EFFECTS OF IONIZING RADIATION ON AQUEOUS SOLUTIONS OF THE DETERGENT ALKYLBENZENESULFONATE AND SEVERAL LOWER HOMOLOGS

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This thesis is dedicated to my wife Edith and my sons Norrin and Marc for their perseverance.

ABSTRACT

A study was conducted of the degradation of benzene-, p-toluene-, and alkylbenzenesulfonates under the action of ionizing radiation from a 3400 curie, Cobalt-60 irradiator.

Effects of varying solute concentrations, pH, and dissolved oxygen concentrations were observed as functions of the energy absorbed by the solutions. The rates of oxygen depletion and the rates of hydrogen peroxide, enol, and sulfate production were followed by irradiating the solutions for varying periods of time.

Results of the irradiations indicate that, in aerated solutions, the major mode of degradation is by desulfonation of the molecule. Degradation was accompanied by significant losses in oxygen, possibly a result of direct oxidation of the solute by radiation, rather than by free radical reactions. Enols were also found to occur, but at very low concentrations. The product formed as a result of desulfonation of benzenesulfonic acid appeared to be quinonoid rather than phenolic in nature.

In deaerated solutions, enol yields were found to decrease, while sulfates were not observed. A more rapid decrease in the ultraviolet absorption peaks of these homologs in deaerated solutions was attributed to the formation of dimers.

The study indicates that the use of radiation, as a water or wastewater treatment process for degrading organic compounds, would necessarily be limited to aerated solutions in situations where the large losses of oxygen would not be detrimental.

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CHAPTER 1

INTRODUCTION

1-1 The Broad Problem of Water Pollution

Alkylbenzenesulfonates (ABS) and related compounds used in detergents have been shown to be significant components of domestic and industrial wastewaters, and to be relatively resistant to biochemical degradation in conventional treatment processes. Indeed, the ABS compounds have proved to be excellent tracers to indicate the contamination of water supplies by domestic or industrial wastes.

With the increasing demand for fresh water by industry, agriculture, municipalities, and recreational interests in the face of an inexorably constant supply of fresh water through the hydrologic cycle, it has become apparent that fresh water will have to be used more than once before it is discharged to the sea or evaporated to the atmosphere. Before such re-use is practical, objectionable contaminants must be removed. One such group of contaminants is the surfactant chemicals that constitute the active fraction of commercial synthetic detergents.

While it is possible that the supply of fresh water may be increased by productive research into desalinization of sea water and nucleation of the atmosphere to produce more rainfall, it is apparent that these efforts will be minuscule in relation to the present supply of fresh water and the future needs of industry, agriculture, and municipalities. The only truly feasible way to guarantee suitable fresh water for its many beneficial uses is to assure adequate treatment of wastewaters so that they will not unduly and unreasonably

contaminate the limited fresh-water resources of any region.

It is not the intent of this investigation to review all methods of water and wastewater treatment, for this subject is diverse and complicated. Instead, it is the aim of this study to consider the effects of radiation on ABS and related homologs, with the hope that such research will lead to an economically feasible method of removing such compounds from wastewater.

1-2 Irradiation of Water and Waste Water

A major portion of the accomplishments in this area has been directed toward the effects of radiation on the microorganisms found in water and sewage. Lowe, et al. (1), exposed 5 organisms to a 1.1-kilocurie source of Co-60 in a mixture of double distilled water and autoclaved sewage. It was found that all the organisms could be completely destroyed if large enough doses were used. For a complete kill the most resistant organism was *Bacillus subtilis* which required 2.0×10^6 rads while the most sensitive was the *Escherichia coli* phage T3 which succumbed with 7.5×10^4 rads. (The rad is defined as the unit of absorbed dose equivalent to 100 ergs per gram in any medium.) Settled sewage and sewage sludge were sterilized by 5.0×10^6 and 2.0×10^6 rads respectively. Dosages for less than 100 per cent kill were materially less. With the exception of *B. subtilis* kills up to 90 per cent were achieved at doses no larger than 7×10^4 rads.

Ridenour and Armbruster (2), using a 10-kilocurie Co-60 source, irradiated 10 pure cultures in water. It was found that *E. coli* and *A. aerogenes* were most susceptible and *Bacillus subtilis*

and Streptococcus faecalis were most resistant. All could be reduced more than 99 per cent by a dose of 100,000 reps. (The rep, or roentgen equivalent physical, is defined (3) as the quantity of corpuscular radiation which produces in a gram of tissue, ionization equivalent to the quantity of ionization of one roentgen of gamma radiation in air.) This unit is being replaced by the rad. A dose of 100,000 reps was found sufficient to reduce the total bacterial population of primary sewage effluent by 99 per cent while only one half this dose was required to obtain the same results with a final plant effluent. These bactericidal effects were not influenced by pH in the range 5 to 8.5.

Dunn (4), conducting studies on water and sewage samples with a one-kilocurie Co-60 source and a 3-million electron volt (Mev) Van de Graaff generator, found the generator more effective in 10 seconds than the Co-60 source in up to 25 minutes of exposure. From 88.3 to 99.9 per cent of the bacteria were destroyed by the Co-60 in 25 minutes and from 95.4 to 99.999 per cent within 125 minutes at an exposure rate of 2000 roentgens per minute.

Grune and Eliassen (5), studying effects of radioactive waste disposal, reported no significant effect on the ultimate and 5-day biochemical oxygen demand or its reaction rate after dosing sewage with up to 10 millicuries per liter of radioactive phosphorous, P-32. Unlike the Co-60, which decays by emission of gamma rays, P-32 emits a 1.74 Mev beta ray. In another study, Grune, et al. (6), could see no effect on anaerobic digestion resulting from the addition of up to 1000 microcuries per liter of C-14 or 500 microcuries per liter of Sr-90, both of which decay by beta emission.

During a study of the economic feasibility of sterilizing sewage by irradiation (7, 8), it was observed that the settling characteristics of the sewage were altered when exposed to a dose rate of 845 roentgens (r) per minute from a 200-kilovolt X-ray source. A dose of 65,000 r caused increased deposition of solid matter while a dose of 350,000 r resulted in increased dispersion of the particulate matter. However, only 50,000 r were necessary to cause a 99 per cent coliform reduction while 78,000 r caused a reduction of 99.9 per cent. Irradiation at the Brookhaven reactor with thermal and fast neutrons and gamma rays also increased dispersion of particulates. Cost estimates for a nuclear reactor to sterilize sewage were not found to be competitive with present practices.

A more recent study by Bio Sciences Laboratories (9) using a Co-60 irradiator and synthetic sewage indicated that sedimentation was effected by both total dose and by dose rate. At dose rates of 507 and 643 rads per minute, no change or slight decreases in sedimentation, measured on a weight basis, occurred. At a lower rate of 296 rads per minute and at higher rates of 850 and 1340 rads per minute, increases in sedimentation were observed. The authors thought that this effect might have been caused by a difference in the spectral quality of the gamma energy. This difference would result from scatter occurring at various distances from the source. At the dose rate of 296 rads per minute, a maximum increase in sedimentation was observed with a dose of 70,000 rads. Additional sedimentation studies at lower dose rates of 10.4 and 22.6 rads per minute to accumulated doses of 1270 and 2710 rads respectively showed

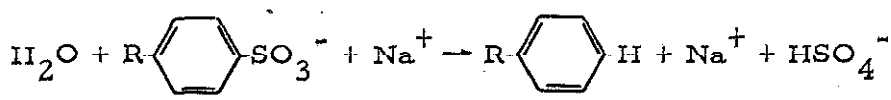
increases in sedimentation resulting from all doses.

In addition to the above-mentioned sedimentation studies, an investigation was also conducted into the effect of ionizing radiation on synthetic detergents. These studies were conducted at dose rates between 10.4 and 1340 rads per minute. Effects of the radiation were determined by foaming measurements, infrared spectroscopy to indicate changes in molecular structure, and chemical assay. The tests for foaming tendency were conducted on solutions of alkylbenzene-sulfonate (ABS), two commercial anionic detergents, and one commercial non-ionic detergent. The absorbed doses ranged from 1,440 to 643,200 rads. All of the solutions indicated a reduction in foaming although this change was more pronounced in the anionic detergents. Solutions of 10 and 35 mg/l were irradiated with doses up to 5,920 and 71,040 rads respectively. Analysis by the methylene blue procedure (see Section 3-10) indicated reduction of the 10 mg/l solution to 3.8 mg/l and the 35 mg/l solution to 6.0 mg/l. The latter was accompanied by a pH decrease of 2.2 units.

Samples containing 14 mg/l ABS were also irradiated to accumulated doses of greater than 10,000 rads at low dose rates of 10.4 and 22.6 rads per minute and high dose rates of 796 rads per minute. At an accumulated dose of 35,000 rads a 99 per cent reduction in ABS concentration was found in the samples irradiated at low dose rates, while approximately 70 per cent was observed in those irradiated at the higher rate. The relationship between ABS remaining and the total absorbed dose was exponential for most dose rates. The G value, defined as the yield or degradation in

molecules per 100 ev of absorbed dose, for the ABS degradation appeared to have an initial value greater than eight for the low dose rate. This value decreased as the degradation progressed, approaching a value of 1.0 for 95 per cent removal. A plot of G(-ABS); i.e., the degradation of ABS in molecules per 100 ev absorbed, as a function of total dose, indicated that the disappearance of the ABS is relatively independent of concentration in very dilute solutions.

Examination of irradiated samples by infrared spectrophotometry was accomplished by incorporating the ABS extracted from solution into potassium bromide pellets. Spectral changes were observed in the 8 to 10 micron range usually assigned to the sulfonate group. This change supported the hypothesis that sulfonate cleavage occurred by the reaction:



A reduction in absorbance was noted at 6.0 microns while a change in the 7 micron region was attributed to alteration in the substituted benzene ring. Changes also occurred in the 3.0 micron area usually assigned to O-H and C-H stretch bonds.

The authors recognized that compounds such as phenolic products from the benzene group or degradation products from the alkyl group and aromatic ring may have been present but the extent of their formation was not investigated.

On the basis of improved sedimentation indicated by the above results, cost comparisons were made for three types of waste treatment facilities, with and without a sedimentation basin containing

Cs-137 as a gamma radiation source. The three cases considered, primary plus secondary treatment, primary treatment only, and an overloaded existing facility, all showed savings when using isotopes at a cost of ten cents per curie. This process would not be competitive at current isotope prices.

1-3 Scope of the Present Study

Anionic detergents met with great success because, unlike soap, the efficiency of the surface-active ingredients is unaffected by hardness in water. Today, detergent-containing compounds constitute approximately 75 per cent of the soap and detergent industry, which handles about 3.5 billion pounds of material annually. Of the 2.4 billion pounds of compounds with detergents, the surface-active ingredients constitute about 900 million pounds (10). The most widely used surface-active agent is the anionic detergent alkylbenzenesulfonate (ABS). This compound is also referred to as dodecylbenzenesulfonate and tetrapropylbenzenesulfonate, the latter because of its synthesis from tetrapropylene.

The alkyl group of the ABS molecule is the key to the manner in which the material will degrade during sewage treatment. The molecule with a branched alkyl chain is not readily degradable while the straight chain formulation will degrade more readily under aerobic conditions. For this reason future household detergents will be formulated from a straight - rather than a branched - chain ABS.

The resistance of ABS to degradation has occasionally resulted in foamy drinking water in areas where water is being reused.

While ABS is not toxic in the usual concentrations found in water, its presence is indicative of the fact that a certain percentage of the water has been used previously. Because of this fact and since higher concentrations will cause foaming and will be accompanied by off-tastes (probably due to other waste products), a limit of 0.5 mg/l was recommended for ABS in the 1962 Drinking Water Standards of the Public Health Service (11).

A prodigious amount of research has been conducted on all phases of the detergent problem, although the study by the Bio Sciences Laboratory appears to be the first in which radiation has been considered as a means of degrading the molecule. The report, however, has left some rather interesting questions unanswered as to effects of such parameters as pH and oxygen concentration on the rate of ABS degradation and on the resulting degradation products. These degradation products have not been identified, and while desulfonation has been proposed as the means by which the molecule is altered, other possibilities should not be neglected. These would include shortening or complete removal of the alkyl chain, opening of the benzene ring, addition of other groups to the ring or the alkyl chain, polymerization of the ABS molecules, and any combination of these possibilities.

The most logical way to answer these questions is to study the effects on aqueous solutions of several of the lower homologs of ABS (namely, benzenesulfonic acid and toluenesulfonic acid) before considering the ABS molecule. It must be realized that some of the products may be produced in quantities too small to analyze, while

no definite analytical procedure may exist for others.

In order to examine the effect of absorbed dose, pH, dissolved oxygen, and sample concentration on the degradation process, it is necessary to propose mechanisms for this process and then to analyze for the particular products resulting from the proposed reactions. This procedure can be accomplished by first reviewing the effects of ionizing radiations on water, aqueous solutions of benzene and aqueous solutions of other substituted benzenes. While the irradiation of water and benzene has been studied with many types of radiations and in many physical states, this study has been limited by time, available equipment, and sphere of interest to the irradiation of aqueous solutions with a Co-60 irradiator.

1-4 Radiations from Cobalt-60

Cobalt-60 (Co-60) is a radioactive isotope formed by neutron bombardment of Co-59. Upon neutron capture by the Co-59 nucleus the mass number is raised to 60 while the 27 protons of cobalt are unchanged. Co-60 has a half-life of 5.24 years decaying to Nickel-60 by emission of a 0.312 Mev beta particle and 1.173 and 1.333 Mev gamma rays.

1-5 Effects of Irradiation on Water (After Allen (12))

The passage of ionizing radiations through water results in the production of electrons by either the photoelectric effect, the Compton effect, or pair production. Fast electrons will give up energy to water in quantities that average about 100 ev. On the basis of a linear energy transfer rate of approximately 0.02 ev per Angstrom, these events will lie about 5000 Angstroms apart. Since the

energy required to decompose a water molecule is 29 ±3ev (13), several molecules will decompose within a radius of 10 to 20 Angstroms forming H• and •OH radicals. These free radicals can recombine to form water, or like radicals may combine to form the molecular products hydrogen peroxide and hydrogen gas. Those radicals not combining will diffuse into the solution and participate in the reactions to be discussed subsequently. These initial events may be written

$$H_2O \rightarrow H\cdot + \cdot OH \qquad (1\text{-}1)$$

and

$$2H_2O \rightarrow H_2 + H_2O_2 \qquad (1\text{-}2)$$

Allen (14) has suggested an additional equation

$$2H_2O \rightarrow 2H\cdot + H_2O_2 \qquad (1\text{-}3)$$

to account for the fact that the hydrogen peroxide yield exceeds the hydrogen yield. Using G values (the yield or degradation of molecules per 100 ev of absorbed energy), a material balance for decomposition gives

$$2G_{H_2O_2} + G_{OH} = 2G_{H_2} + G_H \qquad (1\text{-}4)$$

where subscripted G values will indicate initial yields and those with parentheses, appearing later, will indicate values that would be measured. Although the free radicals are denoted by H• and •OH, their actual structure at different pH values is still under discussion.

Czapski and Schwarz (15) have shown that the reducing radical exists as H• in acid solution and as the solvated electron

H_2O^- or e^-_{aq} in neutral and alkaline solutions, with each having different kinetic behavior. This phenomenon was shown by the ionic strength effect on three rate constant ratios, since the rate constants and ionic strength are related by the Bronsted model of ionic reactions and the Debye theory of ionic solutions. The rate constants will increase, decrease, or remain unchanged with increasing ionic strength depending upon whether the reactants have the same or opposite signs or one is neutral.

Barr and Allen (16) postulated the following reactions for the radiolysis of neutral water in the presence of oxygen:

$$H_2O \rightarrow e^-_{aq},\ \cdot OH,\ H_2,\ H_2O_2 \qquad (1\text{-}5)$$

$$\cdot OH + H_2 \rightarrow H\cdot + H_2O \qquad (1\text{-}6)$$

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \qquad (1\text{-}7)$$

$$e^-_{aq} + H_2O_2 \rightarrow \cdot OH + OH^-_{aq} \qquad (1\text{-}8)$$

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

$$e^-_{aq} + O_2 \rightarrow O_2^- \qquad (1\text{-}10)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (1\text{-}11)$$

where the reducing species were proposed to exist in two forms, as the hydrogen radical and as the hydrated electron (e^-_{aq}). The existence of the hydrated electron was later verified by Hart and Boag (53) using pulse radiolysis to examine the absorption spectrum of this intermediate.

The manner in which the initial yields of the decomposition products have been determined is in most cases quite ingenious.

The yield of molecular hydrogen which is subject to reaction (1-6) has been determined by adding bromide, iodide or nitrite ions to the solution to react with the H• and •OH radicals by

$$Br^- + \cdot OH \rightarrow Br\cdot + OH^- \qquad (1\text{-}12)$$

$$Br\cdot + H\cdot \rightarrow H^+ + Br^- \qquad (1\text{-}13)$$

such that $G(H_2) = G_{H_2}$. This value is 0.45 in both acid and neutral solutions.

The hydrogen atom yield has been determined by the oxidation of ferrous sulfate, where

$$H_2O_2 + Fe^{++} \rightarrow FeOH^{++} + \cdot OH \qquad (1\text{-}14)$$

$$\cdot OH + Fe^{++} \rightarrow FeOH^{++} \qquad (1\text{-}15)$$

The H• atoms reacting with dissolved oxygen by reaction (1-9) give

$$HO_2\cdot + Fe^{++} + H^+ \rightarrow H_2O_2 + Fe^{+++} \qquad (1\text{-}16)$$

with the hydrogen peroxide formed oxidizing two additional ferrous ions. Thus

$$G(Fe^{+++}) = 2G_{H_2O_2} + G_{OH} + 3G_H$$

which in 0.8N H_2SO_4 is a well-established 15.5. From the mass balance of (1-4) this sum becomes $4G_H + 2G_{H_2}$. Since $G_{H_2} = 0.45$ the difference gives $G_H = 3.65$.

The remaining yields have been obtained by reduction of

ceric sulfate or oxygen. In an acid solution of the latter, the following reactions have been supposed:

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot \qquad (1\text{-}7)$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (1\text{-}11)$$

or at low H_2O_2 concentrations

$$\cdot OH + HO_2\cdot \rightarrow H_2O + O_2 \qquad (1\text{-}17)$$

This would indicate the peroxide yield to be

$$G(H_2O_2) = G_{H_2} + \tfrac{1}{2}\,(G_H - G_{OH})$$

In 0.8N H_2SO_4, $G(H_2O_2)$ has been found to be 1.17 which then makes $G_{H_2O_2}$ equal 0.8 and G_{OH} equal 2.95. $G_{H_2O_2}$ varies slightly with pH while G_{OH} decreases to 2.2 in neutral solutions.

In neutral solutions Czapski and Allen (54) determined $G_{e^-_{aq}} = 2.85 \pm 0.15$ while Allan and Scholes (55) found $G_H = 0.6$. When these values are considered with the other primary yields in neutral solutions $G_{OH} = 2.2$, $G_{H_2O_2} = 0.7$ and $G_{H_2} = 0.45$ there is disagreement in the material balance. Allen (56) has suggested the existence of an additional oxidizing radical, possibly the oxygen atom, to account for this discrepancy.

1-6 Effects of Irradiation on Benzene

The presence of a reactive solute in aqueous solutions at

concentrations greater than 10^{-6}M will minimize radical recombination in the bulk of the solution. This effect is due to the low radical concentrations that result from a reaction rate constant on the order of 10^9 liters per mole-sec. At this rate constant radical concentrations will not exceed 10^{-8}M. The literature is replete with articles dealing with the effects of irradiations on aqueous solutions of benzene. There is no complete agreement, however, on the products resulting from this irradiation.

Phung and Burton (17), irradiating unbuffered air-free solutions, observed no hydrogen peroxide production, $G(H_2O_2) = 0$, $G(H_2) = 0.42$ similar to pure water, and phenol and diphenyl yields of 0.36 and 1.22 respectively. Acidification of the solution reduced the diphenyl yield and increased hydrogen peroxide production resulting in the following yields:

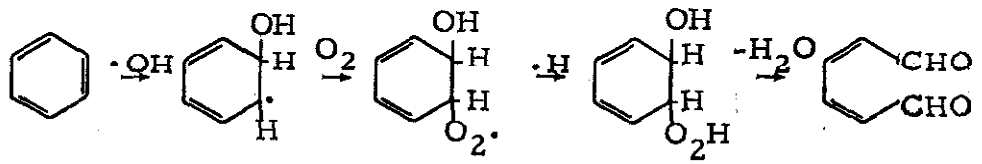
$$G(H_2O_2) = 0.57;\ G(PhOH) = 0.35$$

$$G(H_2) = 0.39;\ G(Ph_2) = 0.96$$

Barelko, et al. (18), found, in the absence of oxygen, $G(PhOH) = 0.5$ and $G(-PhH) = 2.0-2.5$, in good agreement with Phung but disagree with the assumption that the resulting precipitate is diphenyl. They suggest that the precipitate is hydroxydiphenyl and possibly other high molecular weight phenolic compounds.

In aerated or oxygenated solutions, phenol, dihydric phenols, quinones, mucondialdehyde and traces of diphenyl have been measured. Daniels, et.al. (19), irradiating neutral solutions, found the following yields: quinones ~ 0.1, dialdehydes ~ 0.2, phenol $= 2.2$,

and traces of diphenyl. The material assumed to be mucondialdehyde was measured by reaction with 2,4-dinitrophenylhydrazine. The ultraviolet spectra of the para- and 2,4-dinitrophenylhydrazine derivatives of the product resembled those obtained with synthetic mucondialdehyde but were not completely similar. The absence of this product from in vacuo irradiation suggested that molecular oxygen was important in the reaction which was proposed to occur by



(a) (b) (c) (d) (e) (1-18)

Loeff and Stein (20) observed mucondialdehyde and phenol formation in neutral solutions (pH 7.1) with yields of 0.8 and 2.69 respectively. The ratio of the yields remained constant at approximately 3 in a pH range of 0.4 to 7.5 with yields increasing at low pH values. In a later paper (21) they also noted the spectral differences between the hydrozones of the reaction product and the synthetic mucondialdehyde observed by Daniels, et al. An increase in the yield of phenol with increased dose rate was found to be accompanied by a decrease in dialdehyde formation in both acid and neutral solutions. This observation is explained by first examining some mechanisms by which phenol could be produced (17):

$$C_6H_6 + \cdot OH \rightarrow C_6H_5\cdot + H_2O \qquad (1\text{-}19)$$

$$C_6H_5\cdot + O_2 \rightarrow C_6H_5O_2\cdot \qquad (1\text{-}20)$$

$$C_6H_5O_2\cdot + H_2O \rightarrow C_6H_5OH + HO_2\cdot \qquad (1\text{-}21)$$

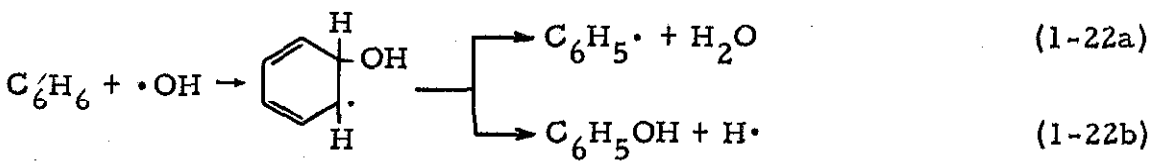
$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (1\text{-}11)$$

or $$C_6H_5\cdot + \cdot OH \rightarrow C_6H_5OH$$

or step (1-18d) above could yield phenol and hydrogen peroxide (18).

The occurrence of these mechanisms is supported by the facts that: (a) the radiation decomposition of initially added H_2O_2 does not affect phenol formation (22); (b) of the two possible mechanisms (23)

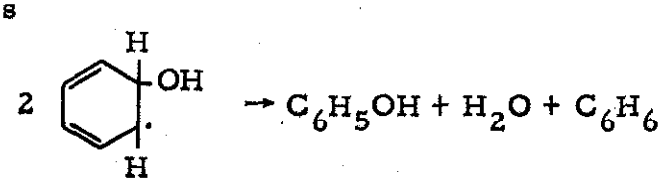


(1-22a)

(1-22b)

reaction (1-22a) is preferred, being exothermic by 16 kcal as compared to 3 kcal for (1-22b), and (c) the higher phenol yield in the presence of oxygen can be attributed to reaction (1-9) inhibiting the recombination of the H• radical with the •OH and phenyl radicals which reduces the yield in oxygen free systems.

To account for the decrease in mucondialdehyde at higher dose rates, it is suggested that two radicals in step (1-18b) may may combine, thus



(1-23)

increasing the phenol yield and decreasing the possibility of a resulting mucondialdehyde molecule.

Goodman and Steigman (24) found still another product showing phenol-like behavior. Their irradiated solutions had an ultraviolet absorption peak at 345 mμ that remained unchanged after phenol, diphenyl, and benzene were extracted with ether. Irradiation of dilute phenol solutions did not reproduce this peak, indicating the product did not arise from phenol. None of the other products reported to arise from the irradiation of benzene have absorption peaks in this area either.

The peak height of the water extract was pH sensitive and two well-defined isobestic points at 280 and 315 mμ suggested an equilibrium between two species. The reaction of this product with Folin's reagent, in the phenol determination, may indicate that reported phenol yields have been too high.

