = N
      T = T0
      H = H0
     WRITE(LOUT,997) NC,T,H
C  997 FORMAT(1H,2X,'NC=',I2,2X,'T=',E12.5,2X,'H=',E12.5)
      IF ((T+H).EQ. T) WRITE(LOUT,15) T
C  15 FORMAT(/46H--- MESSAGE FROM SUBROUTINE DRIVE IN EPISODE, ,
           24H THE O.D.E. SOLVER. ---/22H WARNING.. T + H = T = ,
           E18.8,18H IN THE NEXT STEP./)
C  2 FORMAT(' WARNING... T + H = T = ',1PE16.7,' IN THE NEXT STEP. ')
      HMIN = ABS(H0)
      HMAX = ABS(T0 - TOUT)*TEN
      HMAX = AMIN1(HMAX,HMAXMX)
      EPSC = EPS
      MFC = MF
      JSTART = 0
      SS = ZERO
      N0 = N
      NS0 = N0*N0
      EPSJ = SQRT(UROUND)
      NHCUT = 0
      YCUT = ZERO
      IF (TERROR.GE.8) YCUT=-YMIN
      GOTO 50
C  T0P IS THE PREVIOUS OUTPUT VALUE OF T0 FOR USE IN HMAX.--------
  20  HMAX = ABS(TOUT - T0P)*TEN
      HMAX = AMIN1(HMAX,HMAXMX)
      GOTO 80
  25  HMAX = ABS(TOUT - T0P)*TEN
      HMAX = AMIN1(HMAX,HMAXMX)
C  IF ((T-TOUT)*H .GE. ZERO) GOTO 460
      GOTO 85
C  Throw out old derivative information
  27  JSTART = 0
C?  H=H0 ! Use New Step Size (if MAIN changed it)?
      IF ((T0-TOUT)*H0 .GE. ZERO) GOTO 420
      GOTO 45
C
30 IF ((T-TOUT)*H .GE. ZERO) GOTO 450
IF (MF .NE. MFC) JSTART = -1
NC = N
EPS = EPS
MFC = MF
GOTO 45
C
40 HMAX = H0
HMAX = AMIN1(HMAX,HMAXMX)
C
45 IF ((T+H) .EQ. T) WRITE(LOUT,15) T
C
50 CALL TSTEP(Y, NO)
C
KGO = 1 - KFLAG
WRITE(LOUT,996) KFLAG
C
996 FORMAT(1H ,2X,'KFLAG='I3)
GOTO (60, 100, 200, 300), KGO
C
KFLAG = 0, -1, -2, -3

C
60 CONTINUE
C
C NORMAL RETURN FROM TSTEP.
C
C THE WEIGHTS YMAX(I) ARE UPDATED. IF DIFFERENT VALUES ARE DESIRED, C THEY SHOULD BE SET HERE. IF SS IS TO BE UPDATED FOR CONTROL OF C ERROR PER SS UNITS OF T, IT SHOULD ALSO BE DONE HERE. A TEST IS C MADE TO DETERMINE IF EPS IS TOO SMALL FOR MACHINE PRECISION.
C
C ANY OTHER TESTS OR CALCULATIONS THAT ARE REQUIRED AFTER EACH STEP C SHOULD BE INSERTED HERE.
C
C IF INDEX = 3, Y0 IS SET TO THE CURRENT Y VALUES ON RETURN.
C IF INDEX = 2, H IS CONTROLLED TO HIT TOUT (WITHIN ROUNDOFF C ERROR), AND THEN THE CURRENT Y VALUES ARE PUT IN Y0 ON C RETURN. FOR ANY OTHER VALUE OF INDEX, CONTROL RETURNS TO C THE INTEGRATOR UNLESS TOUT HAS BEEN REACHED. THEN C INTERPOLATED VALUES OF Y ARE COMPUTED AND STORED IN Y0 ON C RETURN.
C IF INTERPOLATION IS NOT DESIRED, THE CALL TO INTERP SHOULD C BE DELETED AND CONTROL TRANSFERRED TO STATEMENT 500 INSTEAD C OF 520.
C
C
C      DO 990 I=1,N
C IF(Y(I,1).LE.1.0E-20) Y(I,1)=1.0E-20
C 990 CONTINUE
C
C D = ZERO
C Initialize to no negative problem
NFLAG = 0
DO 70 I = 1,N
AYI = ABS(Y(I,1))
GOTO (70, 62, 68, 64, 68, 63, 67, 63, 67, IERROR)
C IERROR = 1, 2, 3, 4, 5, 6, 7, 8, 9 --------> DRW --------
C
C Relative Error
62 YMAX(I) = AYI
C No sense in permitting /0.
IF (AYI.EQ.ZERO) YMAX(I)=YMIN
GOTO 70
63 IF (Y(I,1).LT.YCUT.AND.I.GE.NRMIN.AND.I.LE.NRMAX) NFLAG=I
C Relative Error not below YMIN -DRW
64 YMAX(I) = AMAX1(AYI,YMIN)
GOTO 70
67 IF (Y(I,1).LT.YCUT.AND.I.GE.NRMIN.AND.I.LE.NRMAX) NFLAG=I
C SemiRelative Error
68 YMAX(I) = AMAX1(YMAX(I), AYI)
GOTO 70
70 D = D + (AYI/YMAX(I))**2
D = D*(UROUND/EPS)**2
C Halt Condition
IF (D.GT.FLOAT(N)) GOTO 250
IF (INDEX.EQ.3) GOTO 500
IF (INDEX.EQ.2) GOTO 85
C Integration Passed TOUT
80 IF ((T-TOUT)*H .GE. ZERO) GOTO 82
C Negative Value Error
IF (NFLAG.GT.0) GOTO 275
C Keep Going in Time
GOTO 45
C Passed TOUT, set Y0
82 CALL INTERP(TOUT, Y, N0, Y0)
C Done, so T0=TOUT
T0 = TOUT
GOTO 520
85 IF (((T+H)-TOUT)*H .LE. ZERO) GOTO 45
IF (ABS(T-TOUT) .LE. HUNDRD*UROUND*HMAX) GOTO 500
IF ((T-TOUT)*H .GE. ZERO) GOTO 500
H = (TOUT - T)*ONE - FOUR*UROUND
JSTART = -1
GOTO 45

C----------------------------------------
C ON AN ERROR RETURN FROM TSTEP, AN IMMEDIATE RETURN OCCURS IF
C KFLAG = -2, AND RECOVERY ATTEMPTS ARE MADE OTHERWISE.
C TO RECOVER, H AND HMIN ARE REDUCED BY A FACTOR OF .1 UP TO 10
C TIMES BEFORE GIVING UP.
C----------------------------------------