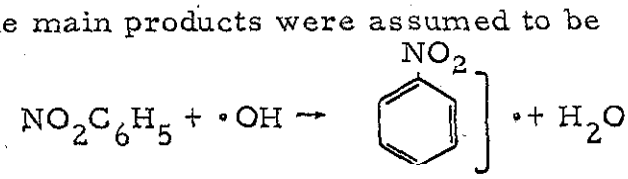
1-7 Effects of Irradiation on Substituted Benzenes

The effects of free radicals on substituted benzenes have been studied both by irradiation and by reaction with Fenton's reagent, a solution of hydrogen peroxide and ferrous salt. The reagent provides free hydroxyl radicals by the reaction:

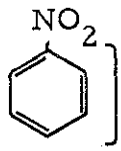
$$H_2O_2 + Fe^{++} \rightarrow \cdot OH + OH^- + Fe^{+++} \qquad (1\text{-}24)$$

One of the purposes of these studies has been to examine the effect of the substituent group on further substitution. If the substituent group has no directive action on free radical substitution then the addition of hydroxyl radicals would be expected to produce isomers

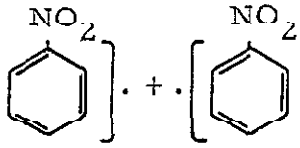
in a statistical distribution of ortho: meta: para equal to 2:2:1. Using Fenton's reagent with aqueous solutions of nitrobenzene, Stein and Weiss (25) found the yield of isomers to be practically equal, thus indicating a para-directing effect. In another paper, Loebl, Stein, and Weiss (26) presented the results of irradiating nitrobenzene in air-saturated solutions with 200-kv X-rays. The ratio of nitrophenol isomers was found to be pH dependent, with the o:m:p ratio at pH 6 approximately 35.5:29:35.5 by per cent. The nitrophenols accounted for 40-50 per cent of the total reaction products. At pH 6 the weight of dinitrodiphenyl was slightly less than the total nitrophenols which together account for 80-85 per cent of the reaction products. The remainder, of phenolic nature, was probably phenol and to a lesser degree dinitrodiphenols and dihydroxynitrobenzenes. The reactions yielding the main products were assumed to be



$$NO_2C_6H_5 + \cdot OH \rightarrow [NO_2C_6H_5]\cdot + H_2O \qquad (1\text{-}25)$$



$$[NO_2C_6H_5]\cdot + \cdot OH \rightarrow NO_2C_6H_4OH \qquad (1\text{-}26)$$



$$\text{and } [NO_2C_6H_5]\cdot + \cdot[NO_2C_6H_5] \rightarrow NO_2C_6H_4C_6H_4NO_2 \qquad (1\text{-}27)$$

While no nitrites were found, nitrates were observed probably as a result of

$$NO_2C_6H_5 + \cdot OH \rightarrow C_6H_5\cdot + HNO_3 \qquad (1\text{-}28)$$

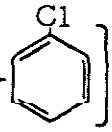
$$\text{while} \quad C_6H_5\cdot + \cdot OH \rightarrow C_6H_5OH \qquad (1\text{-}29)$$

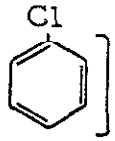
would explain the formation of phenol and

$$C_6H_5\cdot + C_6H_5\cdot \rightarrow C_6H_5C_6H_5, \text{ diphenyl.} \qquad (1\text{-}30)$$

The decline in nitrate yield that occurred after the exhaustion of dissolved oxygen indicated to the authors that the nitrate ion was due to hydroxyl radicals. The nitrate yield was approximately the same at pH 2, 6 and 12, about equal to that of one of the phenolic isomers.

Johnson, et al. (27), studied the hydroxylation of chlorobenzene and found the formation of chlorophenols to be pH sensitive. The chlorophenols result from the reactions

$$C_6H_5Cl + \cdot OH \rightarrow$$  $$\cdot + H_2O \qquad (1\text{-}31)$$

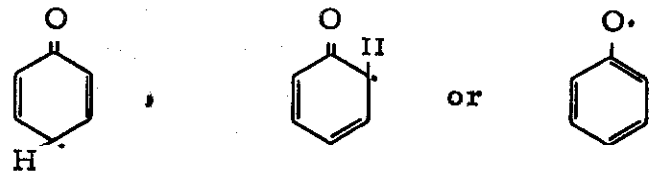
 $$\cdot + \cdot OH \rightarrow ClC_6H_4OH \qquad (1\text{-}32)$$

which is the same mechanism proposed for production of nitrophenols. At pH 6 the per cent of the o:m:p isomers of chlorophenols was 15-20:20-25:55-60. The authors assumed that chloride ions found to be present after irradiation resulted from the reaction

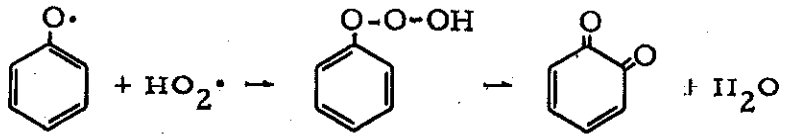
$$C_6H_5Cl + \cdot OH \rightarrow C_6H_5\cdot + HOCl \qquad (1\text{-}33)$$

When the total chlorophenol production was only 5μM, 18μM of the chloride ion was produced. Results tended to indicate that unlike the hydroxylation, removal of the substituent group is independent of pH as was found with nitrobenzene.

Stein and Weiss (28) using Fenton's reagent on aqueous solutions of phenol found quinol and catechol formed in a ratio of about 3:1. Only a trace of resorcinol was observed. X-radiation of aerated phenol solutions resulted in a quinol:catechol ratio of two in neutral and about four in acid solutions. The yields in acid and alkaline solutions were not affected by the absence of air while a smaller yield was noticed in neutral solutions. Irradiation of the acid solution produced o-benzoquinone not from, but in place of, the quinol and catechol. The authors suggested that this reaction occurred by the dehydrogenation of phenol, giving either



where the o-benzoquinone would result from



(1-34)

while quinol and catechol would result from reactions at the other positions. No resorcinol was observed.

Nakken (29), using 200-kv X-rays studied the hydroxylation of p-aminobenzoic acid (PABA) and found the main degradation product at pH 7.4 to be 3-hydroxy-4-aminobenzoic acid with traces of p-hydroxybenzoic acid and aniline. P-aminosalicylic acid was not observed. In oxygen-saturated solutions, the yield of 3-OH-PABA was 0.9 while G(-PABA) = 1.2. These yields were reduced by a factor of 6 without oxygen. In 0.4M sulfuric acid solutions G(-PABA)

was 1.1 and 0.9 with and without oxygen while the yield of 3-OH-PABA was less than 0.2.

Loebl, et al. (30), investigated the hydroxylation of benzoic acid and reported an o:m:p ratio of approximately 5:2:10 for the formation of monohydroxy benzoic acids at pH 3. The salicylic acid yield was found to decrease with pH to approximately pH 8. Diphenyl was also observed.

Downes (31) irradiated benzoic and salicylic acids using C-14 tagged compounds. He reported yields of 0.74:0.42:0.33 for the monohydroxy benzoic acids a ratio of 9:5:4. $G(CO_2)$ equaled 0.73 while the rate of degradation of benzoic acid was observed to be 2.6 molecules per 100 ev. The products accounting for the difference were not investigated. Alkaline solutions of salicylic acid were irradiated resulting in $G(CO_2)$ equal to 1.53. Only the 2,3- and 2,5- dihydroxy benzoic acids were identified, thereby giving results similar to those found for phenol where the meta isomer was not produced.

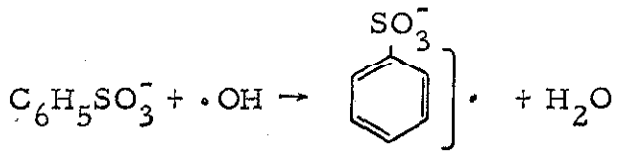
CHAPTER 2

POSSIBLE REACTIONS AND PRODUCTS

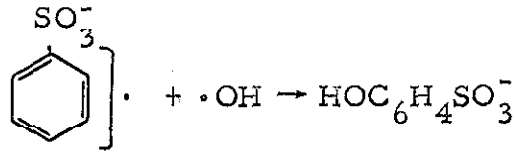
The earlier studies reviewed in Chapter 1 provide an excellent insight into the many possible reactions that may occur during the irradiation of aqueous solutions containing benzene-, p-toluene- and alkylbenzenesulfonate ions. From these studies it is possible to propose the reactions into which the solute will enter and from these the products that should be anticipated. Results of assays for the solute and its reaction products can then indicate to a certain extent the validity of the assumptions that have been made.

2-1 Reactions with Benzenesulfonate Ions

It may be anticipated that the benzenesulfonate ion will react to form phenolsulfonates by the following reactions



(2-1)



(2-2)

in the same manner proposed for the occurrence of the chloro- and nitrophenols, assuming in general that all three isomers will be present. In addition desulfonation would be expected to yield phenol by:

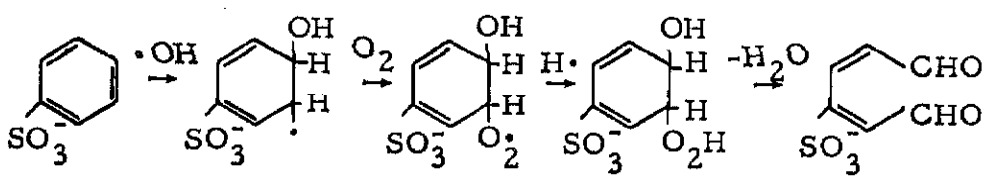
$$C_6H_5SO_3^- + \cdot OH \rightarrow C_6H_5 \cdot + HSO_4^- \qquad (2\text{-}3)$$

$$C_6H_5\cdot + \cdot OH \rightarrow C_6H_5OH \qquad (2\text{-}4)$$

as well as an equal amount of sulfates since this type reaction has been observed to occur in aerated solutions.

In deaerated solutions, a number of biphenyldisulfonic acid isomers may be anticipated. These molecules would occur by dimerization of the radicals produced in reaction (2-1). This reaction would be analogous to (1-27) which resulted in the formation of dinitrodiphenyl.

Another reaction that should be considered would be that resulting in the opening of the aromatic ring in a reaction similar to (1-18).



(2-5)

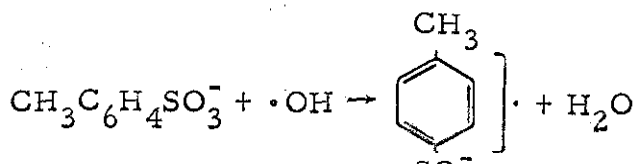
Whether this reaction can occur with the substituent group in any position or whether it is possible to abstract a bisulfate group rather than a water molecule in the last step of the process is unknown.

In addition to the compounds discussed above, it is likely that other compounds such as dihydroxybenzenesulfonic acid and dihydroxybiphenylsulfonic acid will be formed but with a much smaller yield.

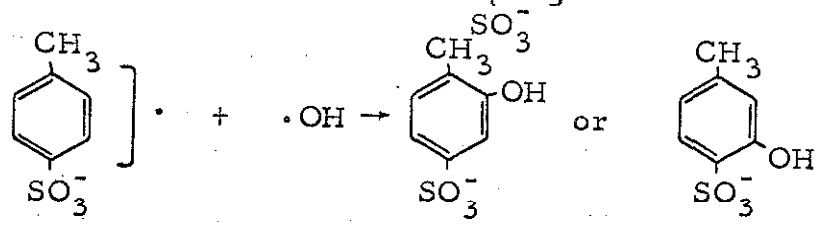
2-2 Reactions with p-Toluenesulfonate Ions

Reaction products from irradiation of p-toluenesulfonic acid would be expected to be similar to those from benzenesulfonic

acid. The monohydroxy compounds would be expected from the reactions:



$$CH_3C_6H_4SO_3^- + \cdot OH \rightarrow \left[\text{(p-tolyl-SO}_3^-\text{)} \right]\cdot + H_2O \qquad (2\text{-}6)$$



$$\left[\text{(p-tolyl-SO}_3^-\text{)} \right]\cdot + \cdot OH \rightarrow \text{(p-cresol-SO}_3^-\text{)} \text{ or } \text{(p-cresol-SO}_3^-\text{)} \qquad (2\text{-}7)$$

although as stated earlier Nakken (29) found only one when irradiating p-aminobenzoic acid. In deaerated solutions the free radicals produced in reaction (2-6) may be expected to dimerize forming isomers of bitolyldisulfonic acid. Desulfonation would be expected to occur as above, only yielding a p-cresol rather than phenol by:

$$CH_3C_6H_4SO_3^- + \cdot OH \rightarrow CH_3C_6H_4\cdot + HSO_4^- \qquad (2\text{-}8)$$

$$CH_3C_6H_4\cdot + \cdot OH \rightarrow CH_3C_6H_4OH \qquad (2\text{-}9)$$

while p-phenolsulfonic acid and methanol might be anticipated from:

$$CH_3C_6H_4SO_3^- + \cdot OH \rightarrow CH_3OH + \cdot C_6H_4SO_3^- \qquad (2\text{-}10)$$

$$\cdot C_6H_4SO_3^- + \cdot OH \rightarrow HOC_6H_4SO_3^- \qquad (2\text{-}11)$$

Since little has been done on the irradiation of aqueous solutions of saturated hydrocarbons, it is difficult to estimate affects of radiation on the methyl group with any degree of confidence. Phung and Burton (17) found a hydrogen yield of 1.22 in unbuffered deaerated solutions. This yield would indicate hydrogen abstraction of cyclohexane by the hydrogen radical. In aerated solutions $G(H_2)$ was

reported to be 0.43, the yield found on irradiation of pure water, while $G(-O_2)$ was 2.88. Johnson and Weiss (32) irradiated aerated solutions of methane and obtained methyl hydroperoxide and formaldehyde. Since the yield of methyl hydroperoxide decreased with pH while the hydrogen peroxide yield increased, the authors assumed that the reactions producing the methyl hydroperoxide were:

$$CH_4 + \cdot OH \rightarrow CH_3\cdot + H_2O \qquad (2\text{-}12)$$

$$CH_3\cdot + O_2 \rightarrow CH_3OO\cdot \qquad (2\text{-}13)$$

$$CH_3OO\cdot + O_2^- \rightarrow CH_3OO^- + O_2 \qquad (2\text{-}14)$$

$$CH_3OO^- + H^+ \rightleftharpoons CH_3OOH \qquad (2\text{-}15)$$

From these studies it would appear that hydrogen can be abstracted by either the $H\cdot$ or $\cdot OH$ radicals. On this basis one might expect the reactions

$$RCH_3 + \cdot OH \rightarrow RCH_2\cdot + H_2O \qquad (2\text{-}16)$$

or

$$RCH_3 + \cdot H \rightarrow RCH_2\cdot + H_2 \qquad (2\text{-}17)$$

$$RCH_2\cdot + \cdot OH \rightarrow RCH_2OH \qquad (2\text{-}18)$$

yielding a sulfonated benzyl alcohol or possibly

$$RCH_2\cdot + O_2^- \rightarrow RCH_2OO^- + O_2 \qquad (2\text{-}19)$$

R being the phenylsulfonate group. The possibility of ring opening cannot be overlooked, but the molecule, if it resulted from the same mechanism as reaction (2-5), would be most difficult to identify with

any great conviction.

Additional products that may be expected would include the six dihydric p-toluenesulfonic acids, and the mono- and dihydric bitolyldisulfonic acids.

2-3 Reactions with Alkylbenzenesulfonate Ions

Commercial ABS, being a mixture of ortho, meta, and para isomers, might possibly yield ten monohydroxy compounds on irradiation: four each from the ortho and meta isomers and two from the para. These products would be expected to occur in the same manner as proposed for the phenolsulfonates. A number of dihydric isomers may also be anticipated, although the yield of these compounds will probably be quite small. Dimerization would also be expected to occur producing any of the large number of isomers possible by joining two ABS molecules. Desulfonation would yield the ortho-, meta-, and para-hydroxy alkylbenzenes, while hydrogen might be abstracted from any of the twelve carbons on the alkyl chain being replaced by a hydroperoxide or hydroxyl group.

Ring opening, if it were to occur by reaction (2-5), could result in a hexadiene-dial with a sulfonate and a dodecyl group as substituents.

2-4 Limitations of the Present Study

The study has been limited to an examination of the benzenesulfonic acid, p-toluenesulfonic acid and the ABS mixture just discussed, over a range of pH values and concentrations of interest in environmental health engineering. The ability to determine a

particular chemical compound quantitatively is dependent on several factors: availability of equipment, ability to synthesize the compound, for which the analysis was to be conducted, and sensitivity of an analytical method when such a method was available. In several cases one or more of these limitations were contributing factors in preventing the analysis for a particular compound.

CHAPTER 3

APPARATUS AND ANALYTICAL PROCEDURES

3-1 Cobalt-60 Irradiator

The Co-60 irradiator, Figure 3-1, made available through the courtesy of the Jet Propulsion Laboratory, is a U. S. Nuclear Corporation Model GR-9, containing 4000 curies of Co-60 as of February 1963. This would have decayed to about 3400 curies at the time the irradiator was calibrated fourteen months later.

Samples placed in the sample chamber were automatically lowered into the irradiation position, within the lead pig, by a drive motor. The sample could be removed by pushing a button to raise the sample chamber or by a preset timer which would do this automatically at the end of a predetermined time period. The timer could be set to tenth of a minute increments.

3-2 Calibration of the Irradiator

The irradiator was calibrated using the Fricke ferrous sulfate dosimeter. Dosimetry is necessary to estimate the amount of energy absorbed by an irradiated sample. While calorimeters are the primary standards for radiation dosimetry, the secondary standards are numerous, employing many different concepts. Hart, et al. (33), tabulates fifteen of these, covering a range from acid production in chlorinated hydrocarbon solutions to luminescent degradation of anthracene. The use of chemical dosimetry for aqueous solutions has the distinct advantage that the dosimeter geometry can be made to duplicate the sample geometry by simply irradiating both in the

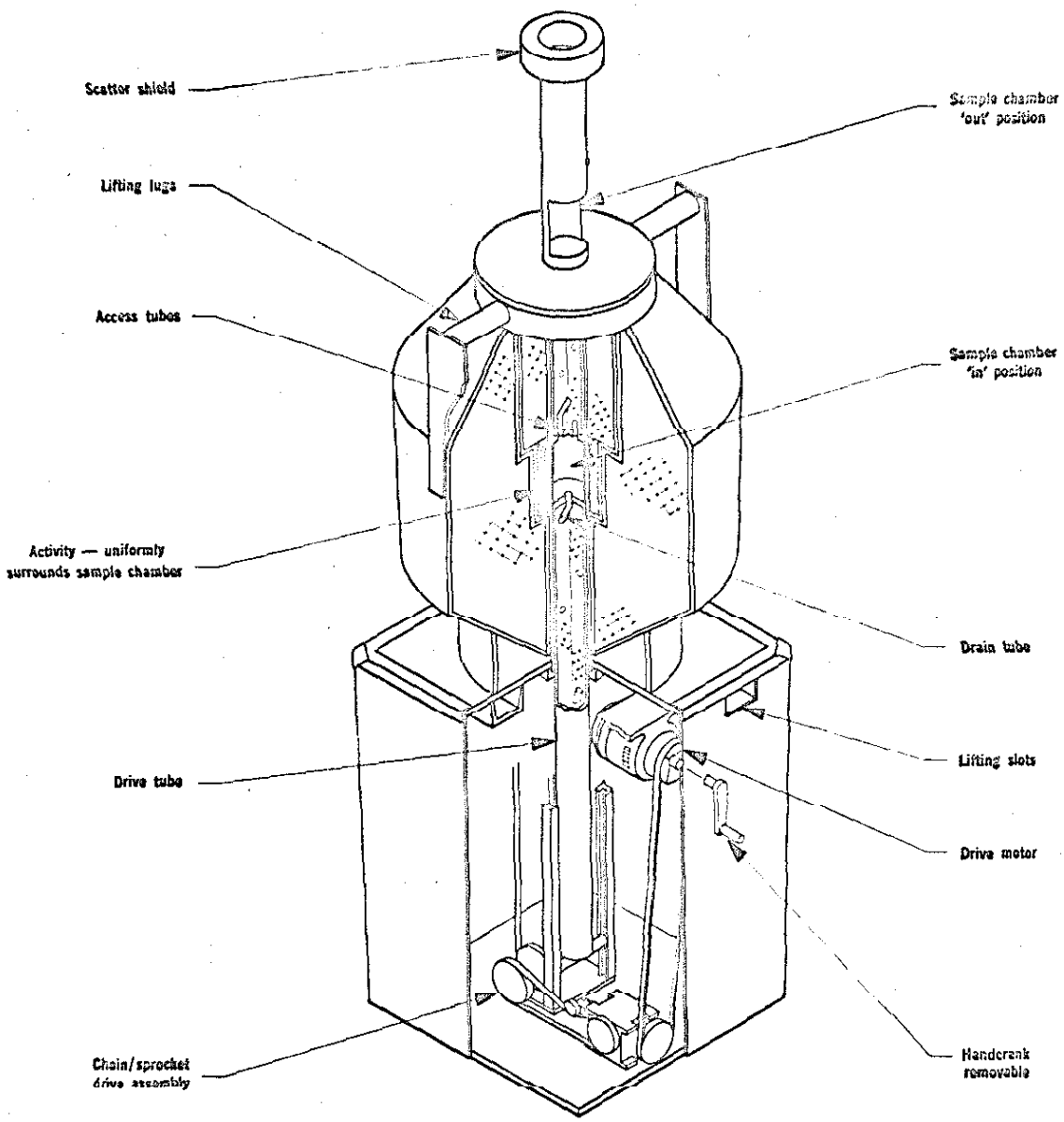


Figure 3-1 Cobalt-60 Irradiator (courtesy of U.S. Nuclear Corp.)

same containers. In this manner, it is possible to eliminate corrections for differences in absorption due to density differences of the solutions and the sample containers.

The most universally accepted chemical dosimeter is the Fricke ferrous sulfate dosimeter, named for Hugo Fricke, the developer. This dosimeter is composed of an air-saturated solution of ferrous sulfate and sodium chloride in 0.8N sulfuric acid prepared by diluting a solution containing 2 g of $FeSO_4 \cdot 7H_2O$, 0.3 g of NaCl, and 110 cc. of concentrated sulfuric acid to five liters, with distilled water. The chloride ion is added for the purpose of inhibiting the effect of impurities.

Under the action of ionizing radiation the following reactions have been assumed (12)

$$H_2O_2 + Fe^{++} \rightarrow FeOH^{++} + \cdot OH \qquad (1\text{-}14)$$

$$\cdot OH + Fe^{++} \rightarrow FeOH^{++} \qquad (1\text{-}15)$$

and in the presence of oxygen:

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

$$HO_2\cdot + Fe^{++} + H^+ \rightarrow H_2O_2 + Fe^{+++} \qquad (1\text{-}16)$$

Therefore, each peroxide molecule accounts for the oxidation of two ferrous ions from reactions (1-14) and (1-15). Each hydroxyl radical will oxidize one ferrous ion in (1-15) and each hydrogen radical will oxidize three ferrous ions. The yield of the dosimeter can be written

$$G(Fe^{+++}) = 3G_H + 2G_{H_2O_2} + G_{OH} \qquad (3\text{-}1)$$

This yield has been studied over a wide range of X- and gamma-ray energies and the accepted yield (G) for energies above 1 Mev is 15.6 ± 0.2 molecules per 100 ev.

Since the ferric ion has an ultraviolet absorption peak at 304 mμ the yield of the dosimeter is readily measured. The molar absorption coefficient for the ferric ion was determined by dissolving a known amount of iron wire, used especially for iron standards, in 6N sulfuric acid, and measuring the absorbance of several different concentrations in 0.8N sulfuric acid. The value of 2200 liters per mole-cm. at 24° C is in good agreement with the work of others (12).

3-3 Chemical Synthesis

Several organic compounds required for comparison with the degradation products could not be obtained commercially, making synthesis necessary. The various methods follow.

3-3-1 Ortho-phenolsulfonic Acid

Ortho-phenolsulfonic acid was prepared by the method of Chase and McKeown (34). This entails mixing equimolar quantities of phenol and concentrated (98%) sulfuric acid while cooling the mixture in a refrigerated water bath. The mixture is allowed to stand at room temperature for 48 hours, after which it is dissolved in water and neutralized to pH 7 with sodium hydroxide. Carbon dioxide is bubbled through the solution to lower the pH, after which the phenol is extracted with ether and the solution evaporated to dryness. The phenolsulfonate is extracted into boiling methanol where

concentration of the extract will precipitate sodium phenolsulfonate containing approximately 80 per cent of the ortho isomer, the remainder being the para isomer. Three further crystallizations should give the pure sodium o-phenolsulfonate.

The purity of the product was estimated to be 93 per cent from the absorption spectra of its ferric chloride complex at 535 mμ. By adding an equal volume of one per cent solution of anhydrous ferric chloride in water to a .001M solution of the phenolsulfonate and measuring absorbance against a ferric chloride blank, between 5-30 minutes after mixing, it was possible to compare the value observed with data presented by the authors. These data were based on molar absorption coefficients of 808 and 76 liters per mole-cm for the ortho- and para-phenolsulfonic acids.

3-3-2 <u>1-Methyl-2-hydroxy-4-benzenesulfonic Acid (I)</u>

This compound was prepared by the method presented by Tatibouet and Setton (35) in which one mole (108 g) of o-cresol is mixed with 300 g of concentrated sulfuric acid and heated for one hour at 150° C. The mixture is then poured over one kg of ice and neutralized with calcium carbonate until carbon dioxide production stops. The solution is filtered and the calcium sulfate precipitate washed, by boiling in one liter of water. This solution is filtered and the cake washed on the filter with an additional one-half liter of water. The filtrates are combined and concentrated under a vacuum until the appearance of calcium sulfate crystals. A half mole (49 g) of concentrated sulfuric acid is added, precipitating the remaining calcium sulfate. The mixture is filtered and the filter

cake washed. This operation leaves a filtrate containing the sulfonic acid and a slight excess of sulfuric acid. It is necessary to eliminate this excess, which would give a slightly soluble aniline sulfate, since the aniline would contaminate the sulfonates.

The excess sulfate is determined by titrating a sample of the filtrate with a barium hydroxide solution, using potassium rhodizonite as an indicator. The required amount of barium hydroxide is added to the solution which is then filtered. The barium sulfate filter cake is washed and discarded.

The amount of barium hydroxide added permits calculation of the efficiency of the sulfonation, since the excess sulfuric acid corresponds to the unreacted amount of o-cresol. At 100 per cent efficiency one mole of the o-cresol would yield one mole of the sulfonate, as the calcium salt. Addition of the one-half mole of sulfuric acid should precipitate essentially all the calcium sulfate. Any excess sulfate results from the lack of calcium attributable to unreacted o-cresol.

The amount of aniline necessary to produce the aniline salt of the sulfonic acid, calculated from the efficiency, is added to the filtrate and the mixture boiled for 30 minutes with 20 g of activated carbon. The solution is filtered while warm, yielding a clear yellow filtrate. The filtrate is concentrated at reduced pressure until the appearance of crystals, at which time it is quickly cooled. Rapid cooling results in precipitation of the aniline salt of 1-methyl-2-hydroxy-5-benzenesulfonic acid (II) which is filtered and washed. A second concentration yields a combination of I and II while the

third concentration yields only the aniline salt of I. The sodium salt is obtained by mixing equimolar quantities of the aniline salt of I with sodium hydroxide, extracting the aniline with ether and crystallizing the salt under reduced pressure.

3-3-3 1-Methyl-3-hydroxy-4-benzenesulfonic Acid (III)

The compound was prepared by heating equimolar quantities of m-cresol and concentrated sulfuric acid on a steam bath for one hour, after which the solution is diluted with water and made alkaline with barium hydroxide. The mixture is filtered and the barium sulfate precipitate washed and discarded. The solution is neutralized with carbon dioxide or sulfuric acid and concentrated. On cooling, the barium salt of III precipitates and is purified by one recrystallization. This method, developed by Haworth and Lapworth (36), enables separation of III from 1-methyl-3-hydroxy-6-benzenesulfonic acid (IV) on the basis of the solubilities of the barium salts, since III was reported to have the much lower solubility, 4.5 g in 100 ml at 20° C. Zehenter, et al. (37), however, indicated that the barium salt of IV was the less soluble of the two. A later study of this separation by Tchitchibabine and Darkovsky (38) reaffirmed the work of Haworth and Lapworth, but indicated that repurification of III lowered the solubility at 20° C to 3.1 g in 100 ml. They reported the solubility at 100° C to be 17.5 g per 100 ml.

3-3-4 Meta-phenolsulfonic Acid

This compound cannot be formed by sulfonation of phenols at other than very high temperatures. Instead, a method recently presented by Karavaev and Spryskov (39) was found to be applicable for

the synthesis of any of the phenolsulfonic acids and could have been used to prepare the ortho isomer, which had been synthesized before this method appeared in the literature.

Metanilic acid is diazotized using the "inverted method," by dissolving this compound in as little water as necessary through neutralization with a concentrated sodium hydroxide solution. (Orthanilic and sulfanilic acids would be used to synthesize the ortho and para isomers.) An equimolar quantity of sodium nitrite is dissolved in this solution to provide the nitrous acid necessary for the diazotization. A sulfuric acid solution (170 cc. concentrated H_2SO_4 per mole of metanilic acid, diluted with 500 ml water) is cooled to 0° C along with the first solution. After cooling, the metanilic acid solution is stirred into the sulfuric acid, while the temperature is maintained below 5° C. This reaction precipitates the diazonium salt, m-diazobenzenesulfonic acid. The mixture is filtered to collect the precipitate. The precipitate is carefully mixed with water, since the dry salt is explosive, and jetted into a boiling solution of sulfuric acid in water. This action decomposes the diazonium salt producing m-phenolsulfonic acid. The solution is treated with lead carbonate to neutralize the sulfuric acid, and then filtered. The filtrate is treated with purified hydrogen sulfide and filtered again. The resulting clear, colorless filtrate is evaporated under a vacuum until crystallization of the m-phenolsulfonic acid.

3-4 Distilled Water

Distilled water used for irradiation was obtained from the distilled water system serving the Keck Laboratories. This water

was redistilled from an alkaline solution of potassium permanganate, in an all-glass system, containing either a platinum gauze or glass wool filter. The distillate was stored in a closed glass carboy for reuse.

3-5 Other Reagents

Benzenesulfonic acid sodium salt - Eastman Organic Chemicals No. 324, recrystallized from methanol.

p-Toluenesulfonic acid sodium salt - Eastman Organic Chemicals No. 524.

p-Phenolsulfonic acid sodium salt - Eastman Organic Chemicals No. 2184.

Alkylbenzenesulfonic acid sodium salt - courtesy of the Soap and Detergent Association. The compound was synthesized from dodecene-1 and had the following assay:

ABS	90.29 per cent
Na_2SO_4	7.86
Free oil	0.69
Water	1.16

Since this compound contains a straight alkyl chain, it corresponds to the degradable detergent now called linear alkylate sulfonate (LAS) by the soap and detergent industry.

3-6 Dissolved Oxygen Determination

Analyses for dissolved oxygen were accomplished polarographically with a Jarrell-Ash model 26-601 Dissolved Oxygen Analyzer. The analyzer uses a temperature-compensated, platinum

and silver-silver oxide, bi-metallic electrode, immersed in a potassium hydroxide solution and covered with a teflon membrane, permeable only to dissolved oxygen. This method has an advantage over other methods for dissolved oxygen analysis in that it is not affected by hydrogen peroxide and the sample is not altered during the determination.

The instrument is calibrated against an air-saturated solution and a solution deaerated with nitrogen gas. Measurements of sample temperature and per cent saturation can then be used to calculate the oxygen concentration of the solution.

3-7 Sulfate Determination

Sulfate production was determined in irradiated solutions of benzenesulfonic acid and p-toluenesulfonic acid by a modification of the turbidimetric procedure in Standard Methods (40). A 50.0-ml sample was pipetted into a 100-ml beaker after which 1.00 ml of concentrated hydrochloric acid was added. The acid was necessary to prevent precipitation of barium carbonate in those cases where the bicarbonate buffer system was used. The solution was stirred at a constant speed, using a magnetic stirrer, during the addition of 3.00 ml of conditioning agent. The conditioning agent was prepared by dissolving 75 g of sodium chloride in a solution containing 300 ml of distilled water and 30 ml of concentrated hydrochloric acid, followed by the addition of 100 ml of isopropyl alcohol and 50 ml of glycerine.

After addition of the conditioning solution, a spoonful of 20-30

mesh barium chloride crystals was added to precipitate barium sulfate. The solution was stirred for exactly one minute, after which time the solution was allowed to stand for thirty minutes. The mixture was then placed in a 10-cm cell and the absorbance resulting from turbidity was measured at a wave length of 420 mμ, against a distilled water blank. Unirradiated samples were also analyzed in order to correct for the slight turbidity produced by the barium salt of the solute. The corrected readings were then compared to a standard curve prepared from solutions of sodium sulfate. The accuracy of this method has been estimated (40) to be about ± 10 per cent under the best laboratory conditions.

This method was not suitable for solutions containing ABS, since the barium salt of ABS is only slightly soluble and interferes with the analysis. Several methods were tried to circumvent this difficulty. Conductimetric titration with barium chloride did not give a sharp enough break between the two salts, while passage through a column of Pittsburgh Chemical Co. Type SGL activated carbon, having an 8 × 30 mesh particle size, removed both sulfates and ABS from the samples.

It was finally decided to remove the ABS from 25.0-ml samples by adding 5 ml of saturated methylene blue solution, 1 ml of hydrochloric acid and then extracting three times with 10 ml-additions of chloroform. The extracted solution was washed into a 50-ml volumetric flask, 3 ml of conditioner was added, and the solution was diluted to 50 ml. The solution was then placed in a plastic centrifuge tube and centrifuged for approximately five

minutes to remove any chloroform that may have remained in suspension. The absorbance of the solution was measured at 424 mμ, in 10-cm cells, against a distilled water blank. The solution was then placed in a beaker, a spoonful of barium chloride was added, and the solution was stirred with a magnetic stirrer for one minute. After standing for thirty minutes the absorbance was read again. The difference between the initial and final readings was attributed to sulfates. This method could indicate 1×10^{-5} M sulfate concentrations, while the original procedure was approximately twice as sensitive.

3-8 Ultraviolet Spectroscopy

All ultraviolet spectroscopy was conducted with the dual beam, Beckman Model DK-2 Recording Spectrophotometer, using silica cells.

As no chemical methods were found for the quantitative determination of benzene- and p-toluenesulfonic acid in aqueous solutions, it was necessary to utilize their spectral properties. Both compounds have well-defined absorbance peaks in the ultraviolet region that obey Beer's Law. Benzenesulfonic acid has a maxima at 216 mμ with a molar absorption coefficient of 8300 liters per mole-cm while p-toluenesulfonic acid has a peak at 221 mμ having a coefficient of 11,000 liters per mole-cm. These peaks were used as an indication of the rate at which these compounds degraded during irradiation. It was realized, however, that the absorbance of the reaction products would interfere with the absolute determination of the amount of solute remaining after irradiation.

3-9 Hydrogen Peroxide Determination

This determination follows the procedure outlined by Hochanadel (41), in which the iodide ion is oxidized by hydrogen peroxide, or organic peroxides, in neutral or slightly acid solution

$$2H^+ + 2I^- + H_2O_2 \rightarrow I_2 + 2H_2O \qquad (3\text{-}2)$$

$$I_2 + I^- \rightarrow I_3^- \qquad (3\text{-}3)$$

The I_3^- can be measured by its ultraviolet absorption peak at 350 mμ. From the reactions it can be seen that one mole of hydrogen peroxide will oxidize one mole of iodide to I_3^-.

The necessary reagent is prepared immediately before use by mixing equal volumes of two solutions. The first solution is prepared by diluting 66 g of potassium iodide, 2 g of sodium hydroxide and 0.2 g of ammonium molybdate to one liter. The second solution is obtained by diluting 20 g of potassium phthalate to one liter. The solutions are stable until mixed, after which the iodide is slowly oxidized by dissolved oxygen.

Hydrogen peroxide was measured by pipetting 10.0 ml of the mixed reagent into a 10.0-ml sample and measuring the absorbance of the resulting solution at 350 mμ.

The molar absorption coefficient was determined using a standard potassium iodate solution reduced in the presence of potassium iodide and acetic acid to I_3^-,

$$6H^+ + IO_3^- + 5I^- \rightarrow 3I_2 + 3H_2O \qquad (3\text{-}4)$$

$$3I_2 + 3I^- \rightarrow 3I_3^- \qquad (3\text{-}5)$$

one mole of IO_3^- producing three of I_3^-. The coefficient for I_3^- was found to be 25,000 liters per mole-cm. The accuracy of this procedure is estimated to be better than ± 5 per cent.

3-10 ABS Determination

ABS was determined using a methylene blue extraction procedure (42). The method is based on the fact that the ABS-methylene blue complex can be extracted by chloroform and the absorbance measured at 660 mμ. Methylene blue will complex with alkylbenzenesulfonates having alkyl chains containing more than six or seven carbon atoms. For this reason the method is not satisfactory for the other homologs investigated. The complex followed Beer's Law to 2.5×10^{-7} moles, the maximum quantity standardized, indicating an absorption coefficient of 97,000 liters per mole-cm.

In the procedure adopted a sample containing approximately 10^{-7} moles of ABS is pipetted into a 250-ml separatory funnel and diluted to 100 ml. One ml of 5N sulfuric acid and 5.0 ml of methylene blue solution are added and mixed. The methylene blue solution was prepared by adding 0.35 g of methylene blue to one liter of 0.01N sulfuric acid. Ten ml of chloroform are added to the solution which is then shaken once a second for 25 seconds and allowed to separate. The chloroform is withdrawn into a 50-ml volumetric flask through an absorbent cotton plug. The extraction procedure is repeated

twice more, the cotton rinsed with additional chloroform and the flask filled to the mark. The solution is allowed to stand for approximately 5 minutes after which the absorbance is measured at 660 mμ, against a chloroform blank, using 2-cm. cells.

The absorbance is compared to a standard curve prepared by running duplicate determinations with 0.5, 1.0, 1.5, 2.0 and 2.5×10^{-7} moles of ABS. Standard Methods (40) indicates an accuracy of about ± 10 per cent for this procedure.

3-11 Hydroxyl Group Determination

Two methods were used for the determination of hydroxylation by ionizing radiation. Both are modifications of the aminoantipyrine methods for phenol determination, as recommended in Standard Methods (40). The same reagents were required in each of the methods of analysis, the major difference being that in one procedure the complex is extracted into chloroform before measuring the absorption while this extraction is not required in the other. The procedures are based on the observation that in alkaline solutions certain phenolic compounds will react quantitatively with 4-aminoantipyrine in the presence of ferricyanide to form an antipyrine dye. If desired, this dye may be concentrated by extraction into chloroform. In either case the absorption may be determined spectrometrically, although the absorption peaks will shift depending upon the particular phenolic compound and whether the complex is in water or chloroform. It was found during the course of this study that some enols cannot be extracted into chloroform.

The reagents required are: an aminoantipyrine solution, prepared daily by dissolving 2.0 g of the compound in distilled water and diluting to 100 ml; a solution of potassium ferricyanide prepared weekly by dissolving 8 g in water and diluting to 100 ml; and a buffer solution containing 50 g of ammonium chloride dissolved in water and diluted to one liter.

3-11-1 Modified Phenol Determination

Pipette a 15.0-ml sample into a beaker, add 0.5 ml of ammonium chloride solution and adjust the pH to 10.0 ± 0.2 with concentrated ammonium hydroxide. Wash the solution into a 25-ml volumetric flask. Add 1.00 ml of aminoantipyrine solution, mix, add 1.00 ml of potassium ferricyanide solution and dilute to the mark. Measure absorbance against an unirradiated sample blank at the absorbance peak, with 5-cm cells. The absorbance can then be compared to a standard curve or set of samples run concurrently with known amounts of the phenolic compound of interest. The molar absorption coefficients (a) found for several of the compounds of interest have been listed in Table 3-1, below. Since these values will depend on the age and strength of the solutions being used, they will vary slightly from day to day. They are presented to indicate the range of values that may be anticipated.

3-11-2 Phenol Determination

This analysis is conducted by pipetting a 100.0-ml sample into a beaker, adding 2 ml of ammonium chloride solution and adjusting the pH to 10 ± 0.2 with concentrated ammonium hydroxide. The solution is then washed into a 250-ml separatory funnel and 3.00 ml

Table 3-1

Molar Absorption Coefficients in Modified Phenol Determination

Compound	a-liters/mole-cm	Peak wavelength-mμ
phenol	13,000	510
o-phenolsulfonic acid	18,000	505
m-phenolsulfonic acid	9,900	500
p-phenolsulfonic acid	950	500
I	6,300	500
III	4,900	500

of aminoantipyrine solution is added. Immediately after mixing, 3.00 ml of potassium ferricyanide solution is introduced. The solution is mixed again and extracted twice with 10-ml portions of chloroform and once with a 7-ml portion. The extract is filtered into a 25-ml volumetric flask through a fritted glass funnel containing a layer of anhydrous, granular, sodium sulfate. The chloroform is diluted to the mark and the absorbance measured against an unirradiated sample blank in 5-cm cells. The absorbance can be compared to those of standards run concurrently. The molar absorption coefficients for some of the compounds used are presented in Table 3-2, below. Again, it should be noted that these will suffer daily variations.

Comparison of the coefficients in both tabulations shows that the compounds behave differently in the two solvents. The most striking differences are the complexes with m- and o-phenol-

sulfonic acid which do not extract into the chloroform.

Table 3-2

Molar Absorption Coefficients in Phenol Determination

Compound	a-liters/mole-cm	Peak wavelength-mμ
phenol	20,000	460
o-phenolsulfonic acid	0	-
m-phenolsulfonic acid	0	-
p-phenolsulfonic acid	800	460
I	2,300	455
III	4,500	455

3-11-3 Hydroxylation of Benzenesulfonic Acid

In the discussion of possible reactions into which the benzenesulfonate ion would be expected to enter, it was indicated that the three monohydroxy isomers, phenol, and some of the dihydroxy isomers should be anticipated. The two phenol tests cannot be expected to give quantitative information on all of these products. They should be useful in obtaining rough estimates assuming that the monohydroxy compounds are predominant.

Table 3-2 shows that the phenol determination will indicate an absorbance resulting from the phenol and p-phenolsulfonic acid produced during irradiation (ignoring the dihydric compounds). Assuming that for each mole of sulfate produced, an equivalent amount of phenol is also produced, these data can be corrected to

indicate p-phenolsulfonic acid alone by subtracting the absorbance of the phenol as estimated from the sulfate determinations.

In a similar manner the data from the modified phenol determination should be corrected to indicate the absorbance of the m- and o-phenolsulfonic acid together. Unfortunately, no method was found to separate these two compounds since even their ultraviolet spectra are almost identical. This fact prohibited estimation of the o:m:p ratio for the formation of the phenolsulfonic acids. The three isomers may have been separable by paper chromatography, possibly using carbon-14 tagged benzenesulfonic acid to locate the isomers, but this method was not attempted.

3-11-4 Hydroxylation of p-Toluenesulfonic Acid

From the data in Tables 3-1 and 3-2, it can be seen that if I and III are present in a solution it should be possible to analyze for both by using the two phenol determinations. This separation is accomplished by analyzing irradiated samples by both methods. Standards of both I and III can be analyzed by both methods at the same time. This method would provide a set of simultaneous equations that should enable the calculation of the amount of the two constituents formed by irradiation. In Chapter 2 it was proposed that, in addition to I and III, p-cresol, p-phenolsulfonic acid, several dihydric p-toluenesulfonic acids, and some hydroxylated dimers might be expected to occur from the irradiation of p-toluenesulfonic acid. Since these analytical methods are insensitive to para-substituted phenols with the exception of such substituents as carboxyl, halogen, methoxyl, hydroxyl or sulfonic acid groups,

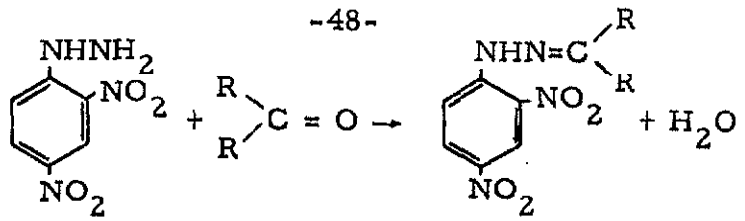
p-cresol and similar para-substituted derivatives will not interfere with this determination. Since a for p-phenolsulfonic acid is so much smaller than that for I or III neglecting this compound should have only a small effect on the results. The effects of the other compounds cannot be estimated without experimental data.

3-11-5 Hydroxylation of ABS

No attempt has been made to determine the amount of each of the ten monohydroxy and numerous dihydroxy isomers that may arise from irradiating ABS. However, a relative indication of the effect of pH, dissolved oxygen and irradiation dose is desirable. To obtain this information, irradiated samples were analyzed by the modified phenol method. This test gives a relative value, since no standard is available. To account for the day-to-day variations, as all samples could not be analyzed at once, an o-phenolsulfonic acid standard was also analyzed each day. Samples could then be converted to a common base, using variations in the o-phenolsulfonic acid as a multiplier.

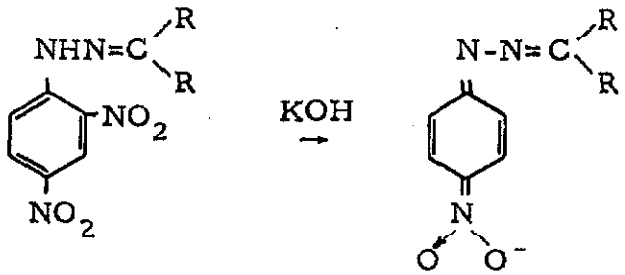
3-12 Aldehyde Analysis

A specific method does not exist for the identification of mucondialdehyde, either with or without substituent groups. A modification of a method presented by Critchfield (43), however, was used as an indication of the existence of an aldehyde or dialdehyde group. The method is based on the reaction of 2,4-dinitrophenylhydrazine with a carbonyl compound to form the hydrazone:



(3-10)

The addition of potassium hydroxide produces a brown-red color, absorbing in the vicinity of 480 mμ, which is presumed to result from a resonating quinoidal ion:



(3-11)

The procedure requires carbonyl-free methanol, prepared by refluxing a solution containing 1 liter of methanol, 3 g of 2,4-dinitrophenylhydrazine, and 1 ml of hydrochloric acid, for four hours. The fraction distilling over to 64.8° C is collected. To 25 ml of the carbonyl-free methanol, 50 mg of 2,4-dinitrophenylhydrazine and two ml of hydrochloric acid are added. The solution is diluted to 50 ml with distilled water. Three ml of this solution, which should be prepared daily, is added to a 5.00-ml sample in a 25-ml volumetric flask. The mixture is allowed to react for 90 minutes, after which 10 ml of distilled water is added. This is followed by the addition of 1.00 ml of a 33 per cent potassium hydroxide solution. The solution is diluted to the mark and the absorbance measured, after 10 minutes, against an unirradiated reagent blank, in 5-cm cells. Using this procedure with 2,4-hexadienal, the color produced did not follow Beer's Law, but yielded the following absorbance-concentration data:

Concentration	Absorbance		
10^{-5} M	440 mμ	475 mμ	560 mμ
0.26	.236	.430	.210
0.51	.331	.640	.323
0.77	.435	.844	.417
1.03	.495	.993	.491
1.29	.512	1.102	.555

The spectra of the hydrazones of p-benzoquinone were quite different. While the 2,4-hexadienal had a sharp peak at 475 mμ, the p-benzoquinone peak decreased slowly with increasing wavelengths, giving the impression of the existance of two adjacent peaks, one at 460 mμ having a molar absorption coefficient, (a), of 8900 liters per mole-cm and another, less pronounced, at about 520 mμ, with a equal to 7400.

Loeff and Stein (21) using a more complicated analytical procedure determined the molar absorption coefficient of the di-p-nitrophenylhydrazone, resulting from synthetic mucondialdehyde, to be 8240 liters per mole-cm at 390 mμ. Their procedure also was used to determine ortho- and para-quinone since these compounds gave derivatives with p-nitrophenylhydrazine having coefficients of 7000 liters per mole-cm at 510 mμ, and 24,000 liter per mole-cm at 470 mμ, respectively.

3-13 Carbon Dioxide Determination

Carbon dioxide was determined manometrically with an American Instrument Company Rotary Warburg apparatus. In this procedure a 100-ml sample is pipetted into a flask which is then attached

to a differential manometer. The flask is placed in a constant temperature water bath set at 20° C and allowed to reach equilibrium. When the sample has reached 20° C the sample is acidified with 1 ml of 6N sulfuric acid. After several hours, when the gas has come to equilibrium, the manometer is adjusted to bring the system to a precalibrated volume, and the height of the column is read. The change in pressure can then be used to calculate the number of moles of gas removed from solution, assuming the perfect gas law is applicable. When the calculated value is corrected for the changes observed in an unirradiated sample the effect of irradiation can be estimated. The technique will not remove all the carbon dioxide from solution, as the gas is very soluble in water.

3-14 Other Analytical Techniques

Many of the analytical procedures presented in this chapter are for the purpose of determining the presence of functional groups, rather than specific compounds. Additional procedures were investigated but could not be applied to this particular study. Methods for the determination of unsaturation, which would have proved useful in determining whether aromatic ring opening actually occurred, were all affected by the presence of enol groups. A colorimetric method for the determination of alcohol, was of no value since the molar absorption coefficient was too small in comparison to the concentrations that were expected.

Analytical procedures for the identification of such specific compounds as biphenyldisulfonic acid and other dimers, as well as

the dihydric benzene- and p-toluenesulfonic acids would have been welcome additions to this chapter. Unfortunately procedures are not available that have the sensitivity required for analysis of small samples at low concentrations.

CHAPTER 4

EXPERIMENTAL PROCEDURES

4-1 Calibration of Irradiator

The irradiator was calibrated using the Fricke dosimeter solution discussed in Section 3-2. This solution and all subsequent solutions were irradiated in four-ounce, narrow-mouth bottles sealed with a molded plastic cap containing a conical polyethylene liner. Twenty dosimeter solutions were irradiated, for periods from eighteen seconds up to five minutes, to determine the absorbed dose rate. From the ferric ion analysis it was determined that the solution was absorbing 6.18×10^{20} ev per liter per minute or 9890 rads per minute, at the time of calibration. As a result of radioactive decay of Co-60, the absorbed dose will decrease by approximately 105 rads per minute per month. This decay resulted in a decrease in dose rate of approximately nine per cent during the course of the study.

4-2 Dose Effects

The effect of absorbed dose on the various solutions being irradiated was easily examined, by varying the time a sample remained in the irradiator. Samples were irradiated for periods up to five minutes, at one-minute intervals, to obtain this information. Two factors influenced the decision as to the maximum time the samples were irradiated: the rate of oxygen consumption, in order that all the oxygen not be consumed in aerated samples, and the rate at which the compounds degraded. The second factor was important since secondary reactions would become significant if the quantity of the reaction products became too large.

4-3 pH Effects

Three buffer systems were used during the study to determine the effect of pH on the rate of degradation. The 0.1M potassium dihydrogen phosphate (KH_2PO_4) solution gave a pH of approximately 4.5 and provided a buffer capacity of 4×10^{-4}M H^+ per unit pH change. The 0.1M sodium bicarbonate system yielded a pH of about 8.2 and the system containing 0.01M each, of the potassium mono- and dihydrogen phosphate, produced a pH of about 6.9. These systems had buffer capacities of 7×10^{-4} and 2×10^{-3}M H^+ per unit pH change, respectively. No attempt was made to adjust the pH of the solutions to a particular value after the solutions had been prepared.

The buffer solutions were each irradiated without any sulfonates being added in order to determine changes that occur owing to the buffer system alone. These data provide a base line from which to examine the changes resulting from the addition of the aromatic sulfonates.

A short study was also conducted on the effect of the molarity of a buffer system on the yield of the reaction products.

4-4 Effects of Solute Concentration

The majority of the reactions occurring in aqueous solutions are indirect; that is, reactions in which the solvent concentration is so much greater than the concentration of the solute that the radiation reacts mainly with the solvent. The indirect reaction would naturally be expected in the present studies since the concentration of the water was about 55.6M, while the highest concentration of solute irradiated was 2.5×10^{-3}M, with the majority being irradiated at 2.5×10^{-4}M

concentrations. In general the difference between results of irradiations causing a direct or an indirect reaction is illustrated by Figure 4-1 where S is a solute that will react efficiently with free radicals (one having a rate constant of about 10^9 liters per mole-cm). In the direct reaction, as the concentration increases the degradation of the solute G(-S), for any fixed dose and dose rate, will also increase. In the indirect reaction, this effect will not be observed. After a certain solute concentration is reached, the solute concentration will no longer affect G(-S), since the radiation is reacting with the same amount of solvent in all cases. It is the reaction products from the solvent reacting with the solute that causes the degradation. Allen (12) indicates that this plateau occurs at a solute concentration of about 10^{-2} to 10^{-3}M.