100 WRITE (LOUT,101)
101 FORMAT (/46H--- MESSAGE FROM SUBROUTINE DRIVE IN EPISODE.,
       1 24H THE O.D.E. SOLVER. ---/
       WRITE(LOUT,105) T,HMIN
105 FORMAT(/35H KFLAG = -1 FROM INTEGRATOR AT T = ,1PE16.6/
       1 1 40H ERROR TEST FAILED WITH ABS(H) = HMIN =,1PE16.6/
       110 IF (NHCU.T.EQ.10) GOTO 150
       NHCU = NHCU + 1
       HMIN = HCUT*HMIN
       H = HCUT*H
       WRITE (LOUT,115) H
115 FORMAT(24H H HAS BEEN REDUCED TO ,1PE16.6,
       1 26H AND STEP WILL BE RETRIED//)
       JSTART = -1
       GOTO 45
GOTO 45
```
C
150 WRITE (LOUT,155)
155 FORMAT('4H PROBLEM APPEARS UNSOLVABLE WITH GIVEN INPUT')
     GOTO 500
C
200 WRITE (LOUT,101)
205 WRITE (LOUT,205) T,H,EPS
205 FORMAT('14H KFLAG= -2 T=,1PE17.7,4H H =,E16.6,6H EPS =,E16.6/
     1 50H THE REQUESTED ERROR IS TOO SMALL FOR INTEGRATOR.')
     GOTO 500
C
250 WRITE (LOUT,101)
255 WRITE (LOUT,255) T,EPS
255 FORMAT('46H INTEGRATION HALTED BY SUBROUTINE DRIVE AT T =,
     1 1PE17.8/43H EPS IS TOO SMALL FOR MACHINE PRECISION AND/
     2 29H PROBLEM BEING SOLVED. EPS =,1PE16.6//)
     KFLAG = -2
     GOTO 500
C
275 WRITE (LOUT,280) T,NFLAG,Y(NFLAG,1)
280 FORMAT(' INTEGRATION SUSPENDED BY NEGATIVE CONCENTRATION AT',
     1 $' T=',1PE10.3/' ELEMENT #',13,' WAS',1PE12.3,6X,'(DRIVES)')
     KFLAG=-7
C
INDEX for Negative Value
     GOTO 500
C
300 WRITE (LOUT,101)
305 WRITE (LOUT,305) T
305 FORMAT('34H KFLAG = -3 FROM INTEGRATOR AT T =,1PE18.8/
     1 45H CORRECTOR CONVERGENCE COULD NOT BE ACHIEVED//)
     GOTO 110
C
400 WRITE (LOUT,101)
405 WRITE (LOUT,405) EPS
405 FORMAT('35H ILLEGAL INPUT.. EPS .LE. 0. EPS = ,E16.6//)
     INDEX = -4
     RETURN
C
410 WRITE (LOUT,101)
415 WRITE (LOUT,415) N
415 FORMAT('31H ILLEGAL INPUT.. N .LE. 0. N = ,I8//)
     INDEX = -4
     RETURN
C
420 WRITE (LOUT,101)
425 WRITE (LOUT,425) T0,TOUT,H0
425 FORMAT('39H ILLEGAL INPUT.. (T0 - TOUT)*H0 .GE. 0. /
     1 5H T0 = ,1PE18.8,7H TOUT = ,E18.8,5H H0 = ,E16.6//)
     INDEX = -4
     RETURN
C
430 WRITE (LOUT,101)
435 WRITE (LOUT,435) INDEX
435 FORMAT('24H ILLEGAL INPUT.. INDEX =,I8//)
     INDEX = -4
     RETURN
C
440 WRITE (LOUT,101)
445 WRITE (LOUT,445) N
445 FORMAT('39H ILLEGAL INPUT. THE NUMBER OF ORDINARY/
```
43H DIFFERENTIAL EQUATIONS BEING SOLVED IS N =, 16/
42H STORAGE ALLOCATION IN SUBROUTINE DRIVE IS/
46H TOO SMALL. SEE COMMENTS IN SUBROUTINE DRIVE.}
INDEX = -4
RETURN

C
450 WRITE (LOUT,101)
455 WRITE (LOUT,455) T,TOUT,H
FORMAT(/46H INDEX = -1 ON INPUT WITH (T - TOUT)*H .GE. 0./
1 44H INTERPOLATION WAS DONE AS ON NORMAL RETURN./
2 41H DESIRED PARAMETER CHANGES WERE NOT MADE./
3 4H T =,E18.8,7H TOUT =,E18.8,4H H =,E16.6//)
CALL INTERP (TOUT, Y, NO, Y0)
T0 = TOUT
INDEX = -5
RETURN

C
460 WRITE (LOUT,101)
465 WRITE (LOUT,465) T,TOUT,H
FORMAT(/45H INDEX = 2 ON INPUT WITH (T - TOUT)*H .GE. 0./
1 44H T =,E18.8,7H TOUT =,E18.8,4H H =,E16.6//)
INDEX = -6
RETURN

C
500 T0 = T
DO 510 I = 1,N
510 Y0(I) = Y(I,1)
INDEX = KFLAG
T0P = T0
H0 = HUSED
IF (KFLAG .NE. 0) H0 = H
RETURN

C
C==============================================================================
C
C SUBROUTINE INTERP (TOUT, Y, NO, Y0)
C==============================================================================
C SUBROUTINE INTERP COMPUTES INTERPOLATED VALUES OF THE DEPENDENT
C VARIABLE Y AND STORES THEM IN Y0. THE INTERPOLATION IS TO THE
C POINT T = TOUT AND USES THE NORDSIECK HISTORY ARRAY Y AS FOLLOWS..
C
C WHERE S = -(T-TOUT)/H.
C==============================================================================
C THIS IS THE SINGLE PRECISION VERSION OF SUBROUTINE INTERP.
C==============================================================================
C CAUTION: NOT ALL MEMBERS OF EP COMI ARE USED IN THIS SUBROUTINE.
C==============================================================================

INTEGER NO
INTEGER JSTART, KFLAG, MF, N
INTEGER I, J, L
REAL TOUT, Y, Y0
REAL EPS, H, HMAX, HMIN, SS, T, UROUND
REAL S, S1
REAL ONE
DIMENSION Y0(N0), Y(N0,13)

C COMMON /EPCOM1/ T, H, HMIN, HMAX, EPS, SS, UROUND, N, MF, KFLAG, JSTART
DATA ONE /1.0E0/
DO 10 I = 1, N
  10 Y0(I) = Y(I,1)
L = JSTART + 1
S = (TOUT - T)/H
S1 = ONE
DO 30 J = 2, L
  20 S1 = S1*S
  30 Y0(I) = Y0(I) + S1*Y(I,J)
CONTINUE
RETURN
END