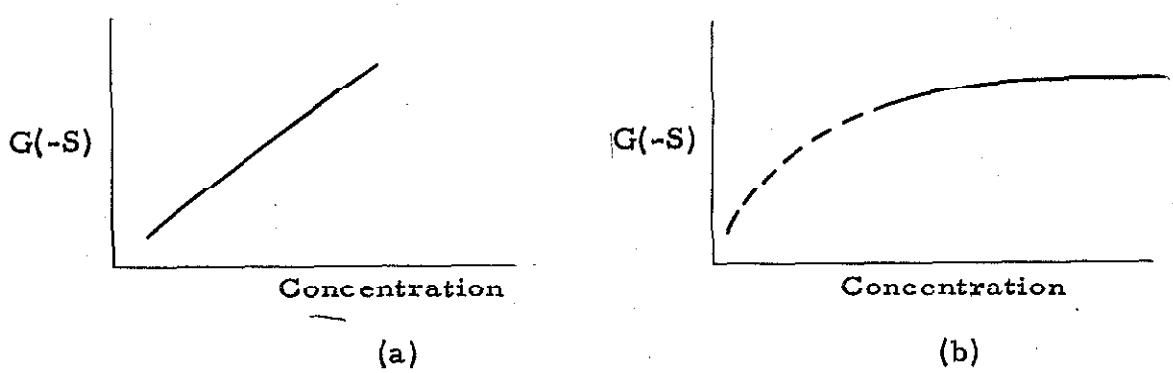


Figure 4-1. Effects of irradiation at a fixed dose on degradation of solute. (a) Direct action; (b) Indirect action.

The major portion of the samples irradiated were at 2.5×10^{-4}M concentrations. Limited studies were also conducted at higher concentrations of 1.0×10^{-3} and 2.5×10^{-3}M and at a lower concentration of 2.5×10^{-5}M. At 2.5×10^{-5}M it becomes very difficult to measure

the presence of reaction products since the original concentration is very low. The higher concentrations, while making analytical procedures much easier, are usually much higher than would be of interest in water and wastewater treatment.

4-5 Effects of Dissolved Oxygen

In Chapter 1 it was indicated that dissolved oxygen plays an important part in the irradiation of water, since it reacts with the hydrogen radical to give the perhydroxyl radical

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

This combination prevents the hydrogen radical from entering into reactions with other solutes that may be present. The effect of oxygen concentration was investigated using saturated solutions, corresponding to about 8.7 mg/l or 2.7×10^{-4}M, solutions of about 40 per cent saturation and deaerated solutions. The entire range is of interest since fresh-water treatment usually occurs with saturated or near saturated solutions while wastewater is frequently devoid of dissolved oxygen.

Deaeration of solutions of benzene- and p-toluenesulfonic acid was accomplished using nitrogen which was bubbled through a gas-washing bottle containing distilled water. Increasing the moisture content of the gas eliminated evaporation losses, thereby maintaining a constant solute concentration. The gas was then passed through a fritted glass diffuser into the solution. The oxygen concentration was measured at intervals until the desired per cent saturation was obtained. The solution was then siphoned or pipetted into the sample

bottles. The samples on which oxygen determinations were to be conducted were filled with the siphon to overflowing and then capped, making sure that no air bubbles were trapped within the bottle.

The ABS solutions could not be deaerated by the above procedure since excessive foaming would have resulted. These solutions were prepared by adding distilled water to the volumetric flasks, deaerating the water and then pipetting the detergent solution into the flask. The solutions were mixed carefully and siphoned into the bottles to be irradiated.

4-6 Analysis of Samples

After irradiation, samples were analyzed for dissolved oxygen immediately upon being returned to the laboratory. The measurement was made as soon as the bottle was opened. Any oxygen transferred to the sample as the bottle was first opened was removed when insertion of the probe caused the bottle to overflow. This analysis was immediately followed by the hydrogen peroxide determination since this compound would be expected to deteriorate. The remaining analyses were conducted as time permitted under the assumption that more stable compounds were involved.

CHAPTER 5

RESULTS AND DISCUSSION

5-1 Irradiation of Buffer Systems

The results from irradiation of aerated solutions of the three buffer systems are presented in Table 5-1 and Figures 5-1 and 5-2. The production of hydrogen peroxide was greatest in the pH 4.5 buffer system and lowest in the pH 8.2 system. Similarly oxygen depletion was most pronounced at pH 4.5 and least evident at pH 8.2. The oxygen depletion, after absorbing 29.6×10^{20} ev/l, and the initial observed yield of hydrogen peroxide, $G(H_2O_2)$, are listed below. Both decrease almost linearly with increasing pH.

pH	Oxygen Depletion	$G(H_2O_2)$
4.5	3.9×10^{-5}M	1.33
6.7	2.5×10^{-5}M	1.03
8.2	1.3×10^{-5}M	0.80

The oxygen depletion, resulting from the reactions

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (1\text{-}11)$$

was less than the hydrogen peroxide produced in all cases. Additional hydrogen peroxide arises from the decomposition of water.

Assuming that the buffer does not react with the free radicals, the system will be governed by reactions (1-5) through (1-11). In the case of the irradiation of aerated water it is possible to estimate the

Table 5-1

Irradiation of Aerated Buffer Systems

Sample No.	Absorbed Energy 10^{20} ev/l	H_2O_2 10^{-5}M	pH	D.O. 10^{-4}M	Buffer
7-30-0	0.0	0.00	6.70	-	0.01M KH_2PO_4
-1	5.9	1.26	6.73	-	0.01M K_2HPO_4
-2	11.8	2.06	6.70	-	
-3	17.7	2.77	6.70	-	
-4	23.6	3.45	6.71	-	
-5	29.5	4.01	6.71	-	
9-02-0	0.0	-	-	2.80	
-1	5.8	-	-	2.68	
-2	11.7	-	-	2.64	
-3	17.5	-	-	2.64	
-4	23.4	-	-	2.59	
-5	29.2	-	-	2.55	
7-30-6	0.0	0.00	4.50	-	0.10M KH_2PO_4
-7	5.9	1.52	4.47	-	
-8	11.8	2.46	4.44	-	
-9	17.7	3.34	4.45	-	
-10	23.6	4.23	4.44	-	
-11	29.5	4.86	4.42	-	

Table 5-1 (Cont'd)

Sample No.	Absorbed Energy 10^{20}ev/l	H_2O_2 10^{-5}M	pH	D.O. 10^{-4}M	Buffer
9-01-0	0.0	-	-	3.00	0.10M KH_2PO_4
-1	5.8	-	-	2.96	
-2	11.7	-	-	2.94	
-3	17.5	-	-	2.91	
-4	23.4	-	-	2.89	
-5	29.2	-	-	2.87	
7-31-6	0.0	0.00	8.21	-	0.10M $NaHCO_3$
-7	5.9	0.74	8.18	-	
-8	11.8	1.51	8.19	-	
-9	17.7	2.17	8.19	-	
-10	23.6	2.76	8.18	-	
-11	29.5	3.23	8.19	-	
9-03-0	0.0	-	-	3.00	
-1	5.8	-	-	2.96	
-2	11.7	-	-	2.94	
-3	17.5	-	-	2.91	
-4	23.4	-	-	2.89	
-5	29.2	-	-	2.87	

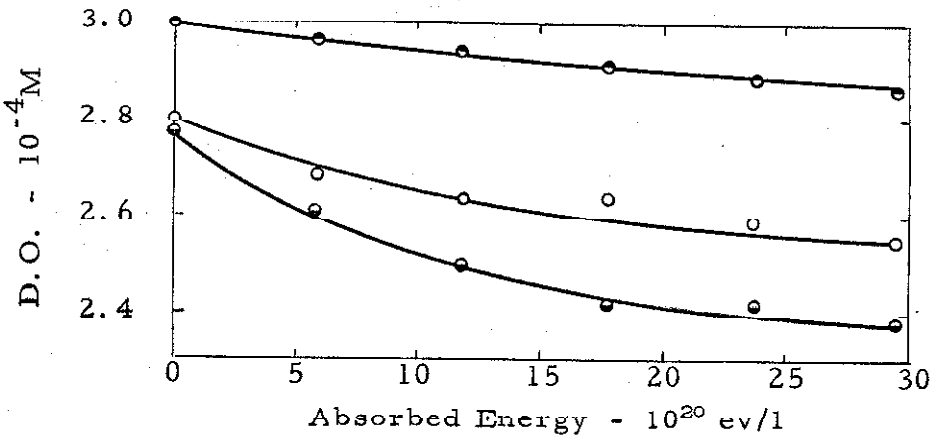


Figure 5-1. Dissolved oxygen depletion vs. absorbed energy, in buffered water.

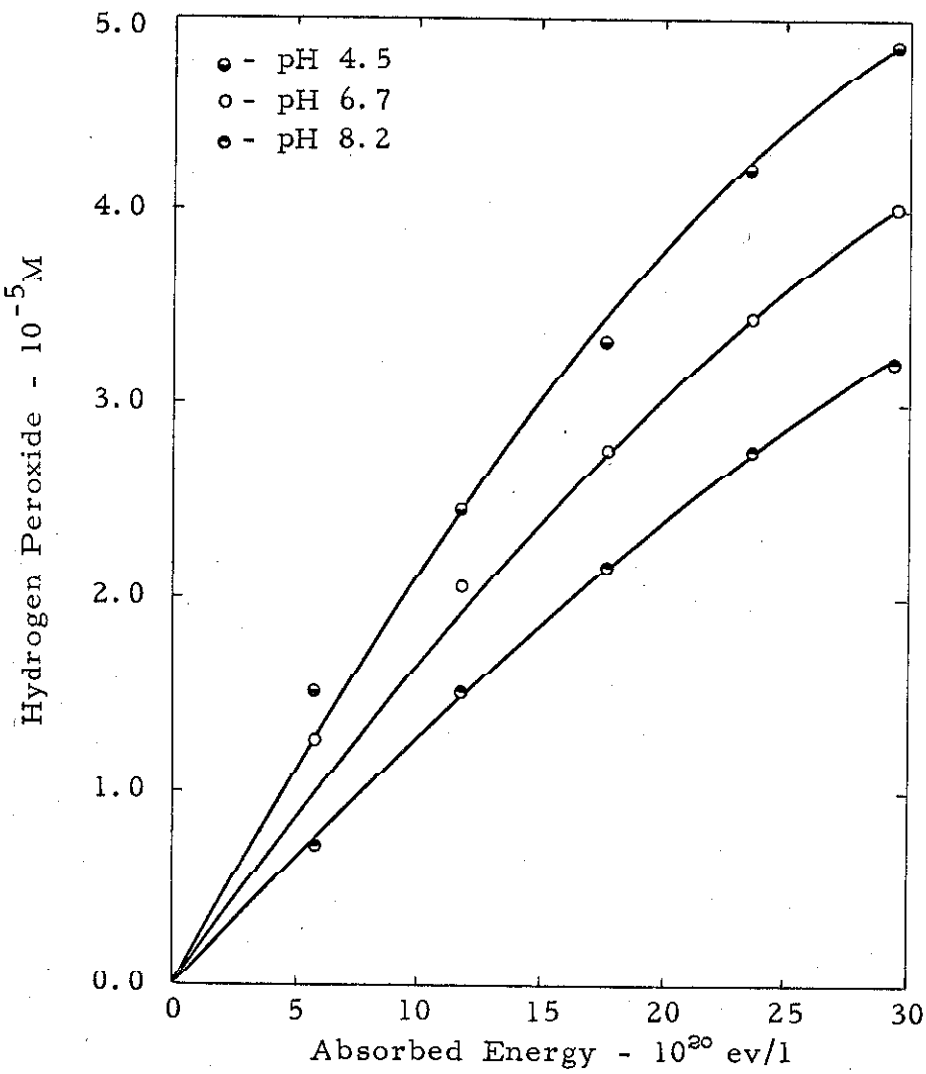


Figure 5-2. Hydrogen peroxide vs. absorbed energy, in buffered water.

initial $G(H_2O_2)$ on the assumption that in the early stages of irradiation the hydrogen radical reacts only with oxygen since the rate constant for this reaction is higher than for the reaction with hydrogen peroxide which is not present initially. It is also assumed that the hydroxyl radical reacts with both molecular hydrogen and hydrogen peroxide. Under these circumstances the reactions governing the system will be

$$H_2O \rightarrow H\cdot \text{ (or } e^-_{aq}), \cdot OH,\ H_2,\ H_2O_2 \qquad (1\text{-}5)$$

$$\cdot OH + H_2 \rightarrow H\cdot + H_2O \qquad (1\text{-}6)$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot \qquad (1\text{-}7)$$

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (1\text{-}11)$$

Since all free radicals produced must recombine to form stable products, it is possible to construct a material balance from the above relations. The number of molecules per 100 ev produced or depleted by a reaction will be indicated by that reaction number. Thus

$$G_{OH} = (6) + (7) \qquad (5\text{-}1)$$

Relation (5-1) indicates that the hydroxyl radicals produced from the decomposition of water, (1-5) will be used completely in reactions (1-6) and (1-7). In a similar manner for the hydrogen or reducing radical

$$G_H + (6) = (9) \tag{5-2}$$

and for $HO_2\cdot$

$$(7) + (9) = 2(11) \tag{5-3}$$

Another relationship exists since both molecular hydrogen and hydrogen peroxide are competing for the hydroxyl radicals in reactions (1-6) and (1-7). This equation is

$$\frac{k_6\,(H_2)}{k_7\,(H_2O_2)} = \frac{(6)}{(7)} \tag{5-4}$$

where k represents the rate constant for the reaction. The compounds in parentheses connote their molar concentrations. The observed yields should be

$$G(H_2O_2) = G_{H_2O_2} + (11) - (7) \tag{5-5}$$

and

$$G(H_2) = G_{H_2} - (6) \tag{5-6}$$

while the oxygen depletion will be given by

$$G(-O_2) = (9) - (11) \tag{5-7}$$

Substitution into equations (5-5), (5-6) and (5-7) yields

$$G(H_2O_2) = G_{H_2O_2} + \frac{G_H + G_{OH}}{2} - \frac{G_{OH}}{1 + \frac{k_6(H_2)}{k_7(H_2O_2)}} \tag{5-8}$$

$$G(H_2) = G_{H_2} - G_{OH} + \frac{G_{OH}}{1 + \frac{k_6(H_2)}{k_7(H_2O_2)}} \tag{5-9}$$

$$G(-O_2) = \frac{G_H + G_{OH}}{2} - \frac{G_{OH}}{1 + \frac{k_6(H_2)}{k_7(H_2O_2)}} \qquad (5\text{-}10)$$

Addition of equation (5-8) to (5-9) gives

$$G(H_2) + G(H_2O_2) = G_{H_2O_2} + G_{H_2} + \frac{G_H - G_{OH}}{2}$$

indicating that this sum is a constant. Allen (12) integrates the quotient $G(H_2O_2)/G(H_2)$ and finds that H_2O_2/H_2 is a constant, thus making $G(H_2O_2)$, $G(H_2)$ and $G(-O_2)$ constants. Using a reported value for k_6/k_7 of 1.0 he finds $H_2O_2/H_2 = 7.45$. If this value is substituted into equations (5-8) and (5-10) along with the following values for the yields of degradation products

$$G_H = 2.9 \qquad G_{H_2O_2} = 0.71$$

$$G_{OH} = 2.2 \qquad G_{H_2} = 0.45$$

$G(H_2O_2)$ and $G(-O_2)$ are found to be 1.3 and 0.6 molecules per 100 ev respectively. If the rate of oxygen depletion is constant, a depletion of 2.9×10^{-5}M would be expected for 29.6×10^{20} ev/l. This value is quite close to the 2.5×10^{-5}M that was found for the depletion at pH 6.7.

Although the data are not at great variance with this simple model, the model does not explain the initial variation in $G(H_2O_2)$ apparently attributable to pH. This variation might result from several different effects which will be presented although not examined further:

(a) The high dose rate, from the 3400-curie source, may have caused absorbed doses that were too large for valid application of this simple model, even with short irradiation times.

(b) Little is known as to the variation of k_6/k_7 with pH or other effects.

(c) The yields of the radicals and the molecular degradation products as well as the form of the reducing radicals are known to change with pH, and thus could be expected to show some variation over the range from pH 4.5 to pH 8.2.

(d) The assumption has been made that the buffer compound will not enter into the reaction. Jortner, et al. (60), however, have indicated that the solvated electron will react with dihydrogen phosphate yielding the hydrogen radical by

$$e^-_{aq} + H_2PO_4^- \rightarrow H + HPO_4^= \qquad (5\text{-}11)$$

Hasselstrom and Henry (44) observed the formation of oxalic acid from the irradiation of a 0.1 per cent solution of sodium bicarbonate. Although there was no indication as to whether this was the result of a direct or an indirect reaction, the degradation of the bicarbonate ion by indirect action would require additional reactions in the model. This has been studied more closely in the presence of benzenesulfonic acid. The results, which indicate buffer effects from the sodium bicarbonate, are discussed further in Section 5-2-2.

(e) Loeff and Stein (21) indicate that the perhydroxyl radical is affected by changes in pH. They indicate its pK value to be approximately 4. Therefore the equilibrium

$$HO_2\cdot \rightleftharpoons H^+ + O_2^- \qquad (5\text{-}12)$$

may affect the yield of reaction (1-11) if the possibility of an electron transfer process such as

$$O_2^- + \cdot OH \rightarrow O_2 + OH^- \qquad (5\text{-}13)$$

is considered. This equilibrium could account for a difference in results between pH 4.5 and the higher values, but would not be expected to contribute to the differences observed between pH 6.7 and 8.2.

5-2 Irradiation of Benzenesulfonic Acid Solutions

5-2-1 Aerated Solutions at Different pH Values

Benzenesulfonic acid was irradiated in the three buffer systems discussed earlier. The majority of the investigation was conducted using a 2.5×10^{-4}M solute concentration. Table 5-2 and Figures 5-3 and 5-4 present the data on hydrogen peroxide production and oxygen depletion in aerated solutions. In each case the addition of the solute has resulted in a small increase in the production of hydrogen peroxide over that observed in the buffered solutions without solute present. This increase in hydrogen peroxide production was accompanied by a much larger increase in oxygen utilization which was not observed in the buffer solutions and was not accounted for as hydrogen peroxide. Below, the oxygen depletion in the buffer system is compared to that of the benzenesulfonic acid solutions for an absorbed dose of

Table 5-2

Irradiation of Aerated Solutions of

2.5×10^{-4}M Benzenesulfonic Acid

Sample No.	Absorbed Energy 10^{20} ev/l	H_2O_2 10^{-5}M	pH	D.O. 10^{-4}M	Buffer
7-27-0	0.0	0.00	4.53	-	0.10M KH_2PO_4
-1	5.9	1.73	4.52	-	
-2	11.8	3.29	4.53	-	
-3	17.7	4.68	4.51	-	
-4	23.6	5.30	4.51	-	
-5	29.5	6.23	4.51	-	
9-01-10	0.0	-	-	2.72	
-11	5.9	-	-	2.49	
-12	11.7	-	-	2.17	
-13	17.5	-	-	1.79	
-14	23.4	-	-	1.56	
-15	29.3	-	-	1.17	
7-29-0	0.0	0.00	6.85	-	0.01M KH_2PO_4
-1	5.9	1.52	6.85	-	0.01M K_2HPO_4
-2	11.8	2.53	6.85	-	
-3	17.7	3.10	6.85	-	
-4	23.6	3.79	6.85	-	
-5	29.5	4.15	6.85	-	

Table 5-2 (Cont'd)

Sample No.	Absorbed Energy 10^{20}ev/l	H_2O_2 10^{-5}M	pH	D.O. 10^{-4}M	Buffer
9-01-20	0.0	-	-	2.72	0.01M K_2HPO_4
-21	5.9	-	-	2.49	0.01M KH_2PO_4
-22	11.7	-	-	2.17	
-23	17.5	-	-	1.85	
-24	23.4	-	-	1.53	
-25	29.3	-	-	1.11	
7-31-0	0.0	0.00	8.14	-	0.1M $NaHCO_3$
-1	5.9	1.02	8.20	-	
-2	11.8	1.86	8.12	-	
-3	17.7	2.70	8.12	-	
-4	23.6	3.66	8.12	-	
-5	29.5	4.35	8.15	-	
9-01-30	0.0	-	-	2.70	
-31	5.9	-	-	2.50	
-32	11.7	-	-	2.33	
-33	17.5	-	-	2.14	
-34	23.4	-	-	2.02	
-35	29.3	-	-	1.76	
11-13-0	0.0	0.00	-	2.90	
-1	5.7	1.08	-	2.95	
-2	11.4	1.90	-	2.81	
-3	17.1	2.85	-	2.55	
-4	22.8	3.66	-	2.31	
-5	28.5	4.35	-	2.09	

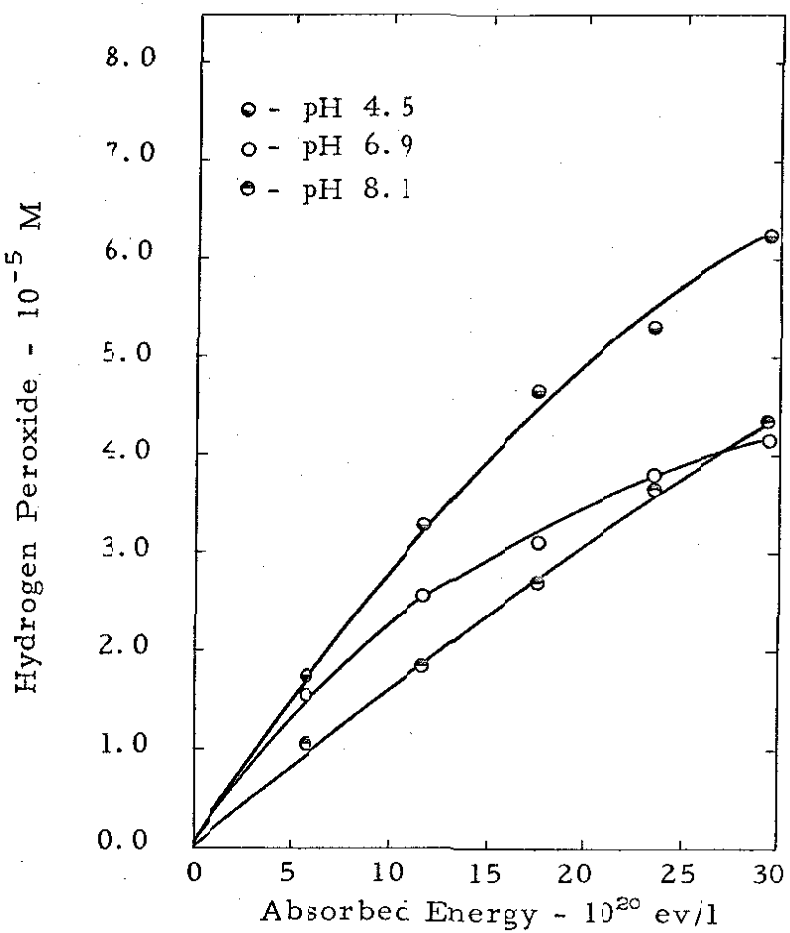


Figure 5-3. Hydrogen peroxide production in aerated benzenesulfonic acid solutions.

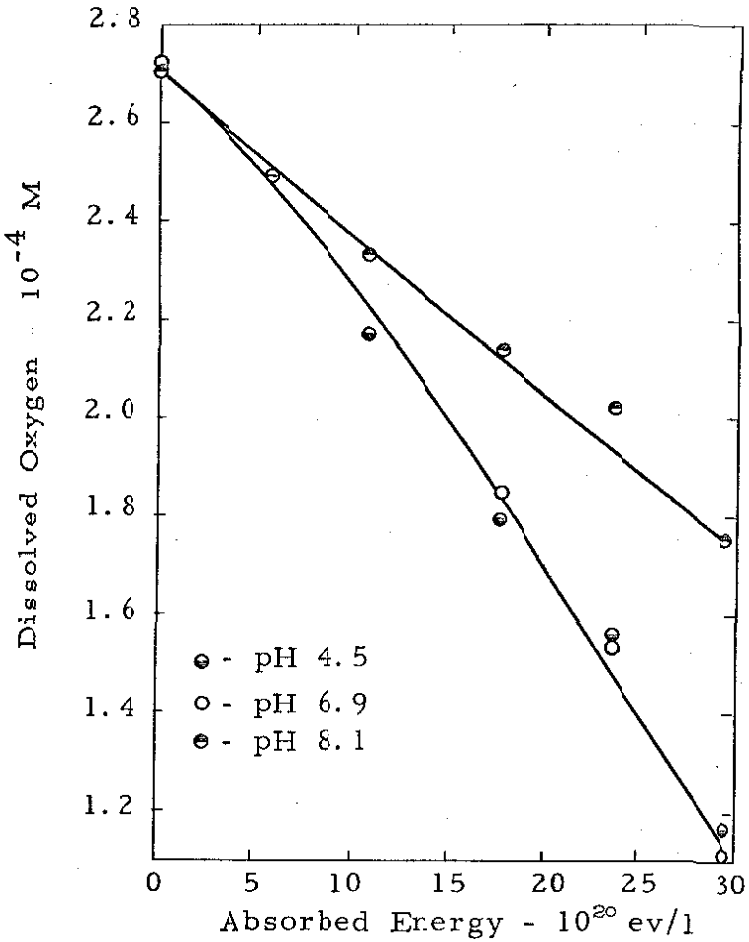


Figure 5-4. Dissolved oxygen depletion in benzenesulfonic acid solutions.

approximately 29.5×10^{20} ev/l.

pH	Oxygen depletion, 10^{-5}M Buffer only	Buffer + Solute	$G(-O_2)$
4.5	3.9	15.5	3.2
6.7	2.5	16.1	3.2
8.1	1.3	8.9	2.0

The average $G(-O_2)$ was calculated using the curves in Figure 5-4. The discussion of possible reaction products in Chapter 2 anticipated the utilization of oxygen in the formation of aldehydes associated with the ring opening in reaction (2-5). In that reaction one mole of oxygen would result in one mole of aldehyde, but would not be expected to account for such a large oxygen depletion. The other source of oxygen depletion would be expected to occur in the production of hydrogen peroxide by

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (1\text{-}11)$$

In these reactions the oxygen loss can be accounted for in the formation of hydrogen peroxide where a material balance would indicate

$$G(-O_2) = (9) - (11) \qquad (5\text{-}14)$$

Even on the basis of a G_H as high as the 3.6 indicated by Allen (56), $G(-O_2)$ would only be 0.5 G_H, or 1.8 molecules per 100 ev, much less than observed. Even with an aldehyde yield of 0.8, as reported by Loeff and Stein (21), $G(-O_2)$ would only be about 2.6 molecules

per 100 ev. This comparison would tend to indicate that some step or steps in the reaction mechanism are causing the reduction of oxygen, possibly to water. Figure 5-4 also indicates that in the case of the phosphate buffer systems the rate of oxygen depletion becomes greater as the oxygen concentration is lowered. This fact is not observed with the bicarbonate buffer system, which gives the appearance of undergoing a linear oxygen depletion during irradiation.