C
C============================================
C
C SUBROUTINE TSTEP (Y, N0)
C============================================
C
C TSTEP PERFORMS ONE STEP OF THE INTEGRATION OF AN INITIAL VALUE
C PROBLEM FOR A SYSTEM OF ORDINARY DIFFERENTIAL EQUATIONS.
C COMMUNICATION WITH TSTEP IS VIA THE FOLLOWING VARIABLES..
C
C Y
C AN N0 BY LMAX ARRAY CONTAINING THE DEPENDENT VARIABLES
C AND THEIR SCALED DERIVATIVES. LMAX IS CURRENTLY 6 FOR
C THE VARIABLE STEP BACKWARD DIFFERENTIATION FORMULAS,
C AND 13 FOR THE VARIABLE STEP ADAMS FORMULAS.
C (LMAX -1) = MAXDER, THE MAXIMUM ORDER USED.
C SEE SUBROUTINE COSET. Y(I,J+1) CONTAINS THE
C J-TH DERIVATIVE OF Y(I), SCALED BY H**(J)/FACT(J)
C FOR J = 0,1,...,NQ, WHERE NQ IS THE CURRENT ORDER.
C N0 A CONSTANT INTEGER .GE. N, USED FOR DIMENSIONING
C PURPOSES.
C T THE INDEPENDENT VARIABLE, UPDATED ON EACH STEP TAKEN.
C H THE STEP SIZE TO BE ATTEMPTED ON THE NEXT STEP.
C H IS ALTERED BY THE ERROR CONTROL ALGORITHM DURING
C THE SOLUTION OF THE PROBLEM. H CAN BE EITHER POSITIVE
C OR NEGATIVE, BUT ITS SIGN MUST REMAIN CONSTANT
C THROUGHOUT THE PROBLEM RUN.
C HMIN, THE MINIMUM AND MAXIMUM ABSOLUTE VALUES OF THE STEP
C HMAX SIZE TO BE USED FOR THE STEP. THESE MAY BE CHANGED AT
C ANY TIME, BUT THE CHANGE WILL NOT TAKE EFFECT UNTIL THE
C NEXT CHANGE IN H IS MADE.
C EPS THE RELATIVE ERROR BOUND. SEE DESCRIPTION IN
C SUBROUTINE DRIVE.
C SS THE SIZE OF THE TIME INTERVAL TO BE USED FOR ERROR
C CONTROL. A DEFAULT VALUE OF 0 IS USED TO PRODUCE
C CONTROL OF ERROR PER STEP. SEE SUBROUTINE DRIVE.
C UROUND THE UNIT OF ROUNDOFF FOR THE COMPUTER BEING USED.
C N THE NUMBER OF FIRST ORDER ORDINARY DIFFERENTIAL
C EQUATIONS BEING SOLVED.
C MF THE METHOD FLAG. SEE DESCRIPTION IN SUBROUTINE DRIVE.
C KFLAG A COMPLETION CODE WITH THE FOLLOWING MEANINGS..
C 0 THE STEP WAS SUCCESSFUL.
-1 THE REQUESTED ERROR COULD NOT BE ACHIEVED
   WITH ABS(H) = HMIN.
-2 THE REQUESTED ERROR IS SMALLER THAN CAN
   BE HANDLED FOR THIS PROBLEM.
-3 CORRECTOR CONVERGENCE COULD NOT BE
   ACHIEVED FOR ABS(H) = HMIN.
ON A RETURN WITH KFLAG NEGATIVE, THE VALUES OF T AND
THE Y ARRAY ARE AS OF THE BEGINNING OF THE LAST
STEP AND H IS THE LAST STEP SIZE ATTEMPTED.
JSTART AN INTEGER USED ON INPUT AND OUTPUT.
   ON INPUT, IT HAS THE FOLLOWING VALUES AND MEANINGS...
   0 PERFORM THE FIRST STEP.
   .GT.0 TAKE A NEW STEP CONTINUING FROM THE LAST.
   .LT.0 TAKE THE NEXT STEP WITH A NEW VALUE OF
   H AND/OR MF.
ON EXIT, JSTART IS SET TO NO, THE CURRENT ORDER OF THE
METHOD.
YMAX AN ARRAY OF N ELEMENTS WITH WHICH THE ESTIMATED LOCAL
ERRORS IN Y ARE COMPARED.
ERROR AN ARRAY OF N ELEMENTS. ERROR(I)/TQ(2) IS THE
ESTIMATED LOCAL ERROR IN Y(I) PER SS UNITS OF
T OR PER STEP (OF SIZE H).
SAVE1, SAVE2 TWO ARRAYS FOR WORKING STORAGE,
   EACH OF LENGTH N.
PW A BLOCK OF LOCATIONS USED FOR THE PARTIAL DERIVATIVES
   OF F WITH RESPECT TO Y, IF MITER IS NOT 0. SEE
   DESCRIPTION IN SUBROUTINE DRIVE.
IPIV AN INTEGER ARRAY OF LENGTH N, WHICH IS USED FOR PIVOT
   INFORMATION FOR THE LINEAR ALGEBRAIC SYSTEM IN THE
   CORRECTION PROCESS, WHEN MITER = 1 OR 2.

THE COMMON BLOCK EPCM10, DECLARED BELOW, IS PRIMARILY INTENDED
FOR INTERNAL USE, BUT IT CAN BE ACCESSED EXTERNALLY.

PARAMETER ( NMAX =120 )
PARAMETER ( NMAXSQ = NMAX*NMAX )
INTEGER N0
INTEGER IPIV, JSTART, KFLAG, L, LMAX, METH, MF, N, NFE, NJE,
   1 NO, NOINDEX, NOUSED, NSTEP
INTEGER I, IBACK, IER, IREDO, J, J1, J2, M, MFIELD, MIO,
   1 MITER, MITER1, NEWJ, NSTEPJ
INTEGER ISTEPJ, KFC, KFH, MAXCOR
REAL Y
REAL EL, EPS, ERROR, H, HMAX, HMIN, HUSED, PW,
   1 SAVE1, SAVE2, SS, T, TAU, TQ, UROUND, YMAX
REAL BND, CNQUOT, CON, CONP, CRATE, D, DRC,
   1 D1, E, EDN, ETA, ETAMAX, ETAMIN, ETAQ, ETAQM1,
   2 ETAQP1, EUP, FLOTL, FLOTN, HOLD, HRL1, PHRL1,
   3 PRL1, R, RC, RL1, R0, R1, TOLD
REAL ADDON, BIAS1, BIAS2, BIAS3, CRDOWN, DELRC,
   1 ETACF, ETAMXP, ETAMX1, ETAMX2,
   2 ETAMX3, ONEFPM, SHORT, THRESH
REAL ONE, PT5, ZERO
C* Multiple Declaration of ETAMIN fixed - DRW
DIMENSION Y(N0,13)
C
COMMON /EPCOM1/ T, H, HM, H, EPS, SS, UROUND, N, MF, KFLAG, JSTART
COMMON /EPCOM2/ YMAX (NMAX)
COMMON /EPCOM3/ ERROR (NMAX)
COMMON /EPCOM4/ SAVE1 (NMAX)
COMMON /EPCOM5/ SAVE2 (NMAX)
COMMON /EPCOM6/ FW (NMAXSQ)
COMMON /EPCOM7/ IPIV (NMAX)
COMMON /EPCOM9/ HUSED, NQUSED, NSTEP, NFE, NJE
COMMON /EPCOM10/ TAU (13), EL (13), TQ (5), LMAX, METH, NQ, L, NQINDX
COMMON /EPCOM99/ NCSTEP, NCFE, NCJE

C

DATA ISTEPJ / 20 / , KFC / -3 / , KFH / -7 / , MAXCOR / 3 / 
DATA ADDON / 1.0E-6 / , BIAS1 / 2.5E1 / , BIAS2 / 2.5E1 / ,
1 BIAS3 / 1.0E2 / , CRDOWN / 0.1E0 / , DELRC / 0.3E0 / ,
2 ETA1CF / 0.25E0 / , ETAMIN / 0.1E0 / , ETA1MF / 0.2E0 / ,
3 ETA1MX1 / 1.0E4 / , ETAM2X1 / 1.0E4 / , ETAM2X3 / 1.5E0 / ,
4 ONEPSM / 1.00001E0 / , SHORT / 0.1E0 / , THRESH / 1.3E0 / 
DATA ONE / 1.0E0 / , PT5 / 0.5E0 / , ZERO / 0.0E0 / 
KFLAG = 0 
TOLD = T 
FLOTH = FLOAT(N) 
IF (JSTART .GT. 0) GOTO 200 
IF (JSTART .NE. 0) GOTO 150 
C-------------------------------------------
C ON THE FIRST CALL, THE ORDER IS SET TO 1 AND THE INITIAL 
C DERIVATIVES ARE CALCULATED. ETA1MAX IS THE MAXIMUM RATIO BY 
C WHICH H CAN BE INCREASED IN A SINGLE STEP. IT IS 1.E04 FOR THE 
C FIRST STEP TO COMPENSATE FOR THE SMALL INITIAL H, THEN 10 FOR 
C THE NEXT 10 STEPS, AND THEN 1.5 THEREAFTER. IF A FAILURE 
C OCCURS (IN CORRECTOR CONVERGENCE OR ERROR TEST), ETA1MAX IS SET AT 1 
C FOR THE NEXT INCREASE. ETA1MIN = .1 IS THE MINIMUM RATIO BY WHICH 
C H CAN BE REDUCED ON ANY RETRY OF A STEP. 
C-------------------------------------------
C
CALL DIFFUN (N, T, Y, SAVE1)
DO 110 I = 1, N
  110 Y(I, 2) = H*SAVE1(I) 
METH = MF/10 
MITER = MF - 10*METH 
MITER1 = MITER + 1 
MFOLD = MF 
NQ = 1 
L = 2 
TAU(1) = H 
PRL1 = ONE 
RC = ZERO 
ETA1MAX = ETAM2X1 
NQINDEX = 2 
C For unknown reasons, these variables are sometimes 
C uninitialized and cause the program to crash under 
C Microsoft FORTRAN, despite a BLOCK DATA initialization. 
C WRITE(99, 789) NSTEP, NCSTEP 
C789 FORMAT ('NSTEP=', I8, 'NCSTEP=', I8) 
C Cumulative Values 
NCSTEP = NCSTEP+NSTEP 
NF = NCFE+NFE 
NJE = NCJE+NJE 
NSTEP = 0 
NSTEPJ = 0
C-26

NFE = 1
NJ = 0
GOTO 200

C IF THE USER HAS CHANGED H, THEN Y MUST BE RESCALED. IF THE
C USER HAS CHANGED MITE, THEN NEWJ IS SET TO MTER TO FORCE
C THE PARTIAL DERIVATIVES TO BE UPDATED, IF THEY ARE BEING USED.
C

150 IF (MF .EQ. MFIELD) GOTO 170
    MIO = MTER
    METH = MF/10
    MTER = MF - 10*METH
    MFIELD = MF
    IF (MITER .EQ. MIO) GOTO 170
    NEWJ = MTER
    MTER1 = MTER + 1
170 IF (H .EQ. HOLD) GOTO 200
    ETA = H/HOLD
    H = HOLD
    IREDO = 3
    GOTO 185
180 ETA = AMAX1(ETA, HMIN/ABS(H), ETAMIN)
185 ETA = AMIN1(ETA, HMAX/ABS(H), ETAMAX)
    R1 = ONE
    DO 190 J = 2, L
        R1 = R1*ETA
    DO 190 I = 1, N
190      Y(I,J) = Y(I,J)*R1
    H = H*ETA
    RC = RC*ETA
    IF (IREDO .EQ. 0) GOTO 690

C THIS SECTION COMPUTES THE PREDICTED VALUES BY EFFECTIVELY
C MULTIPLYING THE Y ARRAY BY THE PASCAL TRIANGLE MATRIX. THEN
C COSET IS CALLED TO OBTAIN EL, THE VECTOR OF COEFFICIENTS OF
C LENGTH NQ + 1. RC IS THE RATIO OF NEW TO OLD VALUES OF THE
C COEFFICIENT H/EL(2). WHEN RC DIFFERS FROM 1 BY MORE THAN
C DELRC, NEWJ IS SET TO MTER TO FORCE THE PARTIAL DERIVATIVES
C TO BE UPDATED, IF USED. DELRC IS 0.3. IN ANY CASE, THE PARTIAL
C DERIVATIVES ARE UPDATED AT LEAST EVERY 20-TH STEP.
C

200 T = T + H
    DO 210 J1 = 1, NQ
        DO 210 J2 = J1, NQ
            J = (NQ + J1) - J2
        DO 210 I = 1, N
210      Y(I,J) = Y(I,J) + Y(I,J+1)
    CALL COSET
    BND = FLOTN*(TQ(4)*EPS)**2
    RL1 = ONE/EL(2)
    RC = RC*(RL1/PRL1)
    PRL1 = RL1
    IF (NSTEP .GE. NSTEPJ+1STEPJ) NEWJ = MTER
    DRC = ABS(RC-ONE)
    IF (DRC .LE. DELRC) GOTO 215
    NEWJ = MTER
CRATE = ONE
RC = ONE
GOTO 220

215 IF ((MITER .NE. 0) .AND. (DRC .NE. ZERO)) CRATE = ONE

C UP TO 3 CORRECTOR ITERATIONS ARE TAKEN. A CONVERGENCE TEST IS MADE
C ON THE ROOF MEAN SQUARE NORM OF EACH CORRECTION, USING BND, WHICH
C IS DEPENDENT ON EPS. THE SUM OF THE CORRECTIONS IS ACCUMULATED IN
C THE VECTOR ERROR. THE Y ARRAY IS NOT ALTERED IN THE CORRECTOR
C LOOP. THE UPDATED Y VECTOR IS STORED TEMPORARILY IN SAVE1.
C---------------------------------------------------------------------

- 220 DO 230 I = 1,N
  230    ERROR(I) = ZERO
    M = 0
    CALL DIFFUN (N, T, Y, SAVE2)
    NFE = NFE + 1
    IF (NEWJ .LE. 0) GOTO 290
C---------------------------------------------------------------------

- C IF INDICATED, THE MATRIX P = I - H*R1*L IS REEVALEUATED BEFORE
C STARTING THE CORRECTOR ITERATION. NEWJ IS SET TO 0 AS AN
C INDICATOR THAT THIS HAS BEEN DONE. IF MITER = 1 OR 2, P IS
C COMPUTED AND PROCESSED IN PSET. IF MITER = 3, THE MATRIX IS
C P = I - H*R1*L, WHERE D IS A DIAGONAL MATRIX. R1 IS 1/EL2.
C---------------------------------------------------------------------

- NEWJ = 0
RC = ONE
NJF = NJF + 1
NSTEPJ = NSTEP
GOTO (250, 240, 260), MITER
240 NFE = NFE + N
250 CON = -H*R1
    CALL PSET(Y, NO, CON, MITER, IER)
    IF (IER .NE. 0) GOTO 420
    GOTO 350
260 R = R1*SHORT
    DO 270 I = 1,N
  270 PW(I) = Y(I,1) + R*(H*SAVE2(I) - Y(I,2))
    CALL DIFFUN(N, T, PW, SAVE1)
    NFE = NFE + 1
    HRL1 = H*R1
    DO 280 I = 1,N
      R0 = H*SAVE2(I) - Y(I,2)
      PW(I) = ONE
      D = SHORT*R0 - H*(SAVE1(I) - SAVE2(I))
      SAVE1(I) = ZERO
      IF (ABS(R0) .LT. UROUND*YMAX(I)) GOTO 280
      IF (ABS(D) .EQ. ZERO) GOTO 420
      PW(I) = SHORT*R0/D
      SAVE1(I) = PW(I)*R1*R0
    280 CONTINUE
    GOTO 370
290 GOTO (295, 350, 350, 310), MITER1
C---------------------------------------------------------------------

- C IN THE CASE OF FUNCTIONAL ITERATION, Y IS UPDATED DIRECTLY FROM
C THE RESULT OF THE LAST DIFFUN CALL.
C-28

295 D = ZERO
   DO 300 I = 1,N
C
C    WRITE(LOUT,999) I,YMAX(I)
C 999 FORMAT(1H 2X,'I=',I2,2X,'YMAX=',E12.5)
C
    R = RL1*(H*SAVE2(I) - Y(I,2))
C
    The next line often gave an Undefined Real Error.
C    Let's try to fix it without changing anything else. - DRW
C
    D = D + ((R - ERROR(I))/YMAX(I))**2
C
    DTERM = ABS ((R-ERROR(I)) / YMAX(I) )
    IF (DTERM.LT.1.E15) DTERM = DTERM*DTERM
    D = D + DTERM
    SAVE1(I) = Y(I,1) + R
300 ERROR(I) = R
   GOTO 400