In Figure 5-3 the high pH solution again indicates a relationship that is almost linear. The other systems, however, show a decreasing rate of hydrogen peroxide production and appear to be leveling off to a maximum value. These figures thus indicate that molecular oxygen is being withdrawn from the system at a steadily increasing rate. In fact, Phung and Burton (17) on irradiating benzene found $G(-O_2)$ to be 5.3 in aerated solutions. Investigations by others, cited earlier (26-31), on the irradiation of substituted benzenes, did not follow the progress of peroxide formation or oxygen depletion closely. These studies were primarily interested in identifying and measuring the formation of degradation products and as such only proposed reaction mechanisms to account for the formation of the products examined.

The sulfate determination indicated the presence of this anion in aerated solutions that had been irradiated, while none was found in deaerated solutions. The data are presented in Table 5-3 and Figure 5-5. The absorbance of the deaerated samples actually showed a slight decrease in turbidity with absorbed energy,

Table 5-3

Sulfate Production from Irradiated

2.5×10^{-4}M Benzenesulfonic Acid Solutions

Absorbed Energy 10^{20} ev/l	Sulfate Production pH 4.5 10^{-5}M	pH 6.9 10^{-5}M	pH 8.1 10^{-5}M
5.9	0.5	0.2	0.0
11.8	0.9	0.6	0.0
17.7	1.2	1.0	0.9
23.6	1.6	1.3	1.0
29.5	3.1	2.1	3.2

indicating the decrease in benzenesulfonic acid by a decrease in the amount of barium salt precipitating. These data would seem to indicate that desulfonation is due to the perhydroxyl radical rather than the hydroxyl radical, since the former would be present only in aerated solutions as a result of reaction (1-9), while the latter is formed as a primary product in the decomposition of water. Under these circumstances the reaction could be

$$PhSO_3^- + HO_2\cdot \rightarrow PhO\cdot + HSO_4^- \qquad (5\text{-}15)$$

where Ph represents the phenyl radical. This mechanism, which accounts for the formation of the sulfate ion, does not involve a change in the oxidation state of the sulfur from +6. Figure 5-5 indicates an increasing rate of sulfate production, similar to that observed in the case of oxygen depletion. This relationship will be discussed further in Section 5-2-3. Again the results in the

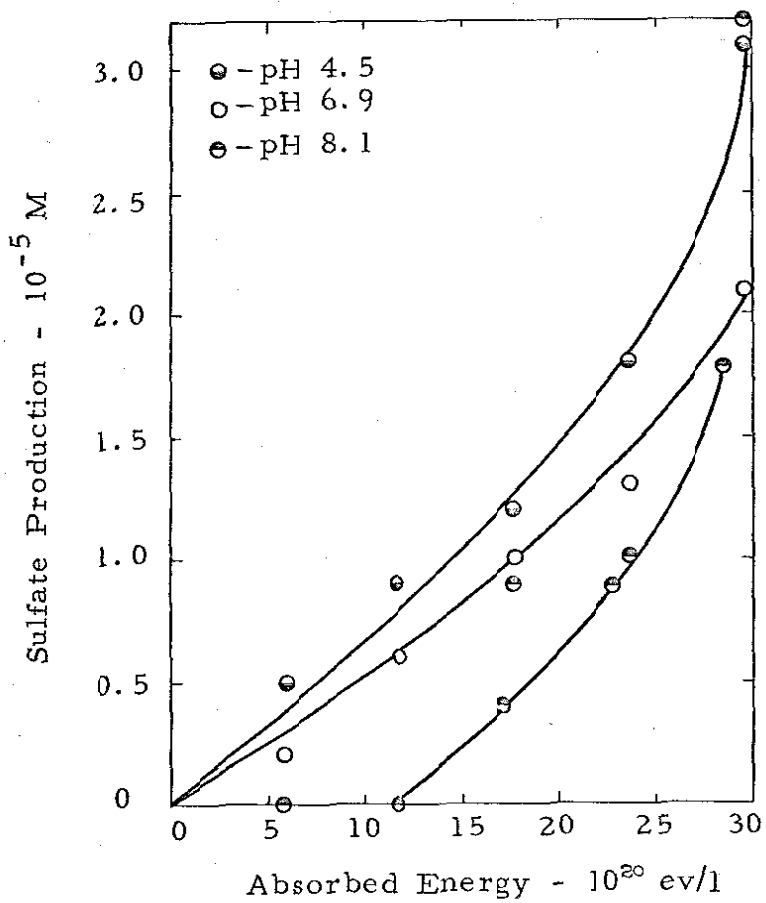


Figure 5-5. Sulfate production vs. absorbed energy in solutions of benzenesulfonic acid.

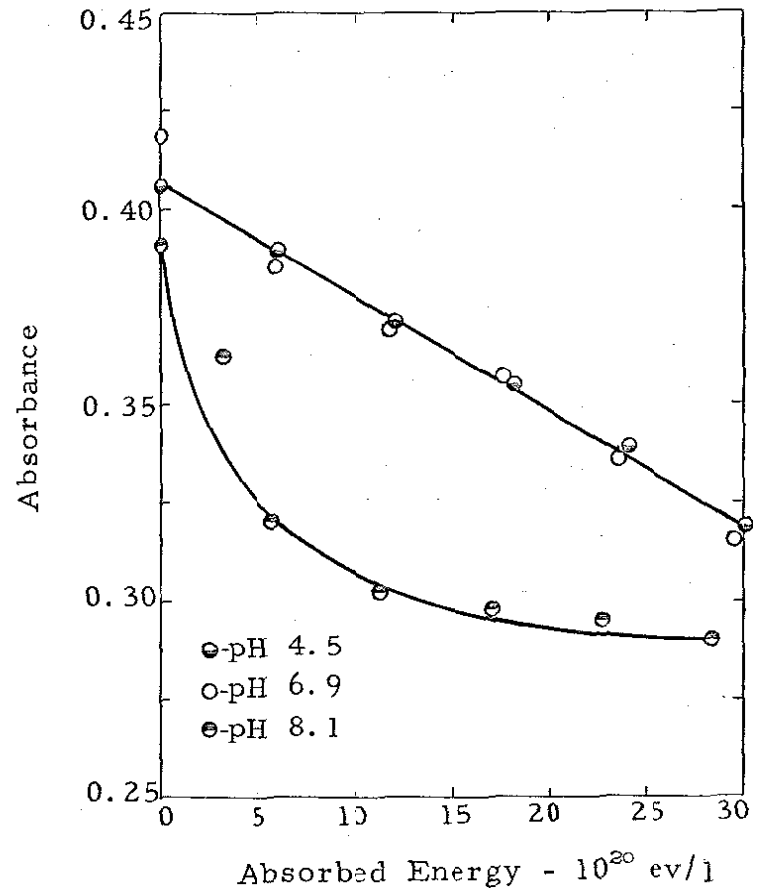


Figure 5-6. Absorbance at 216 mμ vs. absorbed energy in 2.5×10^{-4}M solutions of benzenesulfonic acid.

bicarbonate system are found to differ with the other buffer systems, with no sulfate production being indicated until after the system had absorbed a dose of over 11×10^{20} ev/l.

This difference in the bicarbonate system is again observed in Figure 5-6, which indicates the behavior of the 216 mμ benzenesulfonate absorption peak. The decreases in the absorption peak at the two lower pH values are in good agreement, but completely different from that observed in the bicarbonate system. This decrease, which appears linear in the phosphate systems, is not directly proportional to the amount of benzenesulfonate present, since the reaction products formed by the addition of a hydroxyl group to the benzene ring will also absorb at this wavelength. Thus what is actually being measured is the difference between the absorbance of the reactant and the products.

The observed change in absorbance would not be expected to be very great since benzenesulfonic acid has a molar absorption coefficient of 8300 liters per mole-cm at 216 mμ compared to 7000 and 4800 liters per mole-cm for the para- and ortho-phenolsulfonic acids. If all the reactant degraded by hydroxylation alone, the absorbance would not be reduced by 50 per cent at this wavelength. The linear decrease in absorbance does indicate that the rate of degradation of the reactant is linear or very nearly linear.

The ultraviolet spectra of a series of samples, between 209 and 300 mμ, are illustrated in Figure 5-7. These samples, irradiated at pH 6.7, and diluted to bring the spectra within an absorbance range of one unit, show that below approximately 222 mμ the

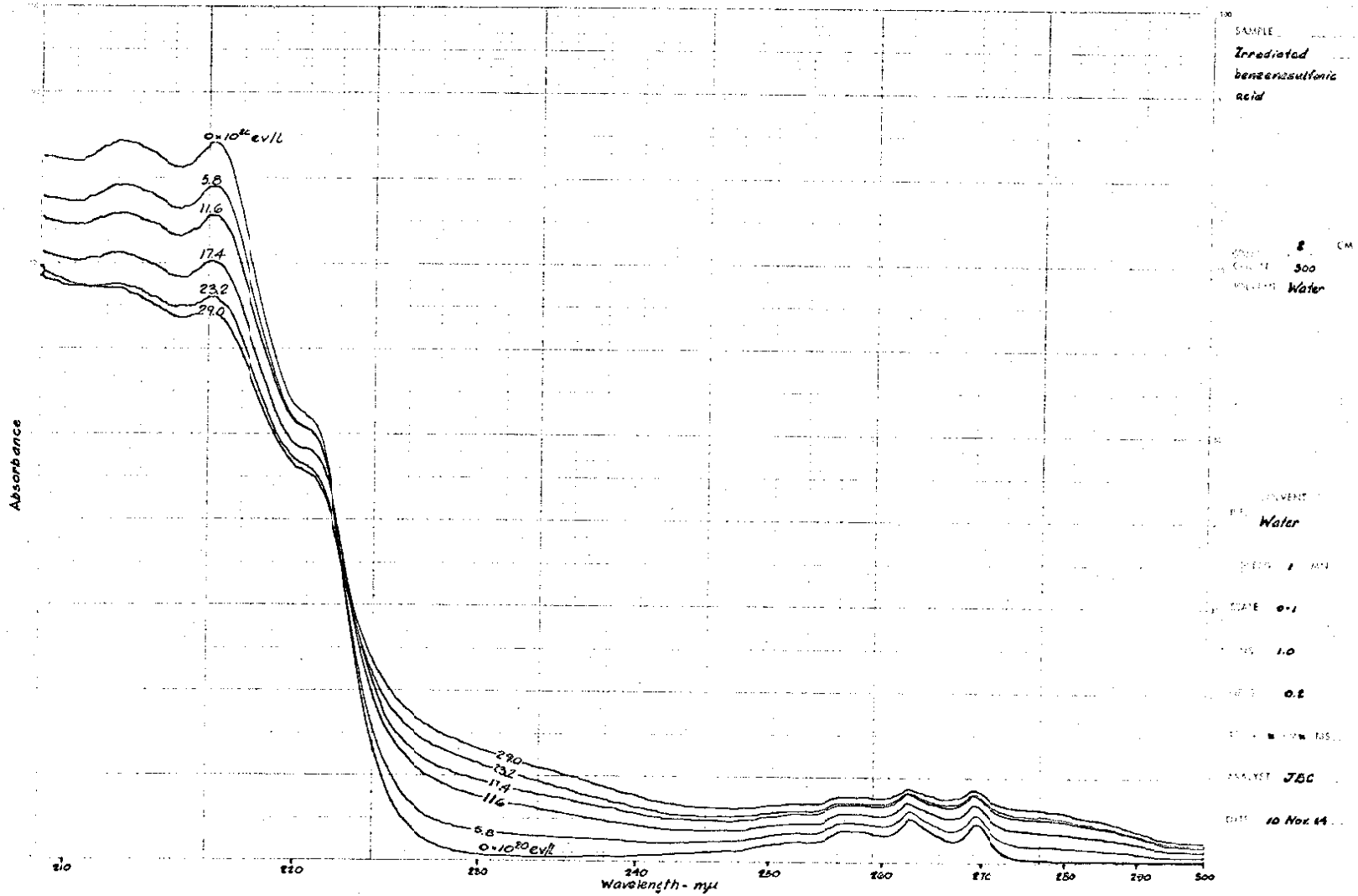


Figure 5-7. Variation in the ultraviolet spectrum of benzenesulfonic acid solutions irradiated at pH 6.9.

absorbance decreases while above this wavelength the absorbance is increasing. A major part of this effect results from the formation of the enols which have much higher absorbances at the longer wavelengths than does benzenesulfonic acid. This effect is more obvious in Figure 5-8, a series of undiluted samples, also presented as a function of absorbed energy. The influence of ring opening on these spectra cannot be estimated since sulfonated mucondialdehydes could not be synthesized.

The peaks being formed at approximately 280 mμ are the minor peaks of the m- and o-phenolsulfonic acids while the increases in the vicinity of 230 mμ would result from the formation of the p-phenolsulfonic acids. The increase in absorption at 280 mμ gives the appearance of being linear. No information can be obtained from the major peaks of the m- and o-phenolsulfonic acids since these fall in the same region as the major peak of the benzenesulfonic acid.

Examination of the data resulting from the two phenol tests indicated that the amount of absorbance that would be expected to occur from phenol, if this were formed when the benzenesulfonate ion was desulfonated, was not observed. Drying and reconstituting samples to volatilize the phenol did not show a decrease in the ultraviolet absorption spectra resulting from the removal of this product. Reexamination of the analytical procedure, for the purpose of determining if the presence of an inorganic salt such as potassium phosphate would reduce the absorbance of a hydroxyl group, provided no additional information. Extraction of an

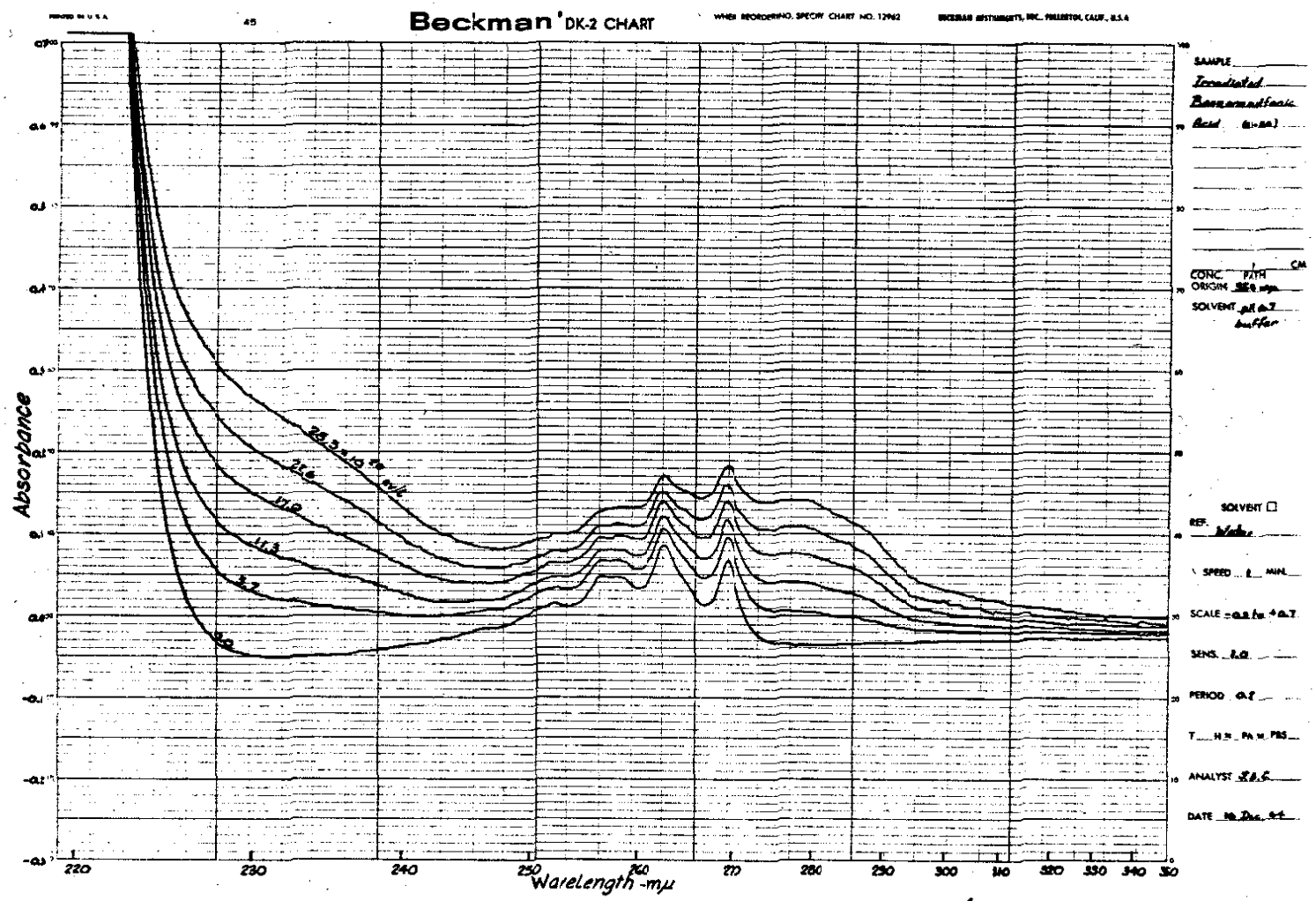


Figure 5-8. Variation in the ultraviolet spectrum of 2.5×10^{-4}M benzenesulfonic acid as a function of absorbed energy.

irradiated sample with ether to concentrate any phenols that might be present did not yield the ultraviolet spectrum of phenol when examined spectrophotometrically. On the basis of these facts it is concluded that phenol, if formed at all, is certainly not produced in an amount equivalent to that of the sulfates formed. Therefore, the production of p-phenolsulfonic acid indicated in Table 5-4 is based on the assumption that no phenol is present and the amount of the dihydroxy compounds is negligible, which may not necessarily be the case.

The sum of the m- and o-phenolsulfonic acids, also presented in Table 5-4, are conservative figures. These figures were arrived at by subtracting out the effect of the p-phenolsulfonic acids, as calculated from the phenol determination, and then using the absorption coefficient of the ortho isomer. Since there was no

Table 5-4

Phenolsulfonic Acid Isomers from Irradiation of

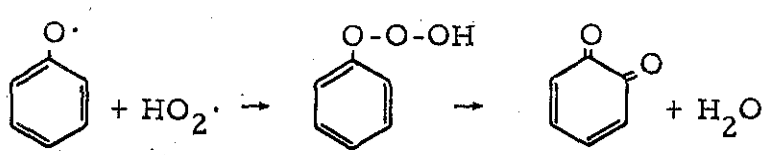
2.5×10^{-4}M Benzenesulfonic Acid Solutions

Absorbed Energy 10^{20} ev/l	pH 4.5 o+m 10^{-5}M	pH 4.5 p 10^{-5}M	pH 6.9 o+m 10^{-5}M	pH 6.9 p 10^{-5}M	pH 8.1 o+m 10^{-5}M	pH 8.1 p 10^{-5}M
5.9	0.31	0.75	0.47	1.06	0.12	0.28
11.8	0.55	1.46	0.76	2.34	0.23	0.28
17.7	0.71	2.52	1.04	3.51	0.33	0.65
23.6	0.82	2.91	1.35	4.52	0.40	0.75
29.5	0.97	3.62	1.37	6.24	0.47	0.93

practical method for separating the ortho from the meta isomer, the use of this coefficient which is higher than that of the meta isomer gives the most conservative estimate. Again, the assumption of negligible phenols and dihydroxy compounds has been made.

In the three buffer systems the yield of the para isomer is larger than the sum of the ortho and meta isomers and is approximately linear with dose. The G values for the p-phenolsulfonic acid, in order of increasing pH were found to be 0.7, 1.2 and 0.2 molecules per 100 ev, respectively. The increase in the ortho and meta isomers was not linear with dose, but decreased slightly as the absorbed energy increased. The initial G values for the sum of these isomers, again in order of increasing pH, were 0.3, 0.5 and 0.14 respectively.

Analyses for the formation of aldehydes (see Section 3-12) revealed that the shape of the spectra more closely resembled that of p-benzoquinone than the 2,4-hexadienal. Admittedly a sample of the exact aldehyde that was expected (a sulfonated mucondialdehyde) was not available, but, in view of the fact that phenol was not found in the quantity anticipated, it would appear that the PhO· radical proposed to arise from reaction (5-15) may yield a quinone. The reaction, proposed by Stein and Weiss (28) in their study of the irradiation of phenol is repeated below.



(1-34)

Reaction (1-34) could account for the formation of either o- or p-benzoquinone and would also account for the disappearance of additional quantities of oxygen. Stein and Weiss found that in acid solution the ortho isomer was produced in place of the para isomer and catechol. This factor could account for changes in the spectra observed in the different buffer systems, with the closest agreement being at the highest pH, where the para, rather than the ortho isomer, would be formed. Unfortunately, o-quinone is not available commercially, so this hypothesis could not be examined more closely.

The absorbance peak of the 2,4-dinitrophenylhydrazones from the alkaline samples and from the p-benzoquinones, occurred at 460 mμ. Loeff and Stein (21) reported the p-benzoquinone peak at 470 mμ, although they used p-nitro- rather than 2,4-dinitrophenylhydrazine. In irradiated acid solutions, the hydrazone peak shifts from 510 to 490 mμ with increasing irradiation time. They also report the o-quinone peak occurring at 510 mμ. In the neutral solutions the predominant peak was at 490 mμ with the spectra appearing to be a compromise of those observed in the acid and alkaline solutions.

On the basis of the molar absorption coefficient of 8900 liters per mole-cm for the para isomer, the yield in alkaline solutions would be

Abs. Energy 10^{20} ev/l	p-Benzoquinone 10^{-5}M
5.7	0.4
11.4	0.6
17.1	0.9
22.8	1.2
28.5	1.3

This yield is slightly higher than the sulfate production, but in view of the fact that ring opening was also hypothesized, higher values should be expected. The absorbance in the acid solutions was greater than in the neutral solutions, with both being higher than the alkaline solutions. The sulfate production also followed this pattern as has the reported production of mucondialdehyde (21). A higher absorption coefficient for the hydrazone of the o-quinone could also have caused the observed increase.

In an attempt to extract irradiation products into an organic solvent, a series of samples were dried over a steam bath. Examination of the residue indicated that irradiation caused the solute to take on a brownish color which increased in intensity with the amount of absorbed energy. Pursuing this phenomenon further, it was found that the changes observed in the ultraviolet spectrum of benzenesulfonic acid in Figures 5-7 and 5-8 could also be brought about by the addition of hydrogen peroxide to a solution containing benzenesulfonic acid. This action also resulted in the formation of a brown residue. Hookway and Selton (45) have found that benzene-, p-toluene-, and other sulfonic acids would decompose in the presence of hydrogen peroxide, without the addition of metallic ions, producing sulfuric acid, carboxylic acid and carbon dioxide. Merz and Waters (46) oxidized benzenesulfonic acid with hydrogen peroxide in the presence of ferrous ions and were able to demonstrate the formation of phenolsulfonate, by bromination. Bottomly and Blackman (47) oxidized a wide variety of aromatics to CO_2 and water with hydrogen peroxide in hot, dilute, aqueous

solutions in the presence of either cupric or ferric ions. When heated to 90° C, the solution darkened to a dense brown color with the evolution of carbon dioxide and oxygen. With this treatment, benzene was converted into graphitic acid possibly by addition, or polymerization of aromatic radicals, into a two-dimensional structure between which oxygen atoms are trapped.

The production of a form of graphitic acid could explain the increased oxygen consumption, brown residue and increase in absorbance at the wavelengths longer than 300 mμ.

5-2-2 Effect of Sodium Bicarbonate Buffer

A short study was conducted on the effects of varying the concentration of the sodium bicarbonate buffer system, since the changes observed with this system appear to be significantly different from those observed in the phosphate systems. Some of the effects of decreasing the concentration of the buffer, while maintaining the concentration of benzenesulfonic acid constant at 2.5×10^{-4}M are shown in Table 5-5. All samples were irradiated to an absorbed dose of 23.4×10^{20} ev/l. A marked effect can be

Table 5-5

Effect of $NaHCO_3$ Buffer Concentration on 2.5×10^{-4}M Benzenesulfonic Acid Solutions

$NaHCO_3$ M	Initial pH	H_2O_2 10^{-5}M	$\Delta D.O.$ 10^{-4}M	p-$HOC_6H_4SO_3^-$ 10^{-5}M
0.10	8.2	2.9	-0.7	0.5
0.05	8.2	3.6	-0.8	1.2
0.01	8.1	3.8	-1.2	2.1
0.001	7.7	4.2	-1.3	2.6

observed as the buffer concentration is lowered; the hydrogen peroxide production increases, oxygen depletion increases and the yield of p-phenolsulfonic acid also increases. At the low bicarbonate concentrations, the pH does not reach the 8.2 that can be obtained with the higher buffer concentrations.

A semi-logarithmic plot of these data suggests that the changes in the above parameters could be considered to vary exponentially with buffer concentration. Additional information would be necessary before this relationship could be shown definitely to be the case. However, in view of the findings of Hasselstrom and Henry (44) that radiation does affect sodium bicarbonate, it appears that there is a competition between this buffer and the benzenesulfonic acid for the free radicals. Since the buffer concentration was several orders of magnitude higher in the first studies discussed, the effects being observed were those of a predominantly sodium bicarbonate system. In this system, the hydrogen peroxide being formed and the oxygen depletion were most probably a result of the reactions leading to the formation of oxalic acid, rather than those of interest here. Thus, as the sodium bicarbonate concentration decreased the system was moving along a line similar to that of Figure 4-1(b) which has the form

$$G(-S) = G(-So)\,(1-e^{-k(S)}) \qquad (5\text{-}16)$$

In this equation G(-So) would be the maximum degradation rate at some solute concentration (So), above which additional solute has no effect.

Since there is certainly not enough information to substantiate the reactions occurring in the sodium bicarbonate system, other data have not been corrected for this effect. However, if the data are extrapolated to zero buffer concentration, the following extrapolated values are in much closer agreement with results obtained at the other pH values.

pH	H_2O_2 10^{-5}M	ΔD.O. 10^{-4}M	p-$HOC_6H_4SO_3^-$ 10^{-5}M
8.2	4.25	-1.30	2.70
6.7	3.79	-1.19	4.50
4.5	5.30	-1.16	2.91

5-2-3 Effect of Dissolved Oxygen

The effect of the variation in dissolved oxygen was examined at pH 6.9 using 2.5×10^{-4}M benzenesulfonic acid solutions at three different initial oxygen concentrations. The concentrations corresponded to fully saturated, 40 per cent saturated, and deaerated solutions. The results of irradiation are presented in Table 5-6 and the hydrogen peroxide production and absorbance at 216 mμ are plotted in Figures 5-9 and 5-10 respectively. In Figure 5-9 the hydrogen peroxide production reaches a maximum in both the 40 per cent and the deaerated solutions. This point corresponds to $G(H_2O_2)$ equal to zero. The effect of oxygen concentration is clearly seen in the figure. In order for the hydrogen peroxide yield to reach a maximum, a reaction must be in progress that is consuming the compound at a rate that is greater than its yield of 0.71 molecules

Table 5-6

Dissolved Oxygen Effect on Irradiation

of Benzenesulfonic Acid at pH 6.9

D.O. 10^{-4}M	Absorbed Energy 10^{20} ev/l	H_2O_2 10^{-5}M	$SO_4^=$ 10^{-5}M	Absorbance 216 mμ	Absorbance 500 mμ
2.72	0.0	0.00	0.0	.418	.000
2.49	5.9	1.52	0.5	.385	.288
2.17	11.8	2.53	0.9	.369	.478
1.85	17.7	3.10	1.2	.357	.665
1.53	23.6	3.79	1.6	.336	.857
1.11	29.5	4.15	2.1	.316	.916
1.06	0.0	0.00	0.0	.440	.000
.65	5.8	1.04	0.8	.383	.240
.22	11.6	1.38	1.6	.376	.440
.00	17.5	1.42	3.2	.373	.531
.00	23.3	1.11	3.6	.360	.600
.00	29.1	0.96	-	.304	.558
.09	0.0	0.00	0.0	.418	.000
.00	5.8	0.31	0.0	.377	.066
.00	11.6	0.31	0.0	.350	.100
.00	17.5	0.22	0.0	.310	.134
.00	23.3	0.15	0.0	.285	.165
.00	29.1	0.08	0.0	.255	.205

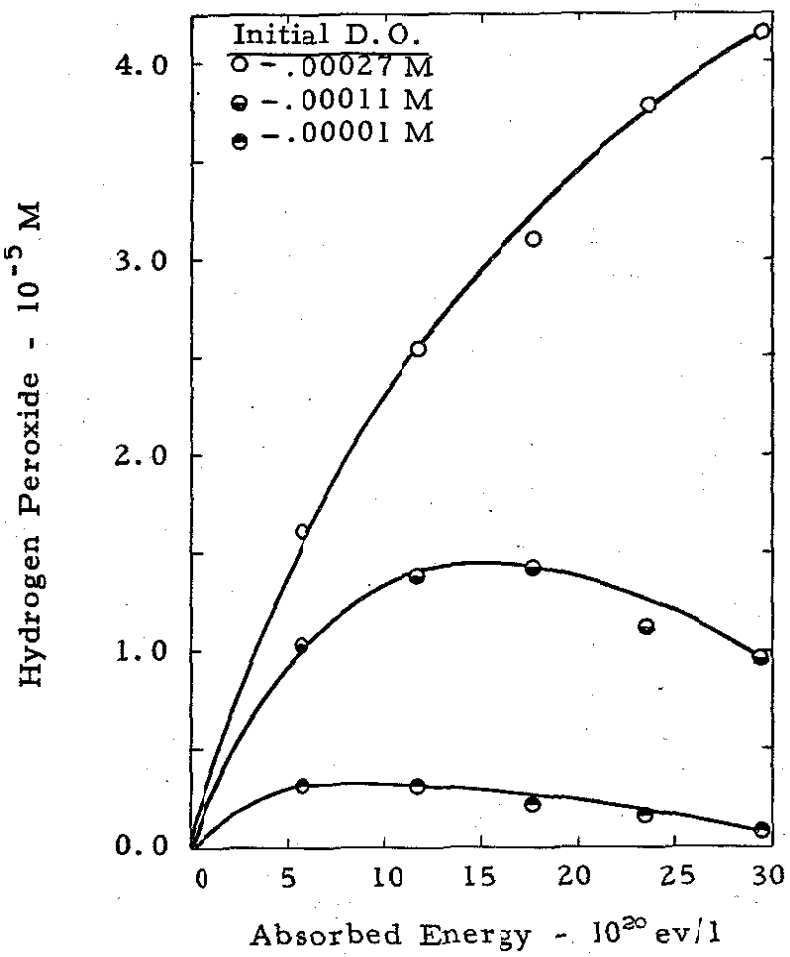


Figure 5-9. Hydrogen peroxide vs. absorbed energy in pH 6.9 solutions of benzenesulfonic acid.

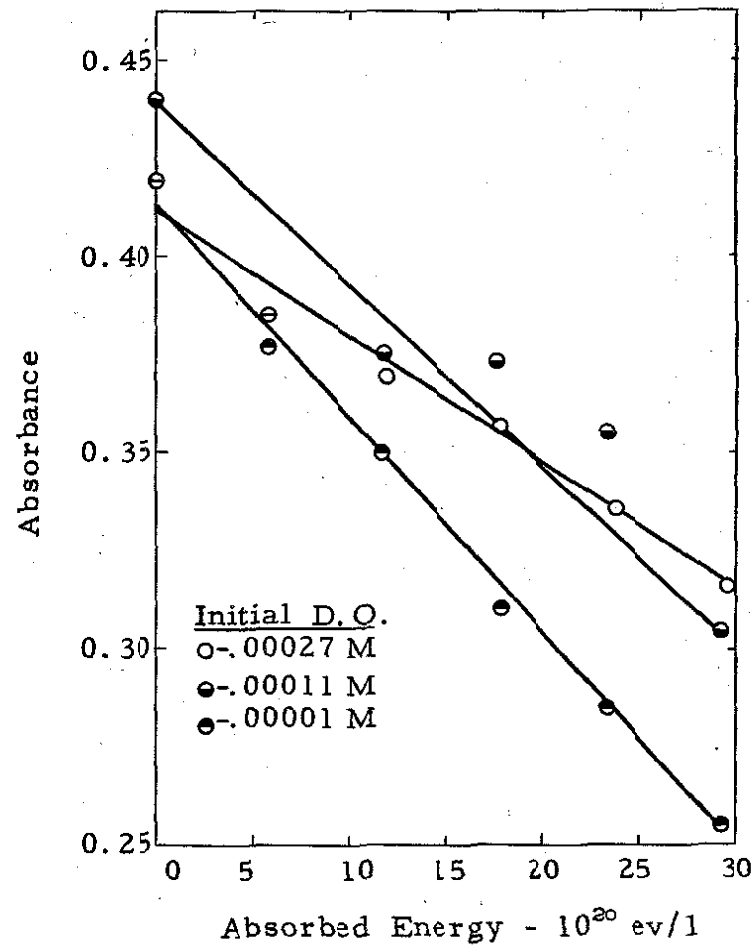


Figure 5-10. Absorbance at 216 mμ vs. absorbed energy in pH 6.9 solutions of 2.5×10^{-4}M benzenesulfonic acid.

per 100 ev, from the decomposition of water. This reaction would be

$$H\cdot + H_2O_2 \rightarrow H_2O + \cdot OH \qquad (1\text{-}8)$$

In Figure 5-9, the comparison of the reduction in absorbance between aerated and deaerated solutions indicates that the rate of decrease is greater in the deaerated solutions, although the results from the 40 per cent samples were quite erratic. Several different factors could account for this decrease in absorbance which still appears quite linear. Assuming that the products and the reactant obey Beer's Law, then the absorbance would be

$$A = a'bc' + a''bc'' \qquad (5\text{-}17)$$

where a' is the absorption coefficient for the reactant and a'' is some average absorption coefficient for the reaction products. If the cell length, b, is considered to be 1 cm, then the rate of change of the absorbance with absorbed energy would be

$$\frac{dA}{dE} = a'\frac{dc'}{dE} + a''\frac{dc''}{dE} \qquad (5\text{-}18)$$

On examining equation (5-18) term by term, it is seen that a' will remain constant while $\frac{dc'}{dE}$, which is proportional to G(-BH), BH symbolizing the solute, may change. This change can occur as a result of the absence of the perhydroxyl radical, since the hydroxyl radical will still react with the solute by

$$BH + \cdot OH \rightarrow B\cdot + H_2O \qquad (5\text{-}19)$$

The hydrogen radical, however, must vanish via another mechanism.

The reaction

$$BH + H\cdot \rightarrow B\cdot + H_2 \qquad (5\text{-}20)$$

is rejected, as Phung and Burton (17) observed that molecular hydrogen production was not increased by irradiation of deaerated benzene solutions. The decrease in the production of hydrogen peroxide, however, indicates that some of the hydrogen radicals react with hydrogen peroxide while still others could react with the phenylsulfonate radical, returning them to their original state. The overall effect should be to decrease $\frac{dc'}{dE}$ and to also decrease phenolsulfonate production.

In addition to the phenylsulfonate radical entering reaction (2-2) to produce the phenolsulfonate, it will also be expected to dimerize in deaerated solutions

$$B\cdot + B\cdot \rightarrow BB \qquad (5\text{-}21)$$

resulting in biphenyldisulfonic acid, thus reducing the number of radicals available for hydroxylation. The reduction in the formation of phenols can be seen in Figure 5-11, where the absorbance resulting from the modified phenol determination has been plotted. The reduction is first seen to occur after irradiation causes depletion of the dissolved oxygen in the samples originally at a 1.1×10^{-4}M concentration. The samples originally containing 0.1×10^{-4}M dissolved oxygen develop less than 25 per cent of the absorbance of the saturated samples.

Reaction (5-21) will reduce $\frac{dc''}{dE}$ since one mole of reactant now goes to one half mole of product. In aerated solutions $\frac{dc''}{dE}$

was probably approximately equal to $\frac{dc'}{dE}$, since most of the reaction products would absorb to some extent at the 216 mμ wavelength. The reduction in $\frac{dc''}{dE}$ will be offset to some extent by the fact that the molar absorption coefficient for biphenyldisulfonic acid is larger than that of the phenolsulfonic acids it is replacing.

Figure 5-12 shows that the rate of oxygen depletion increases as the oxygen concentration decreases. The initial rate of oxygen depletion for the saturated solutions was $G(-O_2)$ equal 2.0. In the solutions at only 40 per cent saturation, this value has increased to 4.3. Figure 5-13 indicates, as did Figure 5-5, that the rate of sulfate production is also increasing as oxygen content decreases.

The observed decrease in the rate of hydrogen peroxide formation at reduced oxygen concentrations could result in part from reaction (1-8)

$$H\cdot + H_2O_2 \rightarrow \cdot OH + H_2O \qquad (1\text{-}8)$$

This reaction along with the reaction (1-7)

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \qquad (1\text{-}7)$$

could account for reduced hydrogen peroxide concentrations, and if the rate of (1-7) is high enough, for an increase in the perhydroxyl radical concentration as well. This increase could account for the increased rate of sulfate production via

$$PhSO_3^- + HO_2\cdot \rightarrow PhO\cdot + HSO_4^- \qquad (5\text{-}15)$$

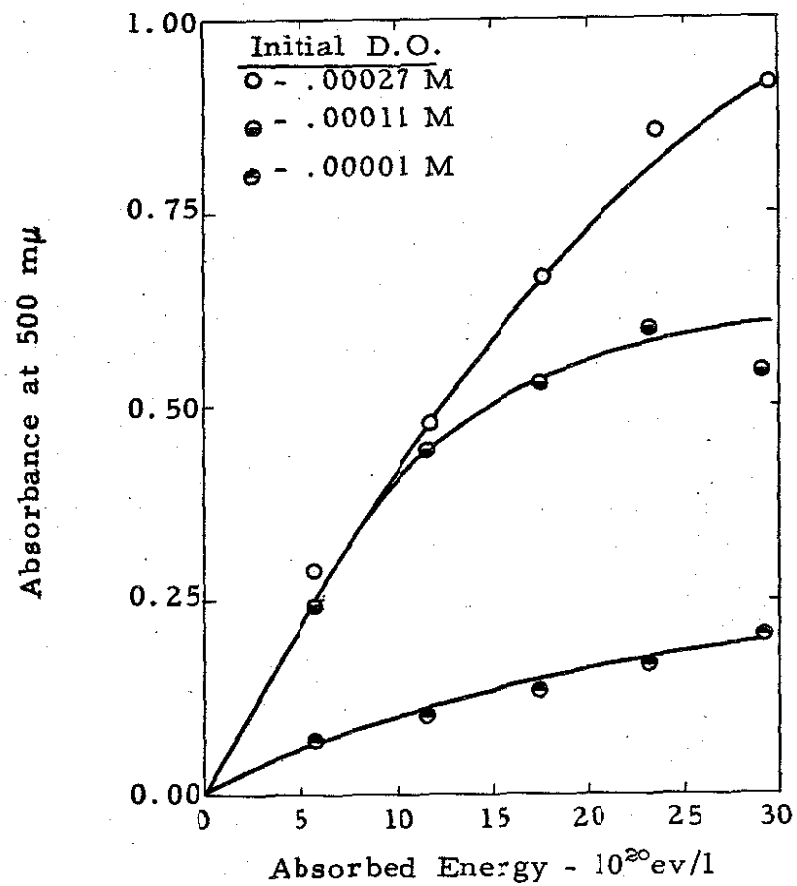


Figure 5-11. Effect of dissolved oxygen on rate of hydroxylation in 2.5×10^{-4}M benzenesulfonic acid.

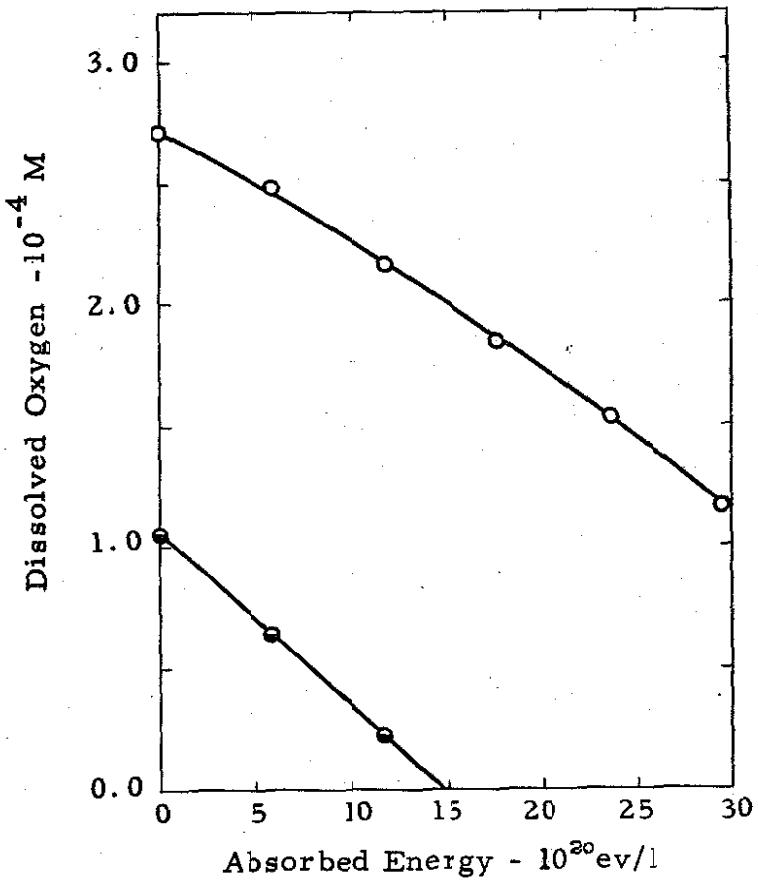


Figure 5-12. Dissolved oxygen vs. absorbed energy in pH 6.9 solutions of benzenesulfonic acid.

However, this increased rate of sulfate production was also observed at the low hydrogen peroxide concentrations in the solutions irradiated at 40 per cent saturation.

As an alternative, the effect could be explained on the assumption that the perhydroxyl radical, $HO_2\cdot$, is the only form of the radical entering into reaction (5-15). Then it is possible that as the oxygen concentration is reduced, more of the solvated electrons have an opportunity to be converted to the hydrogen radical via the reaction

$$H_3O^+ + e^-_{aq} \rightarrow H + H_2O \qquad (5\text{-}22)$$

This reaction would increase the number of hydrogen radicals, thereby increasing the number of $HO_2\cdot$ radicals. This increase would be at the expense of the perhydroxyl radicals of the form O_2^- resulting from the reaction of oxygen with the solvated electron. The additional perhydroxyl radicals would now be available to react with the solute which would result in the observed increase in sulfate ions by reaction (5-15).

If the rate of sulfate production is a function of the oxygen concentration, it would be expected that the relationship would be of a form similar to equations (5-9) or (5-10), that is

$$G(SO_4^=) = a + \frac{b}{1+k(O_2)} \qquad (5\text{-}23)$$

where "a" and "b" are constants relating to the initial yield of free radicals and "k" is proportional to the reaction rate constant. If "a" is assumed equal to zero, as the term does not arise in many

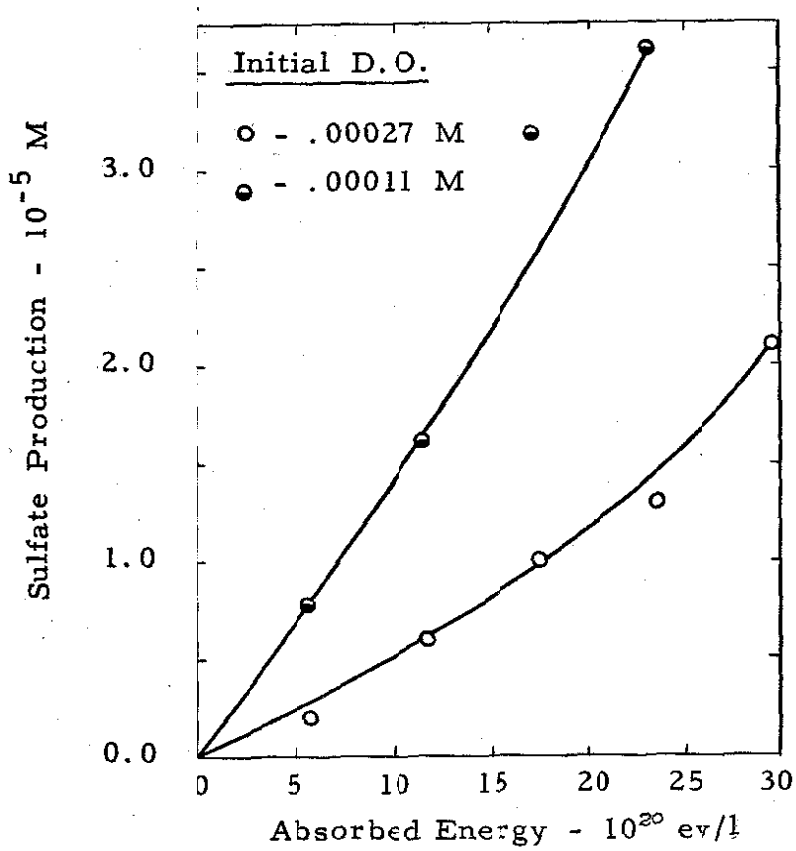


Figure 5-13. Sulfate production as a function of initial D.O. in pH 6.9 solutions of benzenesulfonic acid.

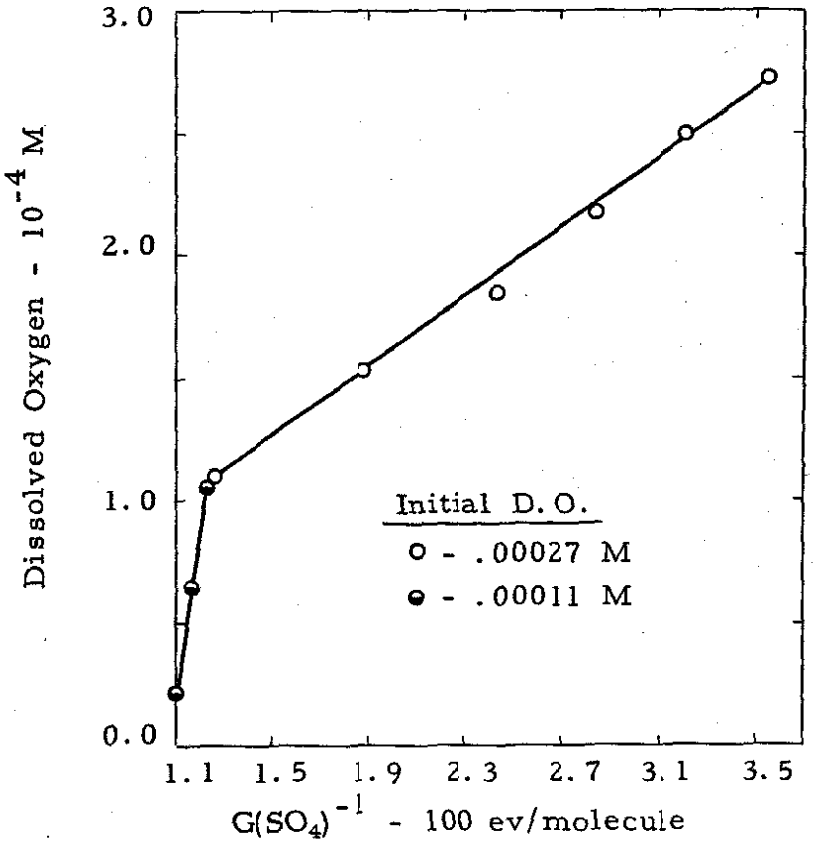


Figure 5-14. Relationship between dissolved oxygen and rate of sulfate production.

cases, a plot of oxygen concentration vs. $G(SO_4^{=})^{-1}$ should be linear in cases where relationship (5-23) exists. The $G(SO_4^{=})$ determined from the slope of the curves in Figure 5-13 and corresponding oxygen concentrations are tabulated below, and plotted in Figure 5-14, for the two cases where sulfates were found. Both groups of data

D.O. 10^{-4}M	$G(SO_4^{=})$	D.O. 10^{-4}M	$G(SO_4^{=})$
2.72	.28	1.06	.81
2.49	.31	.65	.85
2.17	.35	.22	.91
1.85	.41	-	-
1.53	.53	-	-
1.11	.79	-	-

indicate that the relationship does exist, although data for the case of the lower original oxygen concentration is meager and the curve quite steep. The break in the curve results from the fact that the reactions producing sulfates are bimolecular and thus will reflect variations in the initial oxygen concentrations.

The rate of oxygen consumption still exceeds the amount being converted to hydrogen peroxide, sulfates or quinones by the reactions already considered. One additional possibility, not usually examined in studies of radiation induced degradation in aqueous solutions, is that oxygen is converted to carbon dioxide. This reaction might occur either as a result of direct interaction of the radiation with the solute or as a result of oxidation after

opening of the aromatic ring. As a last attempt to explain this loss of oxygen a series of samples at a 2.5×10^{-4}M benzenesulfonic acid concentration were irradiated in a neutral solution. The samples were analyzed by the technique presented in Section 3-13. The concentration of gas found was on the order of 0.3×10^{-4}M for the samples irradiated to a total dose of 27.2×10^{20} ev/l. Unfortunately, this concentration is at the lower limit of the sensitivity of this method so that the evidence is not very conclusive.

The oxidation of carbon to carbon dioxide would account for the observed increase in the rate of oxygen depletion. Since the carbon would be oxidized to carbon dioxide at a much slower rate than that of the free radical reactions, the amount of carbon available for oxidation will increase with time. The carbon would become available as additional direct interactions occurred or additional rings opened. This increase in concentration would result in a corresponding increase in the rate of oxygen depletion. Had the possibility of carbon dioxide formation been considered in studies by earlier investigators, this production would have been examined in greater detail during the course of the investigation. An investigation would also have been conducted into more sensitive measuring techniques.

5-2-4 Effect of Solute Concentration

The solute concentration was varied over three orders of magnitude to estimate the relative position of the 2.5×10^{-4}M concentration used in most of the study, with respect to that needed to eliminate concentration effects. The pH 6.9 samples were each irradiated for four minutes, thus absorbing a dose of 23.6×10^{20} ev/l.