C-IN THE CASE OF A CHORD METHOD, THE RESIDUAL -G(Y SUB N(M))
C IS COMPUTED AND THE LINEAR SYSTEM WITH THAT AS RIGHT-HAND SIDE
C AND P AS COEFFICIENT MATRIX IS SOLVED, USING THE LU DECOMPOSITION
C OF P IF MITER = 1 OR 2. IF MITER = 3 THE SCALAR H*RL1 IS UPDATED.
C
310 PHRL1 = HRL1
   HRL1 = H*RL1
   IF (HRL1 .EQ. PHRL1) GOTO 330
   R = HRL1/PHRL1
   DO 320 I = 1,N
      D $ ONE - R*(ONE - ONE/PW(I))
   IF (ABS(D) .EQ. ZERO) GOTO 440
320 PW(I) = ONE/D
330 DO 340 I = 1,N
340 SAVE1(I) = PW(I)*((RL1*H*SAVE2(I) - (RL1*Y(I,2) + ERROR(I)))
   GOTO 370
350 DO 360 I = 1,N
360 SAVE1(I) = RL1*H*SAVE2(I) - (RL1*Y(I,2) + ERROR(I))
   CALL SOL(N,N0,PW,SAVE1,IPIV)
370 D = ZERO
   DO 380 I = 1,N
380 ERROR(I) = ERROR(I) + SAVE1(I)
   SAVE1(I) = Y(I,1) + ERROR(I)
C-TEST FOR CONVERGENCE. IF M .GT. 0, AN ESTIMATE OF THE SQUARE OF
C THE CONVERGENCE RATE CONSTANT IS STORED IN CRATE, AND THIS IS USED
C IN THE TEST.
C
400 IF (M .NE. 0) CRATE = AMAX1(CRDOWN*CRATE,D/D1)
   IF (D*AMIN1(ONE,CRATE) .LE. BND) GOTO 450
   D1 = D
   M = M + 1
   IF (M .EQ. MAXCOR) GOTO 410
   CALL DIFFUN(N,T,SAVE1,SAVE2)
GOTO (295, 350, 350, 310), MITER1

C THE CORRECTOR ITERATION FAILED TO CONVERGE IN 3 TRIES. IF PARTIAL
C DERIVATIVES ARE INVOLVED BUT ARE NOT UP TO DATE, THEY ARE
C RECALCULATED FOR THE NEXT TRY. OTHERWISE THE Y ARRAY IS RESTORED
C TO ITS VALUES BEFORE PREDICTION, AND H IS REDUCED,
C IF POSSIBLE. IF NOT, A NO-CONVERGENCE EXIT IS TAKEN.

410 NFE = NFE + MAXCOR - 1
   IF (NEWJ .EQ. -1) GOTO 440
420  T = TOLD
     ETAMAX = ONE
     DO 430 J1 = 1,NQ
         DO 430 J2 = J1,NQ
             J = (NQ + J1) - J2
             DO 430 I = 1,N
             Y(I,J) = Y(I,J) - Y(I,J+1)
430   IF (ABS(H) .LE. HMIN*ONEPSM) GOTO 680
     ETA = ETACF
     IREDO = 1
     GOTO 180
440  NEWJ = MITER
     GOTO 220

C THE CORRECTOR HAS CONVERGED. NEWJ IS SET TO -1 IF PARTIAL
C DERIVATIVES WERE USED, TO SIGNAL THAT THEY MAY NEED UPDATING ON
C SUBSEQUENT STEPS. THE ERROR TEST IS MADE AND CONTROL PASSES TO
C STATEMENT 500 IF IT FAILS.

450 IF (MITER .NE. 0) NEWJ = -1
   NFE = NFE + M
   D = ZERO
   DO 460 I = 1,N
460   D = D + (ERROR(I)/YMAX(I))**2
   E = FLOTP* (TQ2/IT2)**EPS**2
   IF (D .GT. E) GOTO 500

C AFTER A SUCCESSFUL STEP, THE Y ARRAY, TAU, NSTEP, AND NOINDEX ARE
C UPDATED, AND A NEW VALUE OF H AT ORDER NQ IS COMPUTED.
C THE VECTOR TAU CONTAINS THE NQ + 1 MOST RECENT VALUES OF H.
C A CHANGE IN NQ UP OR DOWN BY 1 IS CONSIDERED IF NOINDEX = 0.
C IF NOINDEX = 1 AND NQ .LT. MAXDER, THEN ERROR IS SAVED
C FOR USE IN A POSSIBLE ORDER INCREASE ON THE NEXT STEP.
C A CHANGE IN H OR NQ IS MADE ONLY OF THE INCREASE IN H
C IS BY A FACTOR OF AT LEAST 1.3.
C IF NOT, NOINDEX IS SET TO 2 TO PREVENT TESTING FOR THAT MANY
C STEPS. IF NQ IS CHANGED, NOINDEX IS SET TO NQ + 1 (NEW VALUE).

KFLAG = 0
IREDO = 0
NSTEP = NSTEP + 1
HUSED = H
NOUSED = NQ
DO 470 IBACK = 1,NQ
I = L - IBACK

TAU(I+1) = TAU(I)

TAU(I) = H

DO 480 J = 1,L

DO 480 I = 1,N

Y(I,J) = Y(I,J) + ERROR(I)*EL(J)

NQINDEX = NQINDEX - 1

IF ((L .EQ. LMAX) .OR. (NQINDEX .NE. 1)) GOTO 495

DO 490 I = 1,N

Y(I,LMAX) = ERROR(I)

CONP = TQ(5)

495 IF (ETAMAX .GE. ONE) GOTO 520

IF (NQINDEX .LT. 2) NQINDEX = 2

GOTO 690

C-----------------------------------------------------------------------

C THE ERROR TEST FAILED. KFLAG KEEPS TRACK OF MULTIPLE FAILURES.
C T AND THE Y ARRAY ARE RESTORED TO THEIR PREVIOUS VALUES. A NEW
C H FOR A RETRY OF THE STEP IS COMPUTED. THE ORDER IS KEPT FIXED.
C-----------------------------------------------------------------------

500 KFLAG = KFLAG - 1

T = TOLD

DO 510 J1 = 1,NQ

DO 510 J2 = J1,NQ

J = (NQ + J1) - J2

DO 510 I = 1,N

510 Y(I,J) = Y(I,J) - Y(I,J+1)

NEWJ = MITER

ETAMAX = ONE

IF (ABS(H) .GE. HMIN*ONEPSM) GOTO 660

IF (KFLAG .GE. KFC) GOTO 630

IREDO = 2

C COMPUTE RATIO OF NEW H TO CURRENT H AT THE CURRENT ORDER. ---------

520 FLOTL = FLOAT(L)

ETAQ = ONE/((BIAS2*D/E)**(PT5/FLOTL) + ADDON)

IF ((NQINDEX .NE. 0) .OR. (KFLAG .NE. 0)) GOTO 580

ETAQ1 = ZERO

IF (NQ .GE. 1) GOTO 540

C COMPUTE RATIO OF NEW H TO CURRENT H AT THE CURRENT ORDER LESS ONE. --

530 D = ZERO

DO 530 I = 1,N

530 D = D + (Y(I,L)/YMAX(I))**2

EDN = FLOTN*(TQ(1)*EPS)**2

ETAQ1 = ONE/((BIAS1*D/EDN)**(PT5/(FLOTL - ONE)) + ADDON)

540 ETAQP1 = ZERO

IF (L .EQ. LMAX) GOTO 560

C COMPUTE RATIO OF NEW H TO CURRENT H AT CURRENT ORDER PLUS ONE. -------

CNQUOT = (TQ(5)/CONP)*(H/TAU(2))**L

D = ZERO

DO 550 I = 1,N

550 D = D + ((ERROR(I) - CNQUOT*Y(I,LMAX))/YMAX(I))**2

EUP = FLOTN*(TQ(3)*EPS)**2

ETAQP1 = ONE/((BIAS3*D/EUP)**(PT5/(FLOTL + ONE)) + ADDON)

560 NQINDEX = 2

IF (ETAQ .GE. ETAQP1) GOTO 570

IF (ETAQP1 .GT. ETAQM1) GOTO 600
GOTO 590
570 IF (ETAQ .LT. ETAQM1) GOTO 590
580 IF ((ETAQ .LT. THRESH) .AND. (KFLAG .EQ. 0)) GOTO 690
ETA = ETAQ
IF ((KFLAG .LE. -2) .AND. (ETA .GT. ETAMXF)) ETA = ETAMXF
GOTO 180
590 IF (ETAQM1 .LT. THRESH) GOTO 690
CALL ADJUST (Y, NQ)
L = NQ
NQ = NQ - 1
ETA = ETAQM1
NQINDX = L
GOTO 180
600 IF (ETAQP1 .LT. THRESH) GOTO 690
NQ = L
ETA = ETAQP1
L = L + 1
DO 610 I = 1,N
610 Y(I,L) = ZERO
NQINDX = L
GOTO 180