The data in Table 5-7 indicate that the 2.5×10^{-3}M concentration is approaching the region where concentration effects can be neglected since the changes that occur with increasing concentration are becoming smaller. The hydrogen peroxide data are interesting in that the concentration reaches a maximum at 2.5×10^{-5}M with a sharp decrease being observed at the highest solute concentration. The difference between the three lower concentrations is so small that it may be only experimental variation. However, the decrease in the solution containing the highest concentration is too large to be ignored. Increases in the oxygen depletion and sulfate production

Table 5-7

Effect of Solute Concentration

at a Constant Absorbed Energy of 23.6 ev/l

Solute Conc. M	H_2O_2 10^{-5}M	$\Delta D.O.$ 10^{-4}M	$SO_4^{=}$ 10^{-5}M	Absorbance 500 mμ
2.5×10^{-3}	1.77	-1.3	6.0	.72
2.5×10^{-4}	3.98	-1.0	2.7	.55
2.5×10^{-5}	4.16	-0.6	1.2	.10
2.5×10^{-6}	3.80	-0.5	-	-
0.0	3.45	-0.2	-	-

would indicate that when the solute concentration reaches this magnitude there are a sufficient number of solute molecules present to prevent significant radical recombination. Thus the reactions

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \qquad (5\text{-}24)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (1\text{-}11)$$

would be minimized under the scavenging action of the solute. To obtain additional information, a series of samples was irradiated at the higher solute concentration of 2.5×10^{-3}M. The results, presented in Table 5-8, are similar to those in Table 5-7.

Table 5-8

Irradiation of 2.5×10^{-3}M Benzenesulfonic Acid

at pH 6.9

Sample No.	Absorbed Energy 10^{20} ev/l	H_2O_2 10^{-5}M	D.O. 10^{-4}M	$SO_4^{=}$ 10^{-5}M
12-8-10	0.0	0.00	2.89	0.0
-11	5.6	1.08	2.55	2.0
-12	11.3	1.84	2.19	4.5
-13	16.9	2.20	1.78	3.8
-14	22.5	2.56	1.44	6.0
-15	28.2	3.00	0.98	6.7

Comparison of these results with Figures 5-3, 5-4, and 5-5 indicates a lower hydrogen peroxide production, more desulfonation, and greater oxygen depletion. All of these facts would substantiate the indications of decreasing radical recombination. The sulfate production appears quite erratic although it should be noted that part of this effect may be a result of decreased oxygen concentration.

An increase in $G(-O_2)$ as the concentration decreases is again in evidence. The initial $G(-O_2)$ is 3.5 compared to the 2.0 observed at the lower solute concentration of 2.5×10^{-4}M. The hydrogen peroxide concentration at an absorbed does of 22.5×10^{20} ev/l is larger than the comparable value in Table 5-7. Since the other data at this dose are in much closer agreement, it would be assumed that the value in Table 5-7 suffers from experimental error.

5-3 Irradiation of p-Toluenesulfonic Acid

5-3-1 Dissolved Oxygen Effects

The majority of the irradiations of p-toluenesulfonic acid were conducted at pH 6.9 with 2.5×10^{-4}M solute concentrations. The results are presented in Table 5-9. Figure 5-15 indicates the manner in which hydrogen peroxide production progressed as a function of absorbed dose. A comparison with results from the irradiation of benzenesulfonic acid shows that the rate of hydrogen peroxide production is much lower in this case. The maximum concentrations reached are less than 50 per cent of those obtained with benzenesulfonic acid. The initial yields, $G(H_2O_2)$, are also in this proportion, being 1.92 and 0.96 respectively, as compared to that arising from the decomposition of water, $G_{H_2O_2}$, equal to 0.71.

The absorbance of the p-toluenesulfonic acid peak at 221 mμ, illustrated in Figure 5-16, shows the same effect observed earlier, that as the original oxygen concentration decreases, the rate of decrease in absorbance becomes greater. The per cent decrease

Table 5-9

Irradiation of 2.5×10^{-4}M Solutions of

p-Toluenesulfonic Acid at pH 6.9

Sample No.	Absorbed Energy 10^{20} ev/l	H_2O_2 10^{-5}M	D.O. 10^{-4}M	$SO_4^{=}$ 10^{-5}M	Absorbance 221 mμ
9-08-0	0.0	0.00	2.82	0.0	.551
-1	5.8	0.81	2.38	1.2	.490
-2	11.6	1.21	2.06	2.0	.450
-3	17.4	1.41	1.53	2.9	.392
-4	23.2	0.94	0.97	4.9	.383
-5	29.0	0.92	0.22	5.9	.350
9-15-0	0.0	0.00	1.07	0.0	.557
-1	5.8	0.49	0.42	1.7	.505
-2	11.6	0.36	0.02	2.7	.450
-3	17.4	0.21	0.00	3.2	.410
-4	23.2	0.00	0.00	5.0	.374
-5	29.0	0.00	0.00	3.5	.325
9-15-10	0.0	0.00	0.08	0.0	.566
-11	5.8	0.00	0.06	0.0	.488
-12	11.6	0.00	0.05	0.0	.430
-13	17.4	0.00	0.03	0.0	.384
-14	23.2	0.00	0.01	0.0	.348
-15	29.0	0.00	0.00	0.0	.309

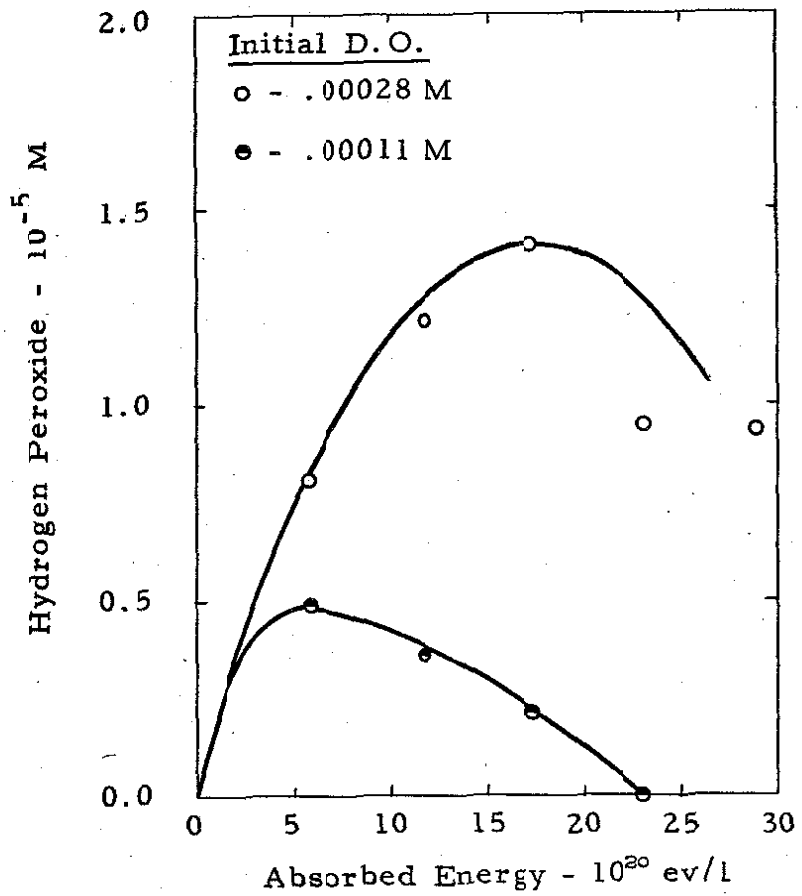


Figure 5-15. Hydrogen peroxide vs. absorbed dose in pH 6.9 solutions of p-toluenesulfonic acid.

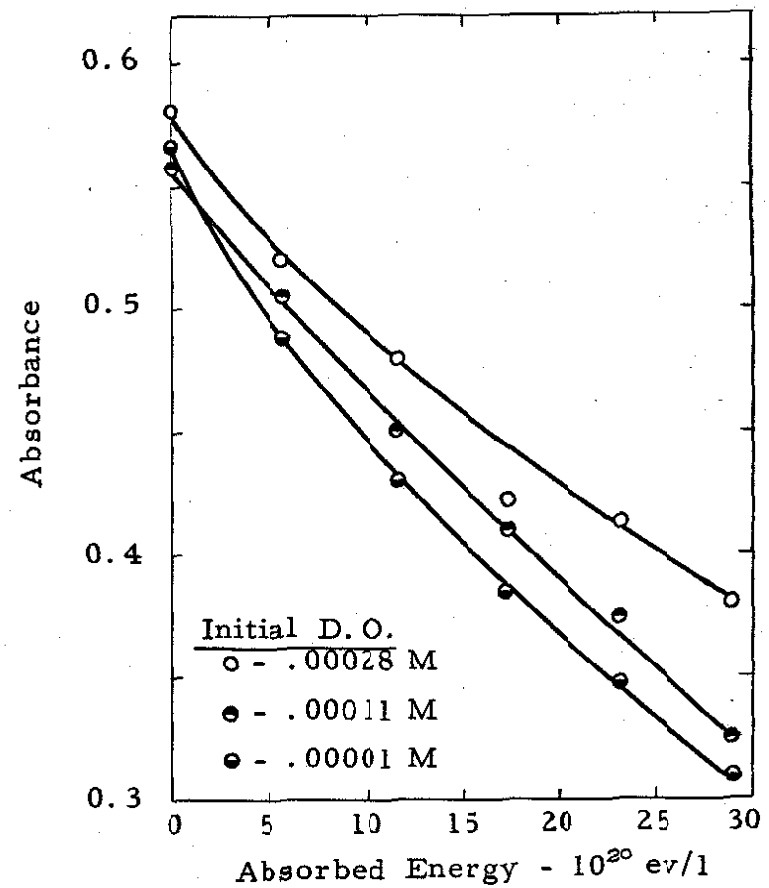


Figure 5-16. Absorbance at 221 mμ vs. absorbed energy in pH 6.9 solutions of p-toluenesulfonic acid.

in absorbance is also greater than that observed with benzenesulfonic acid but could result from the products exhibiting lower absorbance coefficients. Figure 5-17 shows the change in the ultraviolet spectrum of the solute as a function of absorbed energy between the 209 and 300 mμ wavelengths.

The oxygen concentration plotted in Figure 5-18 indicates a much greater rate of depletion than was observed in Figure 5-11. When these data are related to the much larger sulfate production shown in Figure 5-19, the overall picture is one of reactions similar to those observed with benzenesulfonic acid only progressing at a much faster rate. The original rate of oxygen depletion, $G(-O_2)$, in air-saturated solutions was shown to be 2.0 in benzenesulfonic acid while with the present solute this has risen to 3.1, an increase of 50 per cent. This increase cannot be attributed solely to reaction with the additional methyl group possessed by the solute, as proposed by Johnson and Weiss (32). Here, the formation of the methyl hydroperoxide radical

$$CH_3\cdot + O_2 \rightarrow CH_3OO\cdot \qquad (2\text{-}13)$$

could account for some of the additional oxygen depletion, but the increase in sulfates indicates that the attack at the sulfonate position has also increased. The amount of methyl hydroperoxide that may have formed would appear to be small since this product would have been determined with hydrogen peroxide.

Unusual results were obtained from the two phenol determinations. The original intention was to use both determinations to

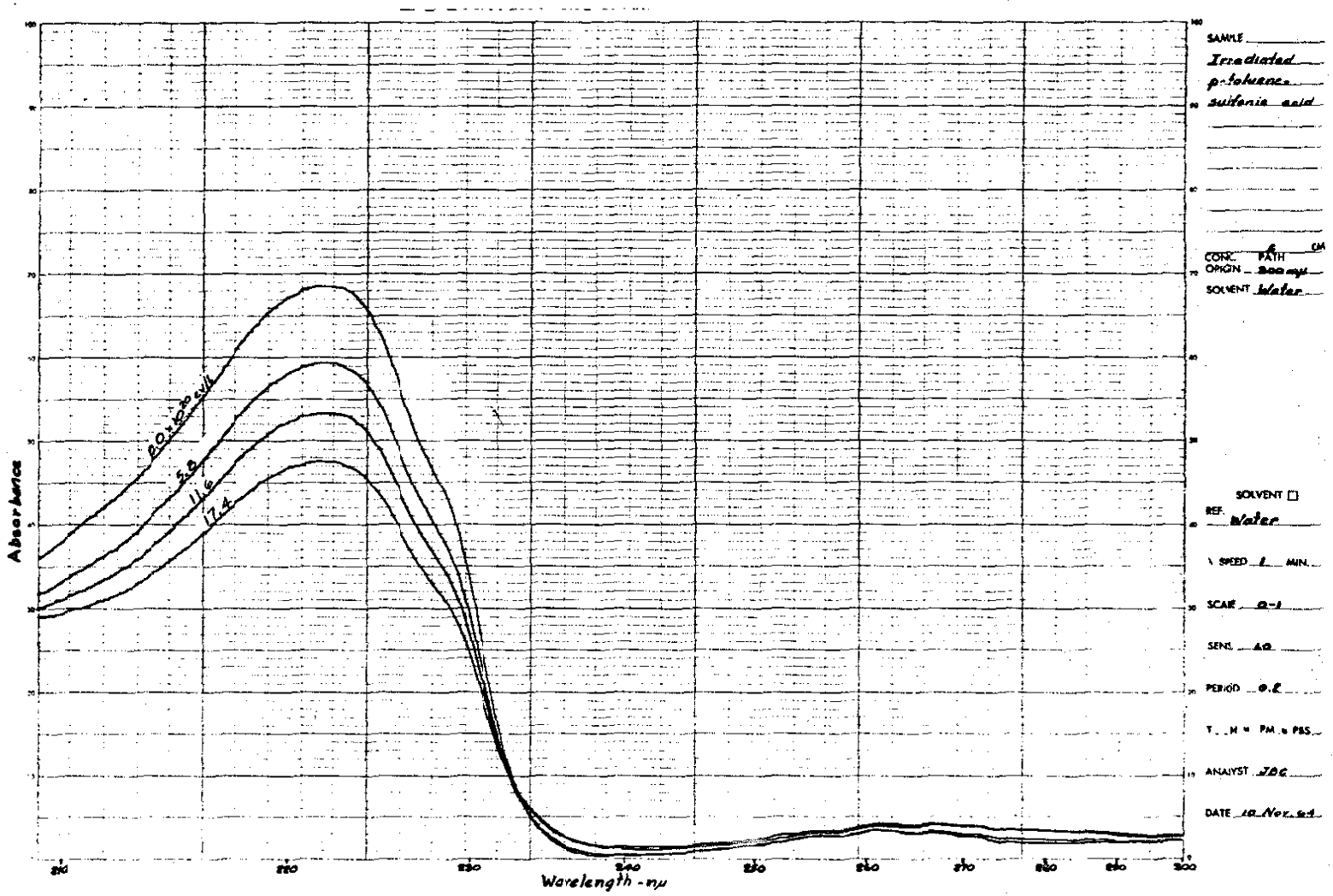


Figure 5-17. Effect of irradiation on the ultraviolet spectrum of p-toluenesulfonic acid.

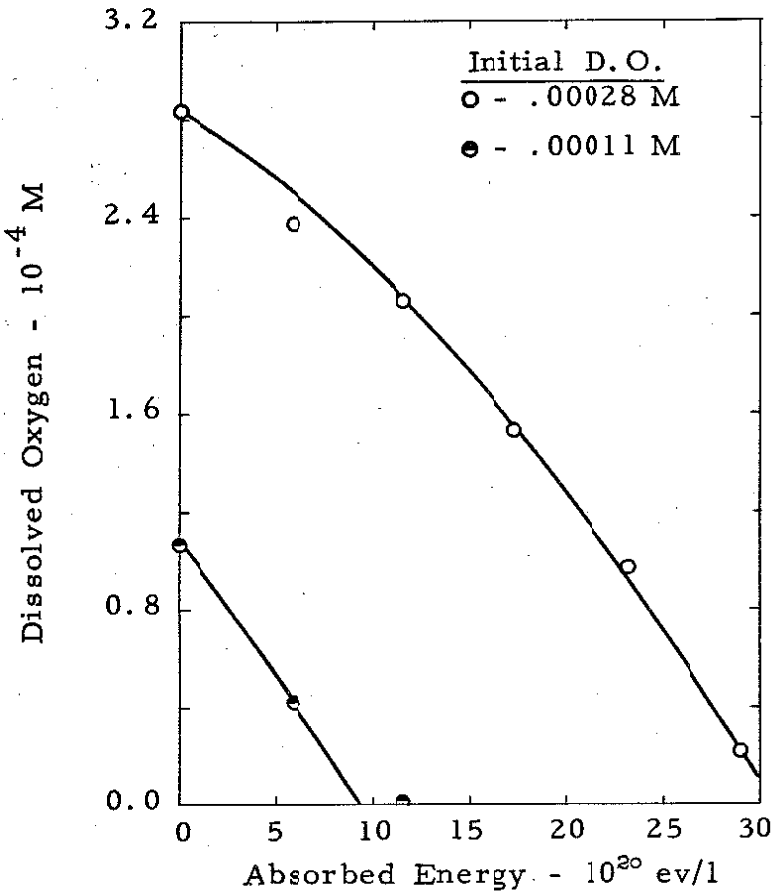


Figure 5-18. Effect of absorbed dose on dissolved oxygen in solutions of p-toluenesulfonic acid at pH 6.9.

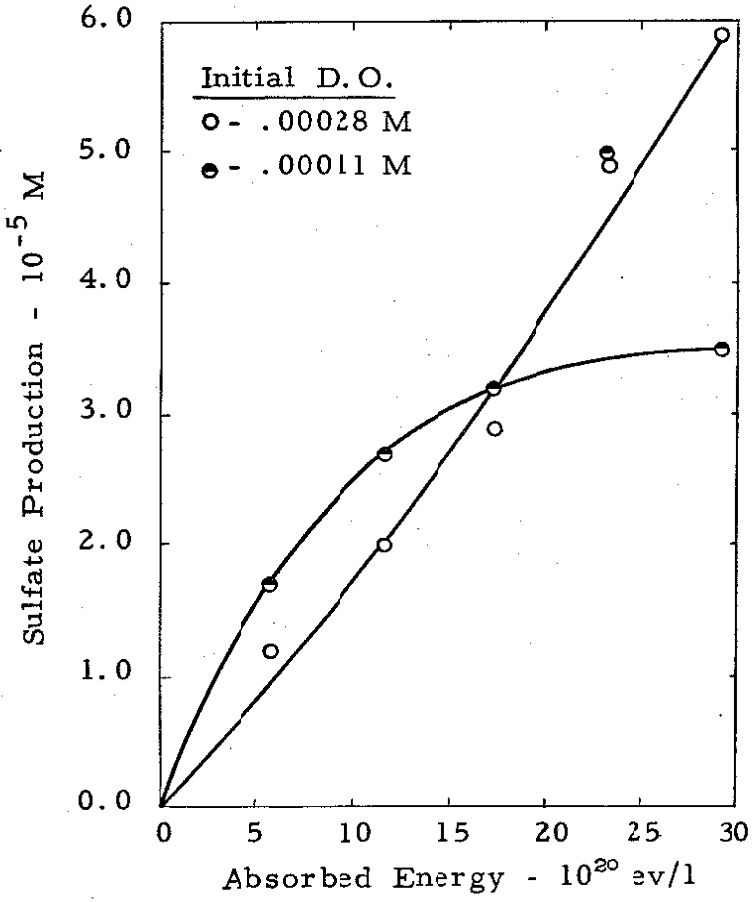


Figure 5-19. Effect of absorbed dose on sulfate production, in solutions of p-toluenesulfonic acid at pH 6.9.

obtain the data necessary to estimate the amount of hydroxylation, ortho- and meta- to the methyl group. This attempt was unsuccessful, however, since a much higher absorbance was obtained in the modified determination than in the method requiring the extraction into chloroform. The modified phenol determination produced results that were an order of magnitude higher than those from the other test. This fact indicates that at least one other hydroxylated compound is being formed. The compound or group of compounds has a much stronger absorbance in water and may not even extract into chloroform. Therefore, in addition to 1-methyl-2-hydroxy- and 1-methyl-3-hydroxy-4-benzenesulfonic acid, some or all of the five dihydroxy compounds are being formed.

The molar absorption coefficient for the 1-methyl-2-hydroxy- and 1-methyl-3-hydroxy-4-benzenesulfonic acid complexes were 2,300 and 4,500 liters per mole-cm respectively. Using the coefficient for the latter, to be conservative, the production of monohydroxy p-toluenesulfonic acid would be

Absorbed Energy 10^{20} ev/l	Monohydroxy Compound 10^{-6}M
5.8	0.1
11.6	0.8
17.4	1.5
23.2	1.9
29.0	2.7

These figures, which indicate a yield of 0.05 molecules per 100 ev,

are lower than those resulting from hydroxylation in the ortho and meta positions of the benzenesulfonic acid.

The spectra of the hydrozones, obtained in the aldehyde analysis of air-saturated samples, differed from that observed with the previous solute. In this case, the spectra closely resembled those of the 2,4-hexadienal, although the peak was shifted to a wavelength of about 490 mμ, as compared to 475 mμ for the 2,4-hexadienal. In addition, as the absorbance of the peak increased, a slight shift in the peak to longer wavelengths was observed. Whether the absorbance data presented below resulted from dialdehydes formed by ring opening, a toluquinone resulting from desulfonation of the solute, as was hypothesized earlier, or a combination of both, was not determined.

Absorbed Energy 10^{20} ev/l	Aldehyde Absorbance
5.7	0.12
11.3	0.42
17.0	0.69
22.6	0.83
28.3	1.10

5-3-2 Variation of Solute Concentration

The solute concentration, at pH 6.9, was varied in the same manner as with the benzenesulfonic acid, and the effects observed were about the same. The results presented in Table

5-10 show the same increase in desulfonation and oxygen utilization as the concentration of the solute increases. As before, there is a

Table 5-10

Effect of Solute Concentration

at a Constant Absorbed Energy of 23.2×10^{20} ev/l

Solute Conc. M	H_2O_2 10^{-5}M	ΔD.O. 10^{-4}M	$SO_4^{=}$ 10^{-5}M	Absorbance 500 mμ
2.5×10^{-3}	0.46	-2.21	11.7	.808
1.0×10^{-3}	0.67	-2.11	8.4	.722
2.5×10^{-4}	0.94	-1.85	4.9	.538
2.5×10^{-5}	2.84	-0.70	2.3	.003
0	3.45	-0.20	-	-

decrease in hydrogen peroxide accompanying the increase in solute concentration. All the effects observed with benzenesulfonic acid can be seen with p-toluenesulfonic acid, the only difference being that in this case all these effects are greater. At the 2.5×10^{-3}M solute concentrations the oxygen utilization is 70 per cent greater, sulfate production almost 100 per cent greater, while hydrogen peroxide has dropped to approximately 25 per cent of that observed with benzenesulfonic acid. The production of hydrogen peroxide may be misleading, since the yield in Figure 5-15 was seen to be decreasing at a dose of 23.2×10^{20} ev/l after having reached a maximum concentration of 1.41×10^{-5}M. The low hydrogen peroxide concentrations observed at the higher solute concentrations are probably the result of decreasing yields following some maximum value.

5-3-3 Hydrogen Ion Effects

An examination was made of the effects the three buffer systems would exhibit when irradiated with the p-toluenesulfonate ion. Samples in the three systems were irradiated to a total dose of 23.2×10^{20} ev/l before examination. The results are indicated in the short table below.

Table 5-11

Effect of 23.2×10^{20} ev/l Absorbed Energy on Buffered Solutions of 2.5×10^{-4}M p-Toluenesulfonic Acid

pH	H_2O_2 10^{-5}M	Δ D.O. 10^{-4}M	$SO_4^{=}$ 10^{-5}M	Absorbance 500 mμ
4.5	2.76	-1.78	5.7	.410
6.9	0.94	-1.85	4.9	.540
8.3	2.16	-0.79	1.6	.105

The dissolved oxygen depletion in both phosphate buffer systems are quite similar and much larger than observed to occur with the bicarbonate buffer system. They bear the same relationship to each other as was observed with the benzenesulfonate ion. Sulfate production increased by almost 100 per cent over that observed with the previous solute. This increased production could account for the high absorbance observed in the aldehyde analyses presented earlier. The absorbance at 500 mμ, resulting from enol formation, varied in the same manner as in the formation of phenolsulfonates with the largest production occurring in the neutral solution and the smallest in the alkaline solution. It must be

realized that other than pH effects probably caused the low yields in the alkaline solutions.

Hydrogen peroxide formation in the phosphate systems is less than half of that observed with benzenesulfonic acid although the decrease was not as large in the case of the bicarbonate buffer. It appears that while the solute is having some effect on the system, the bicarbonate buffer, at a much higher concentration, is still the predominant ion in that system. In the neutral solution, the lower hydrogen peroxide and sulfate yields may be attributable in part to the form of the perhydroxyl radical inhibiting both desulfonation and a certain amount of radical recombination.