C---------------------------------------------------------------------
C CONTROL REACHES THIS SECTION IF 3 OR MORE CONSECUTIVE FAILURES
C HAVE OCCURRED. IT IS ASSUMED THAT THE ELEMENTS OF THE Y ARRAY
C HAVE ACCUMULATED ERRORS OF THE WRONG ORDER. THE ORDER IS REDUCED
C BY ONE, IF POSSIBLE. THEN H IS REDUCED BY A FACTOR OF 0.1 AND
C THE STEP IS RETRIED. AFTER A TOTAL OF 7 CONSECUTIVE FAILURES,
C AN EXIT IS TAKEN WITH KFLAG = -2.
C---------------------------------------------------------------------

630 IF (KFLAG .EQ. KPH) GOTO 670
IF (NQ .EQ. 1) GOTO 640
ETA = ETAMIN
CALL ADJUST (Y, NQ)
L = NQ
NQ = NQ - 1
NQINDX = L
GOTO 180
640 ETA = AMAX1(ETAMIN, HMIN/ABS(H))
H = H*ETA
CALL DIFFUN (N, T, Y, SAVE1)
NFE = NFE + 1
DO 650 I = 1,N
650 Y(I,2) = H*SAVE1(I)
NQINDX = 10
GOTO 200

C---------------------------------------------------------------------
C ALL RETURNS ARE MADE THROUGH THIS SECTION. H IS SAVED IN HOLD
C TO ALLOW THE CALLER TO CHANGE H ON THE NEXT STEP.
C---------------------------------------------------------------------

660 KFLAG = -1
GOTO 700
670 KFLAG = -2
GOTO 700
680 KFLAG = -3
GOTO 700
690 ETAMAX = ETAMX3
IF (NSTEP .LE. 10) ETAMAX = ETAMX2
700
    HOLD = H
    JSTART = NQ
    RETURN
END

C=========================================================================
C
C SUBROUTINE COSET

C=========================================================================

C COSET IS CALLED BY TSTEP AND SETS COEFFICIENTS FOR USE THERE.

C FOR EACH ORDER NQ, THE COEFFICIENTS IN EL ARE CALCULATED BY USE OF
C THE GENERATING POLYNOMIAL LAMBDA(X), WITH COEFFICIENTS EL(I):
C LAMBDA(X) = EL(1) + EL(2)*X + ... + EL(NQ+1)*(X**NQ).
C FOR THE BACKWARD DIFFERENTIATION FORMULAS,
C LAMBDA(X) = PRODUCT (1 + X/XI(I) ) .
C          I = 1
C FOR THE ADAMS FORMULAS,
C (D/DX) LAMBDA(X) = C * PRODUCT (1 + X/XI(I) ) ,
C C = 1
C LAMBDA(-1) = 0,   LAMBDA(0) = 1,
C WHERE C IS A NORMALIZATION CONSTANT.
C IN BOTH CASES, XI(I) IS DEFINED BY
C     H*XI(I) = T SUB N - T SUB (N-I)
C     = H + TAU(I) + TAU(2) + ... TAU(I-1).

C COSET ALSO SETS MAXDER, THE MAXIMUM ORDER OF THE FORMULAS
C AVAILABLE. CURRENTLY THIS IS 5 FOR THE BACKWARD DIFFERENTIATION
C FORMULAS, AND 12 FOR THE ADAMS FORMULAS. TO USE DIFFERENT
C VALUES (.LE. 13), CHANGE THE NUMBERS IN STATEMENTS 1 AND 2 BELOW.

C IN ADDITION TO VARIABLES DESCRIBED PREVIOUSLY, COMMUNICATION
C WITH COSET USES THE FOLLOWING:
C TAU = A VECTOR OF LENGTH 13 CONTAINING THE PAST NQ VALUES
C OF H.
C EL = A VECTOR OF LENGTH 13 IN WHICH COSET STORES THE
C COEFFICIENTS FOR THE CORRECTOR FORMULA.
C TQ = A VECTOR OF LENGTH 5 IN WHICH COSET STORES CONSTANTS
C USED FOR THE CONVERGENCE TEST, THE ERROR TEST, AND
C SELECTION OF H AT A NEW ORDER.
C LMAX = MAXDER + 1, WHERE MAXDER IS THE MAXIMUM ORDER
C AVAILABLE. LMAX IS THE MAXIMUM NUMBER OF COLUMNS
C OF THE Y ARRAY TO BE USED.
C METH = THE BASIC METHOD INDICATOR.
C NQ = THE CURRENT ORDER.
C L = NQ + 1, THE LENGTH OF THE VECTOR STORED IN EL, AND
C THE NUMBER OF COLUMNS OF THE Y ARRAY BEING USED.
C NQINDEX = A COUNTER CONTROLLING THE FREQUENCY OF ORDER CHANGES.
C AN ORDER CHANGE IS ABOUT TO BE CONSIDERED IF
C NQINDEX = 1.

C THIS IS THE SINGLE PRECISION VERSION OF SUBROUTINE COSET.
C
C CAUTION: NOT ALL MEMBERS OF EPCOM1 ARE USED IN THIS SUBROUTINE.

C-----------------------------------------------------------------------------

INTEGER JSTART, KFLAG, L, LMAX, METH, MF, N, NQ, NQINDEX
INTEGER I, IBACK, J, JP1, MAXDER, LMAXN, NQM1
REAL EL, EPS, H, HAX, HMIN, SS, T, TAU, TQ,
1 UROUND
REAL AHDSS, CNQM1, CSUM, ELP, EM, EM0, FLOTI,
1 FLOTL, FLOTNQ, HSUM, HSUM1, PROD, RXI, S, XI
REAL CORTE
REAL ONE, SIX, TWO, ZERO
C* Multiple Declaration of JSTART,KFLAG,L,METH,MF,NQ,NQINDEX, fixed - DR
W
DIMENSION EM(13)
C
COMMON /EPCOM1/ T,H,HMIN,HMAX,EPS,SS,UROUND,N,MF,KFLAG,JSTART
COMMON /EPCM10/ TAU(13),EL(13),TQ(5),LMAX,METH,NQ,L,NQINDEX
DATA CORTE /0.1E0/
DATA ONE /1.0E0/, SIX /6.0E0/, TWO /2.0E0/, ZERO /0.0E0/
AHDSS = ONE
IF (SS .NE. ZERO) AHDSS = ABS(H)/SS
FLOTL = FLOAT(L)
NQM1 = NQ - 1
GOTO (1, 2), METH
1 MAXDER = 12
GOTO 100
C
2 MAXDER = 5
GOTO 200
C
100 IF (NQ .NE. 1) GOTO 110
EL(1) = ONE
EL(2) = ONE
TQ(1) = ONE
TQ(2) = TWO*AHDSS
TQ(3) = SIX*TQ(2)
TQ(5) = ONE
GOTO 300
110 HSUM = H
EM(1) = ONE
FLOTNQ = FLOTL - ONE
DO 115 I = 2, L
115 EM(I) = ZERO
DO 150 J = 1,NQM1
IF ((J .NE. NQM1) .OR. (NQINDEX .NE. 1)) GOTO 130
S = ONE
CSUM = ZERO
DO 120 I = 1,NQM1
120 CSUM = CSUM + S*EM(I)/FLOAT(I+1)
S = -S
TQ(1) = AHDSS*EM(NQM1)/(FLOTNQ*CSUM)
130 RXI = H/HSUM
DO 140 IBACK = 1,J
I = (J + 2) - IBACK
140 EM(I) = EM(I) + EM(I-1)*RXI
150 HSUM = HSUM + TAU(J)
C COMPUTE INTEGRAL FROM -1 TO 0 OF POLYNOMIAL AND OF X TIMES IT. -------
S = ONE
EM0 = ZERO
CSUM = ZERO
DO 160 I = 1,NQ
   FLOTI = FLOAT(I)
   EM0 = EM0 + S*EM(I)/FLOTI
CSUM = CSUM + S*EM(I)/(FLOTI+1)
160 S = -S
C IN EL, FORM COEFFICIENTS OF NORMALIZED INTEGRATED POLYNOMIAL. -------

   S = ONE/EM0
   EL(1) = ONE
DO 170 I = 1,NQ
170   EL(I+1) = S*EM(I)/FLOAT(I)
   XI = HSUM/H
   TO(2) = AHDSS*XI*EM0/CSUM
   TO(5) = XI/EL(L)
   IF (NQINDX .NE. 1) GOTO 300
C FOR HIGHER ORDER CONTROL CONSTANT, MULTIPLY POLYNOMIAL BY 1+X/XI(Q).

   RXI = ONE/XI
DO 180 IBACK = 1,NQ
   I = (L + 1) - IBACK
180   EM(I) = EM(I) + EM(I-1)*RXI
C COMPUTE INTEGRAL OF POLYNOMIAL. -------------------------------

   S = ONE
   CSUM = ZERO
DO 190 I = 1,L
   CSUM = CSUM + S*EM(I)/FLOAT(I+1)
190 S = -S
   TO(3) = AHDSS*FLOTL*EM0/CSUM
GOTO 300
C
200   DO 210 I = 3,L
210   EL(I) = ZERO
   EL(1) = ONE
   EL(2) = ONE
   HSUM = H
   HSUM1 = ZERO
   PROD = ONE
   RXI = ONE
   IF (NQ .EQ. 1) GOTO 240
   DO 230 J = 1,NQM1
        J = 3
230 CONTINUE
C IN EL, CONSTRUCT COEFFICIENTS OF (1+X/XI(1))*...*(1+X/XI(J+1)). ------

   HSUM = HSUM + TAU(J)
   HSUM1 = HSUM1 + TAU(J)
   PROD = PROD*(HSUM/HSUM1)
   RXI = H/HSUM
   JP1 = J + 1
   DO 220 IBACK = 1,JP1
   I = (J + 3) - IBACK
220   EL(I) = EL(I) + EL(I-1)*RXI
240   CONTINUE
RXI = H/HSUM
ELP = EL(2) + RXI
TQ(3) = AHDS*ELP*RXI*(ONE + PROD)*(FLOTL + ONE)
TQ(4) = CORTES*TQ(2)
LMAX = MAXDER + 1
RETURN
END

C
C=================================================================================================
C
C SUBROUTINE ADJUST (Y, N0)
C
C THIS SUBROUTINE ADJUSTS THE Y ARRAY ON REDUCTION OF ORDER.
C SEE REFERENCE 1 FOR DETAILS.
C
C THIS IS THE SINGLE PRECISION VERSION OF SUBROUTINE ADJUST.
C
C CAUTION: NOT ALL MEMBERS OF EPSCOM1 ARE USED IN THIS SUBROUTINE.
C
INTEGER N0
INTEGER JSTART, KFLAG, L, LMAX, METH, MF, N, NQ, NQINDEX
INTEGER I, IBACK, J, JPL1, NQM1, NQM2
REAL Y
REAL EL, EPS, H, HMAX, HMIN, SS, T, TAU, TQ, UROUND
REAL HSUM, XI
REAL ONE, ZERO
DIMENSION Y(N0,13)

COMMON /EPSCOM1/ T,H,HMIN,HMAX,EPS,SS,UROUND,N,MF,KFLAG,JSTART
COMMON /EPSCOM10/ TAU(13),EL(13),TQ(5),LMAX,METH,NQ,L,NQINDEX
DATA ONE /1.0E0/, ZERO /0.0E0/
IF (NQ .EQ. 2) RETURN
NQM1 = NQ - 1
NQM2 = NQ - 2
GOTO (100, 200), METH
C
100 DO 110 J = 1,LMAX
110   EL(J) = ZERO
       EL(2) = ONE
       HSUM = ZERO
       DO 130 J = 1,NQM2
       C CONSTRUCT COEFFICIENTS OF X*(X+XI(1))*...*(X+XI(J)).
       HSUM = HSUM + TAU(J)
       XI = HSUM/H
       JPL1 = J + 1
       DO 120 IBACK = 1, JPL1
             I = (J + 3) - IBACK
120     EL(I) = EL(I)*XI + EL(I-1)
       CONTINUE
C CONSTRUCT COEFFICIENTS OF INTEGRATED POLYNOMIAL. 
C
       DO 140 J = 2,NQM1
140   EL(J+1) = FLOAT(NQ)*EL(J)/FLOAT(J)
       GOTO 300
C
200 DO 210 J = 1,LMAX
210 EL(J) = ZERO
   EL(3) = ONE
   HSUM = ZERO
   DO 230 J = 1,NQM2
   C CONSTRUCT COEFFICIENTS OF X*X*(X+XI(1))*...*(X+XI(J)).
      HSUM = HSUM + TAU(J)
      XI = HSUM/H
      JP1 = J + 1
      DO 220 IBACK = 1,JP1
         I = (J + 4) - IBACK
      220 EL(I) = EL(I)*XI + EL(I-1)
   230 CONTINUE
C
C SUBTRACT CORRECTION TERMS FROM Y ARRAY.
C
C
300 DO 320 J = 3,NQ
   DO 310 I = 1,N
310   Y(I,J) = Y(I,J) - Y(I,L)*EL(J)
320 CONTINUE
RETURN
END
C
C================================================================================================
C
C SUBROUTINE PSET (Y,N0,CON,MITER,IER)
C================================================================================================
C
C PSET IS CALLED BY TSTEP TO COMPUTE AND TO PROCESS THE MATRIX
C P = I - (H/EL(2))**J, WHERE J IS AN APPROXIMATION TO THE
C JACOBIAN. J IS COMPUTED BY EITHER THE USER SUPPLIED
C SUBROUTINE PEDERV, WHEN MITER = 1, OR BY FINITE DIFFERENCES,
C WHEN MITER = 2. J IS STORED IN PW AND REPLACED BY P, USING
C CON = -H/EL(2). THEN P IS SUBJECTED TO AN LU DECOMPOSITION
C FOR LATER SOLUTION OF LINEAR ALGEBRAIC SYSTEMS WITH P AS THE
C COEFFICIENT MATRIX.
C
C IN ADDITION TO VARIABLES DESCRIBED PREVIOUSLY, COMMUNICATION
C WITH PSET USES THE FOLLOWING:
C EPSJ = SQRT(UROUND), USED IN THE NUMERICAL JACOBIAN INCREMENTS.
C NSQ = N0**2.
C
C================================================================================================
C
C CAUTION: NOT ALL EPCOM1 VARIABLES ARE USED IN THIS SUBROUTINE.
C================================================================================================
C
C THIS IS THE SINGLE PRECISION VERSION OF SUBROUTINE PSET.
C================================================================================================
C
PARAMETER ( NMAX =120 )
PARAMETER ( NMAXSQ = NMAX*NMAX )
INTEGER IER, MITER, N0
INTEGER IPIV, JSTART, KFLAG, MF, N, NSQ
INTEGER I, J, J1
REAL CON, Y
REAL EPS, EPSJ, H, HMAX, HMIN, PW, SAVE1, SAVE2,
1 SS, T, UROUND, YMAX
REAL D, R, R0, YJ
REAL ONE, REP, ZERO
C* Multiple Declaration of IER, T, N fixed - DRW
DIMENSION Y(N0,1)

COMMON /EPCOM1/ T, H, HMIN, HMAX, EPS, SS, UROUND, N, MF, KFLAG, JSTART
COMMON /EPCOM2/ YMAX(NMAX)
COMMON /EPCOM4/ SAVE1(NMAX)
COMMON /EPCOM5/ SAVE2(NMAX)
COMMON /EPCOM6/ PW(NMAXSQ)
COMMON /EPCOM7/ IPIV(NMAX)
COMMON /EPCOM8/ EPSJ, NSQ
DATA ONE /1.0E0/, REP /1.0E-3/, ZERO /0.0E0/
IF (MITER .EQ. 2) GOTO 20
C IF MITER = 1, CALL PEDERV AND MULTIPLY BY A SCALAR.  ---------------

    CALL PEDERV (N, T, Y, PW, N0)
    DO 10 I = 1, NSQ
       PW(I) = PW(I)*CON
    GOTO 60
C IF MITER = 2, MAKE N CALLS TO DIFFUN TO APPROXIMATE J.  ---------------

20    D = ZERO
    DO 30 I = 1, N
       D = D + SAVE2(I)**2
       R0 = ABS(H)*SQRT(D)*UROUND/REP
       J1 = 0
       DO 50 J = 1, N
          YJ = Y(J,1)
          R = EPSJ*YMAX(J)
          R = AMAX1(R, R0)
          Y(J,1) = Y(J,1) + R
          D = CON/R
          CALL DIFFUN (N, T, Y, SAVE1)
       DO 40 I = 1, N
          PW(I+J1) = (SAVE1(I) - SAVE2(I))*D
          Y(J,1) = YJ
          J1 = J1 + N0
      50    CONTINUE
C ADD ON THE IDENTITY MATRIX.  -------------------------------

60    J = 1
    DO 70 I = 1, N
       PW(J) = PW(J) + ONE
60    J = J + (N0 + 1)
C GET LU DECOMPOSITION OF P.  -------------------------------

    CALL DEC (N, N0, PW, IPIV, IER)
    RETURN
END

C SUBROUTINE DEC (N, NDIM, A, IP, IER)
C-----------------------------------
C MATRIX TRIANGULARIZATION BY GAUSSIAN ELIMINATION.
C INPUT.
C N = ORDER OF MATRIX.
C NDIM = DECLARED DIMENSION OF ARRAY A.
C A = MATRIX TO BE TRIANGULARIZED.
C OUTPUT:
C A(I,J), I.LE.J = UPPER TRIANGULAR FACTOR, U.
C A(I,J), I.GT.J = MULTIPLIERS = LOWER TRIANGULAR FACTOR, I - L.
C IP(K), K.LT.N = INDEX OF K-TH PIVOT ROW.
C IP(N) = (-1)**(NUMBER OF INTERCHANGES) OR 0.
C IER = 0 IF A NONSINGULAR, OR K IF A FOUND TO BE
C SINGULAR AT STAGE K.
C USE SOL TO OBTAIN SOLUTION OF LINEAR SYSTEM.
C DETERM(A) = IP(N)*A(1,1)*A(2,2)*...*A(N,N).
C IF IP(N)=0, A IS SINGULAR, SOL WILL DIVIDE BY ZERO.
C INTERCHANGES FINISHED IN U, ONLY PARTLY IN L.
C
C C. B. MOLER, ALGORITHM 423, LINEAR EQUATION SOLVER,
C COMM. ASSOC. COMPUT. MACH., 15 (1972), P. 274.
C
C------------------------------------------------------------------
C THIS IS THE SINGLE PRECISION VERSION OF SUBROUTINE DEC.
C------------------------------------------------------------------

INTEGER IER, IP, N, NDIM
INTEGER I, J, K, KP1, M, NM1
REAL A
REAL T
REAL ONE, ZERO
DIMENSION A(NDIM,N), IP(N)
DATA ONE /1.0E0/, ZERO /0.0E0/
IER = 0
IP(N) = 1
IF (N .EQ. 1) GOTO 70
NM1 = N - 1
DO 60 K = 1,NM1
   KP1 = K + 1
   M = K
   DO 10 I = KP1,N
      IF (ABS(A(I,K)) .GT. ABS(A(M,K))) M = I
   IF(K) = M
   T = A(M,K)
   IF (M .EQ. K) GOTO 20
   IF(N) = -IP(N)
   A(M,K) = A(K,M)
   A(K,K) = T
   10 IF (T .EQ. ZERO) GOTO 80
   T = ONE/T
   DO 30 I = KP1,N
      A(I,K) = -A(I,K)*T
   DO 50 J = KP1,N
      T = A(M,J)
      A(M,J) = A(K,J)
      A(K,J) = T
      IF (T .EQ. ZERO) GOTO 50
   30 DO 40 I = KP1,N
      A(I,J) = A(I,J) + A(I,K)*T
   40 CONTINUE
   50 CONTINUE
   70 IF (A(N,N) .EQ. ZERO) GOTO 80
   RETURN
C-39

80 IER = K
  IP(N) = 0
  RETURN
END

C
C===============================================================================
C
C  SUBROUTINE SOL (N, NDIM, A, B, IP)
C
C===============================================================================
C
C SOLUTION OF LINEAR SYSTEM, A*X = B .
C INPUT .
C  N = ORDER OF MATRIX.
C  NDIM = DECLARED DIMENSION OF ARRAY A .
C  A = TRIANGULARIZED MATRIX OBTAINED FROM DEC.
C  B = RIGHT HAND SIDE VECTOR.
C  IP = PIVOT VECTOR OBTAINED FROM DEC.
C DO NOT USE IF DEC HAS SET IER .NE. 0 .
C OUTPUT .
C  B = SOLUTION VECTOR, X .
C
C$ THIS IS THE SINGLE PRECISION VERSION OF SUBROUTINE SOL.
C
C===============================================================================
C
INTEGER IP, N, NDIM
INTEGER K, KB, KM1, KPI, M, NM1
REAL A, B
REAL T
DIMENSION A(NDIM, N), B(N), IP(N)

C IF (N .EQ. 1) GOTO 50
NM1 = N - 1
DO 20 K = 1, NM1
  KPI = K + 1
  M = IP(K)
  T = B(M)
  B(M) = B(K)
  B(K) = T
  DO 10 I = KPI, N
    10 B(I) = B(I) + A(I, K)*T
  CONTINUE
DO 40 KB = 1, NM1
  KM1 = N - KB
  K = KM1 + 1
  B(K) = B(K)/A(K, K)
  T = -B(K)
  DO 30 I = 1, KM1
    30 B(I) = B(I) + A(I, K)*T
  CONTINUE
  B(1) = B(1)/A(1, 1)
RETURN
END

C
C===============================================================================
C
C BLOCK DATA

COMMON /EPCOM9/ HUSED, NQUSED, NSTEP, NFE, NJE
COMMON /EPCO99/ NCSTEP, NCFE, NCJE
COMMON /EPCOMR/ NRMIN, NRMAX
COMMON /EPCOMY/ YMIN, HMAXMX
DATA HUSED, NQUSED, NSTEP, NFE, NJE / 0..0,0,0,0 /
DATA NCSTEP, NCFE, NCJE / 0,0,0 /
DATA NRMIN, NRMAX / 1,500 /
DATA YMIN, HMAXMX / 1.E-20, 1.E6 /
END
SUBROUTINE PEDERV(N,T,Y,PD,N0)

C This is presently intended to be a dummy subroutine in this application
C Used only in EPISODE versions of MAEROS; not adequate if MF=11 or 21

WRITE(*,10) T
10 FORMAT(/5X,’Error -- PEDERV was called at time ’,1PE10.2/) WRITE(*,20)
20 FORMAT(’Hence MITER of MF was set equal to one’) STOP ’STOP on bad MF to DRIVES for Dummy PEDERV’
END