5-4 Irradiation of Alkylbenzenesulfonate

5-4-1 Variation of pH in Aerated Solutions

ABS was irradiated in the same buffer systems as benzenesulfonic acid. The 2.5×10^{-4}M solute concentration, at which the solutions were irradiated, is an order of magnitude higher than would be expected in average waste water, but was considered necessary in order to obtain data as to the possible reaction mechanisms by forming measurable amounts of reaction products. The results of these irradiations are presented in Table 5-12. The dissolved oxygen depletion, plotted in Figure 5-20, is quite similar to that observed with benzenesulfonic acid. The depletion in the bicarbonate system is almost linear but less than that found with the first solute discussed. In the phosphate buffer systems the total oxygen utilization was 1.6 and 1.5×10^{-4}M at pH 4.6 and 6.7 respectively while the corresponding losses in the benzenesulfonic acid system

Table 5-12

Irradiation of 2.5×10^{-4}M Aerated ABS Solutions

Sample	Absorbed Energy 10^{20} ev/l	H_2O_2 10^{-5}M	pH	D.O. 10^{-4}M	Absorbance 224 mμ	Absorbance 500 mμ	ABS 10^{-4}M	$SO_4^{=}$ 10^{-5}M	Buffer
9-21-10	0.0	0.00	4.60	2.90	.670	.000	2.46	2.7	0.1M KH_2PO_4
-11	5.8	1.63	4.60	2.77	.639	.025	2.37	2.9	
-12	11.6	3.10	4.58	2.54	.637	.035	2.40	3.3	
-13	17.4	4.15	4.59	2.19	.635	.051	2.28	5.3	
-14	23.3	5.45	4.57	1.75	.608	.071	2.24	1.3	
-15	29.1	6.43	4.55	1.32	.618	.098	2.10	-	
9-18-0	0.0	0.00	6.70	2.72	.655	.000	2.30	3.0	0.01M KH_2PO_4
-1	5.8	1.22	6.70	2.53	.649	.026	2.28	-	0.01M K_2HPO_4
-2	11.6	2.32	6.70	2.31	.649	.061	2.18	3.7	
-3	17.4	3.58	6.70	2.00	.639	.088	2.10	3.5	
-4	23.3	4.14	6.70	1.63	.624	.114	2.00	3.2	
-5	29.1	4.34	6.70	1.22	.622	.148	1.98	5.0	
9-21-0	0.0	0.00	8.67	2.71	.722	0	2.58	2.0	0.1M $NaHCO_3$
-1	5.8	1.22	8.62	2.56	.694	.010	2.46	3.2	
-2	11.6	2.31	8.39	2.46	-	.010	2.48	3.8	
-3	17.4	3.37	8.54	2.37	-	.010	2.38	3.5	
-4	23.3	4.35	8.30	2.18	.660	.020	2.36	2.9	
-5	29.1	5.22	8.30	2.07	.654	.038	2.28	1.4	

were both 1.6×10^{-4}. A difference does exist in that, in each case, the initial $G(-O_2)$ is less for this solute.

Data on hydrogen peroxide production are illustrated in Figure 5-21. The results at pH 4.6 could be superimposed on those found for benzenesulfonic acid. The data at pH 6.7 is also quite similar to the earlier findings. In the bicarbonate system the curve shows the same slight change in yield with increasing dose observed with the benzenesulfonic acid but the initial yield, $G(H_2O_2)$, is greater than was found previously. The slight decrease in pH, attributable to sulfate production, observed at the high and low pH, is also seen to occur in both solute systems. Comparison of these data indicates that both solutes are experiencing the same effects from the free radicals produced by the radiation, as well as the same or close to the same amount of radical recombination.

In the case of ABS, two methods are available for estimating the rate at which the molecule is being degraded: the absorbance peak at 224 mμ, and the methylene blue test. The data from these determinations have been plotted in Figures 5-22 and 5-23 and the curves fitted by eye. The rate of decrease in absorbance shown in Figure 5-22 is much smaller than observed in the other solutes examined. This effect could result from impurities added with the ABS, a low yield of enol compounds, or the production of enols having molar absorption coefficients comparable to ABS in this region of the UV spectrum. The rates of decrease of absorbance in the phosphate buffer systems are similar, while the bicarbonate system may be decreasing at a slightly faster rate with absorbed

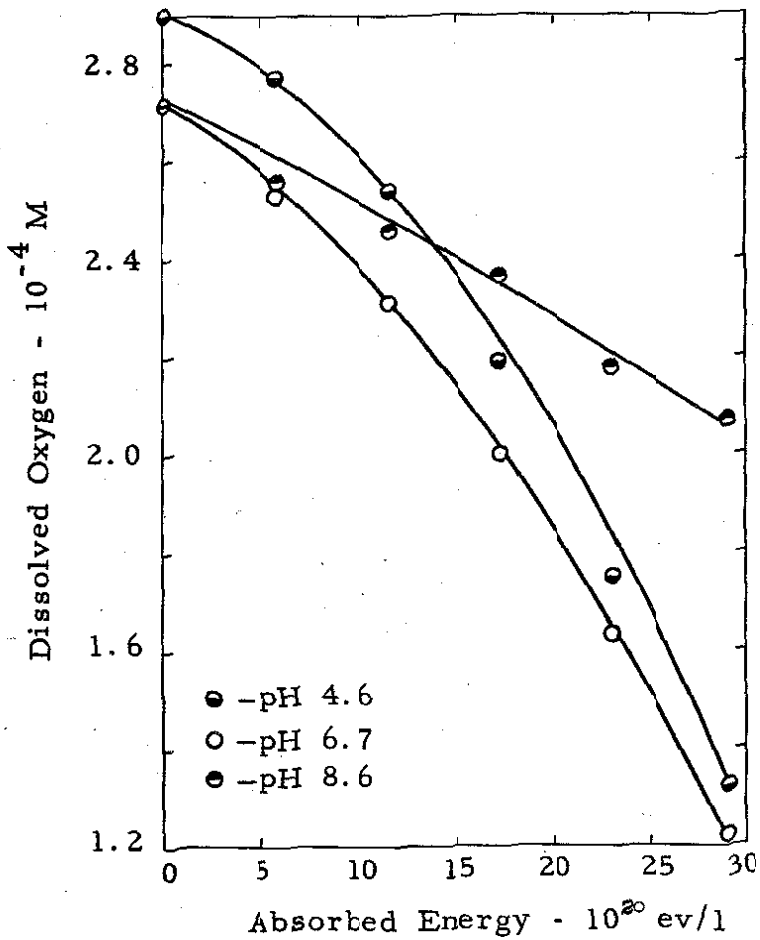


Figure 5-20. Effect of absorbed dose on dissolved oxygen, in solutions of ABS.

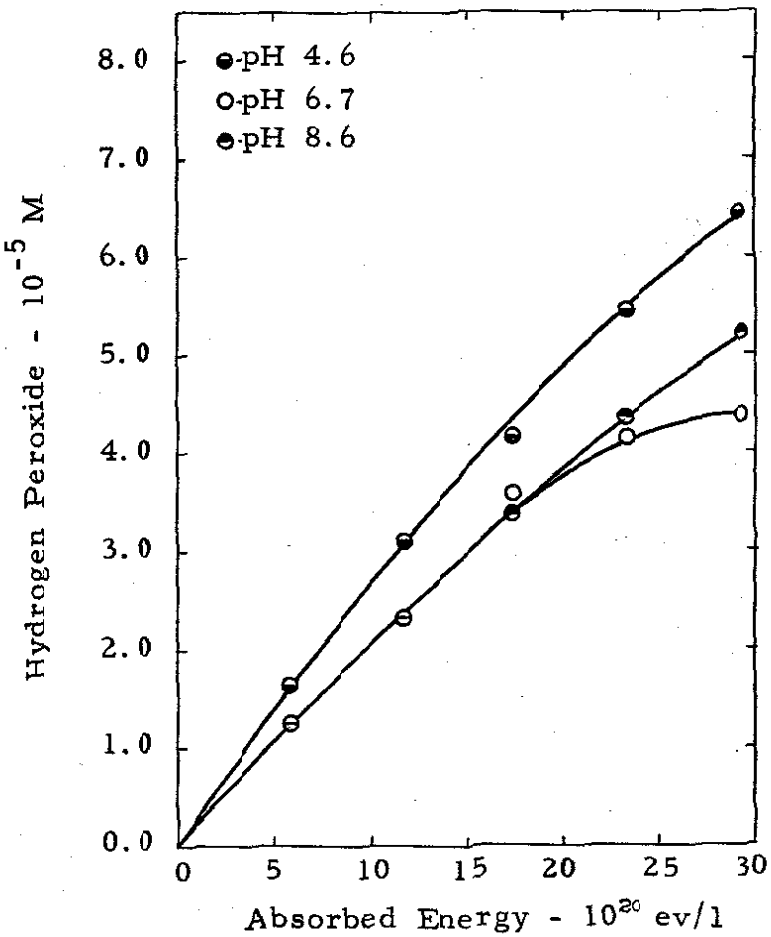


Figure 5-21. Hydrogen peroxide vs. absorbed energy, in solutions of ABS.

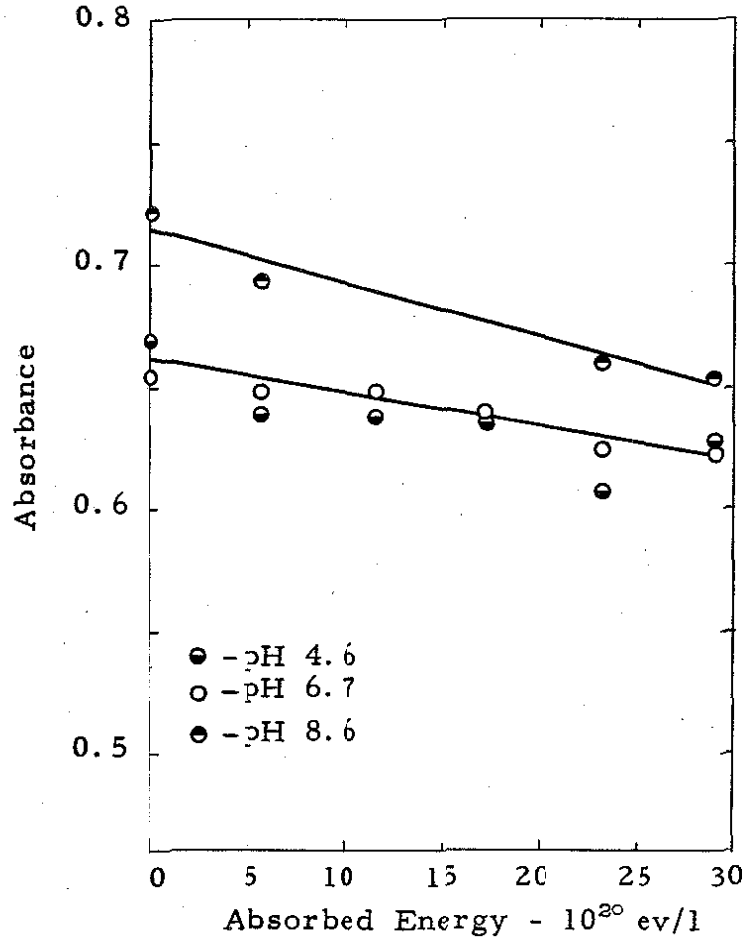


Figure 5-22. Absorbance at 224 mμ vs. absorbed energy.

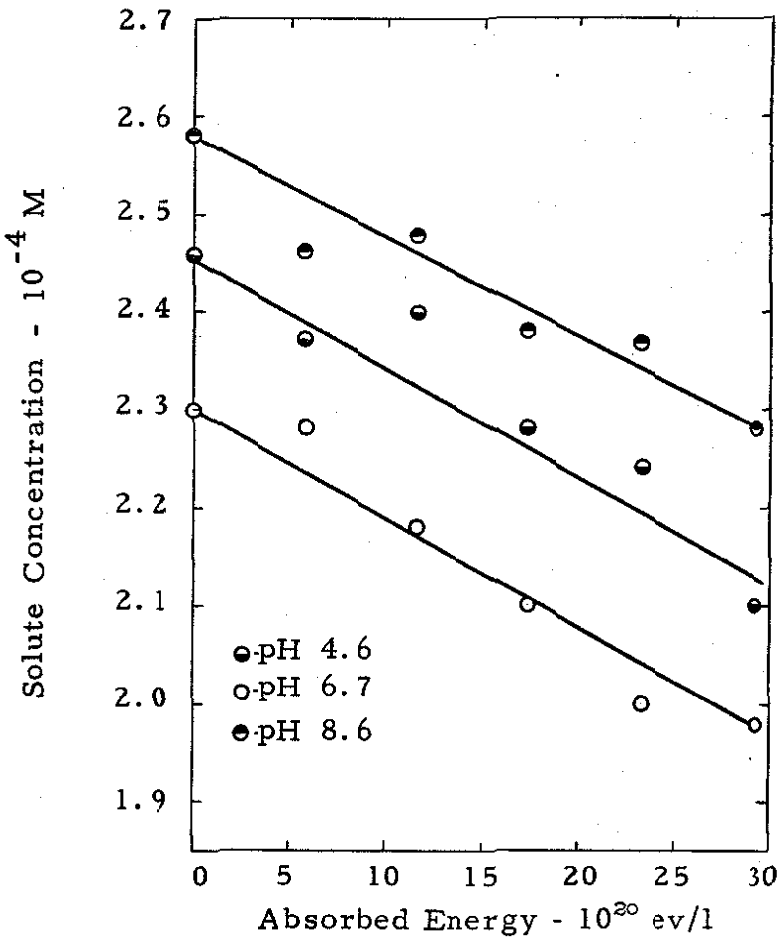


Figure 5-23. ABS concentration vs. absorbed energy using methylene blue procedure.

dose.

Results of the methylene blue determination are probably a better indication of the rate of sulfate production than the sulfate data in Table 5-12. The latter are too erratic to be given much credence. The analytical method required that a large quantity of ABS be removed by extraction into chloroform, since the barium salt of ABS has a low solubility product. This requirement was probably too stringent to be attained with any great degree of precision, as can be seen from the results. While it is not known for certain, it is felt that the methylene blue-ABS complex will probably form even if a hydroxyl group has been added to the benzene ring. Even if this is not the case, the amount of hydroxylation occurring with the other solutes was so small as to be negligible when compared to experimental errors. Under these circumstances the sulfate production would be comparable to that observed for benzenesulfonic acid.

The absorbance of the antipyrine dye at 500 mμ, as an indication of enol formation, is much less than observed in solutions containing the other solutes, with the bicarbonate system again showing the lowest results. This low absorbance could result from a low yield which would be consistent with the small change in absorbance at the 224 mμ ABS peak, or from a low molar absorptivity coefficient for the aminoantipyrine complex. A third possibility is that this method, not being sensitive to compounds similar to para-cresols, is not indicating what could be a significant portion of the hydroxyl compounds.

On the basis of the results of the methylene blue procedure, the rate of degradation of the ABS molecule is very low, about 0.7 molecules per 100 ev. This figure is in agreement with results obtained by Bio Sciences Laboratories (9), however neither their dose rates nor solute concentrations were as high as was used in this study.

The aldehyde analysis, conducted on a series of samples in neutral solution, gave positive results, increasing with absorbed dose, indicating the presence of an aldehyde or quinone. The spectrum closely approximated that described for the p-benzoquinone, with the major peak at about 470 mμ.

5-4-2 Dissolved Oxygen Effects at pH 6.7

The dissolved oxygen concentration of 2.5×10^{-4}M ABS solution was varied at a neutral pH as was done with the other solutes. The solution was not completely deaerated, since it was impractical to bubble nitrogen gas through the solution prior to irradiation. The high detergent concentration would have caused excessive foaming accompanied by the loss of a disproportionate part of the solute in the foam. Instead, the distilled water was deaerated and the ABS added to this solution. Table 5-13 indicates the significant part of the data obtained from solutions originally containing 2.7- and 0.3×10^{-4}M of dissolved oxygen.

The data plotted in Figure 5-24 again illustrate what has been observed to occur with the other solutes, that the absorbance will decrease at a more rapid rate in deaerated solutions. This same effect can be noted in Figure 5-25 where the results of the

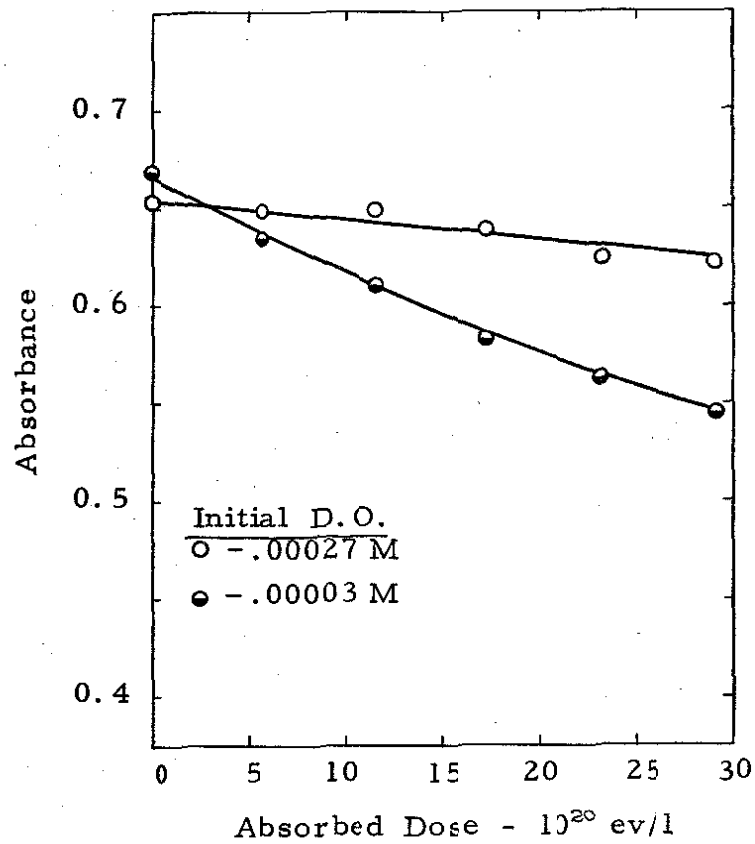


Figure 5-24. Absorbance at 224 mμ vs. absorbed energy in pH 6.7 ABS solutions.

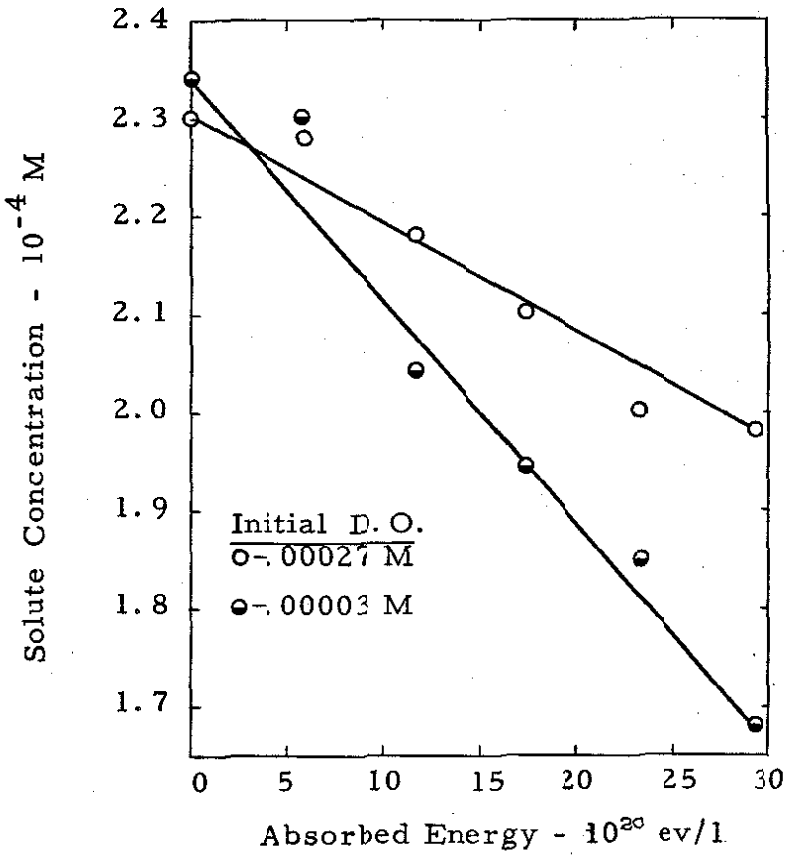


Figure 5-25. ABS concentration vs. absorbed energy in pH 6.7 solutions, using methylene blue procedure.

Table 5-13

Dissolved Oxygen Effects on 2.5×10^{-4}M ABS Solutions

D.O. 10^{-4}M	Absorbed Energy 10^{20} ev/l	H_2O_2 10^{-5}M	ABS 10^{-4}M	Absorbance 224 mμ
2.72	0.0	0.00	2.30	.655
2.53	5.8	1.22	2.28	.649
2.31	11.6	2.32	2.18	.649
2.00	17.4	3.58	2.10	.639
1.63	23.3	4.14	2.00	.624
1.22	29.1	4.34	1.98	.622
0.27	0.0	0.00	2.34	.667
0.03	5.8	0.32	2.30	.633
0.00	11.6	0.15	2.04	.609
0.00	17.4	0.09	1.94	.581
0.00	23.3	0.00	1.90	.566
0.00	29.1	0.00	1.68	.545

methylene blue procedure have been presented. The rate of degradation in the deaerated solutions, 1.4 molecules per 100 ev, is twice that observed in aerated solutions. Assuming that addition of a hydroxyl group to the aromatic ring will not prevent the formation of the methylene blue complex, G(-BH) of 1.4 would represent the rate of dimer or polymer formation. This value is in good agreement with a rate of diphenyl production of 1.22 molecules per 100 ev observed by Phung and Burton (17) on irradiating neutral, air-free, solutions of benzene.

Hydrogen peroxide production in the deaerated solutions is very low, becoming zero after absorbing 23.3×10^{20} ev/l. Had the solution been completely air-free, even this small amount may not have been observed, since Phung and Burton reported their initial $G(H_2O_2)$ as zero.

5-4-3 Variations in Solute Concentration

As was done with the other homologs, several samples were irradiated in neutral solutions at a variety of solute concentrations. The data are presented in Table 5-14. The methylene blue data for the higher solute concentrations are not very significant, since the analytical procedure requires that the original samples be diluted to concentrations which would make experimental error quite appreciable. Thus, at the highest concentration, the three per cent degradation is less than the accuracy of about ± 5 per cent. What is significant is the degradation of the 2.5×10^{-5}M sample,

Table 5-14

Effect of ABS Concentration at a

Constant Absorbed Energy of 23.3×10^{20} ev/l

Solute Conc. M	H_2O_2 10^{-5}M	Δ D.O. 10^{-4}M	Δ Solute Conc. M
2.5×10^{-3}	4.70	-1.07	-0.06×10^{-3}
1.0×10^{-3}	4.28	-1.03	-0.08×10^{-3}
2.5×10^{-4}	4.14	-1.09	-0.30×10^{-4}
2.5×10^{-5}	4.04	-0.85	-2.20×10^{-5}
0.0	3.42	-0.20	-

which has been reduced 88 per cent by a dose of 23.3×10^{20} ev/l. In the four minutes required for the solution to absorb this amount of energy the ABS concentration was reduced from 8.8 mg/l to 1.1 mg/l.

Hydrogen peroxide formation is much greater than was observed with the p-toluenesulfonic acid. At the highest concentration it is about 50 per cent higher than that produced in the comparable benzenesulfonic acid solution. Oxygen depletion on the other hand is less than observed with the other solutes. The high hydrogen peroxide yields, found at the higher solute concentrations, could be indicative of the formation of a small amount of peroxide on the alkyl chain of the ABS molecule. However, one might expect to see a larger oxygen depletion, as compared to the benzenesulfonate ion, if alkyl peroxides were formed by the mechanism proposed by Johnson and Weiss (32). The oxygen and solute depletion data, together, give the appearance that the point at which solute concentration is no longer a factor would be at a lower concentration than appeared to be the case with the other solutes. These data would also indicate a G(-BH) of 1.6 molecules per 100 ev for the degradation of ABS at high solute concentrations.

CHAPTER 6

CONCLUSIONS

6-1 Degradation Mechanisms

From the discussion in Chapter 5 and the summary, Table 6-1, it is seen that the three compounds studied, benzenesulfonic acid, p-toluenesulfonic acid and ABS, will yield the same classes of reaction products, although the quantities produced were different. In aerated solutions hydroxylation was observed to occur to each of the three homologs, with p-toluenesulfonic acid showing evidence of accepting a second hydroxyl radical to form the dihydroxytoluene-sulfonic acids.

Sulfates were also produced by desulfonation of the solutes, with p-toluenesulfonic acid appearing the most susceptible. In the case of benzenesulfonic acid, the amount of sulfate and phenolsulfonates produced was about the same order of magnitude. Results of the phenol and aldehyde analyses, as well as other factors discussed in Chapter 5, gave indications that the product that remained after desulfonation of benzenesulfonic acid was a quinone, rather than phenol.

In addition to the above products, the ABS solutions indicated a higher peroxide yield than the buffer solutions. This yield, shown in Table 6-1, but more obvious at high ABS concentrations, gave indications that peroxides may have been formed on the alkyl chain of that compound.

The effects of the variation in the hydrogen ion concentration were observed in the rates of hydrogen peroxide, sulfate, and enol

Table 6-1

Comparison of Data in 2.5×10^{-4}M Neutral Solutions

with Increasing Absorbed Energy

Approx. Absorbed Energy	Buffer Solution	Benzenesulfonic Acid		p-Toluenesulfonic Acid		ABS	
	H_2O_2	H_2O_2	$SO_4^=$	H_2O_2	$SO_4^=$	H_2O_2	$SO_4^=$
10^{20} ev/l	10^{-5}M	10^{-5}M	10^{-5}M	10^{-5}M	10^{-5}M	10^{-5}M	10^{-5}M
5.9	1.26	1.52	0.5	0.81	1.2	1.22	0.2
11.8	2.06	2.53	0.9	1.21	2.0	2.32	1.2
17.7	2.77	3.10	1.2	1.41	2.9	3.58	2.0
23.6	3.45	3.79	1.6	0.94	4.9	4.14	3.0
29.5	4.01	4.15	2.1	0.92	5.9	4.34	3.2
10^{20} ev/l	$\Delta D.O.$ / 10^{-5}M	$\Delta D.O.$ / 10^{-5}M	Abs. / 500 mμ	$\Delta D.O.$ / 10^{-5}M	Abs. / 500 mμ	$\Delta D.O.$ / 10^{-5}M	Abs. / 500 mμ
5.9	-1.2	-2.3	.288	-4.4	.188	-1.9	.026
11.8	-1.6	-5.5	.478	-7.6	.325	-4.1	.061
17.7	-1.6	-8.7	.665	-12.9	.445	-7.2	.088
23.6	-2.1	-11.9	.857	-18.5	.540	-10.9	.114
29.5	-2.5	-16.1	.916	-26.0	.625	-15.0	.148

formation. The pH did not appear to affect the rate of oxygen depletion, or solute degradation, in the phosphate buffer systems. However, much of the variation observed in the bicarbonate buffer system resulted from this choice of buffer, rather than the pH it produced.

The data would thus indicate that the degradation of the solutes by the irradiation of aerated solutions was affected by the following reactions:

$$H_2O \rightarrow H\cdot \text{ (or } e^-_{aq}), \cdot OH, H_2, H_2O_2 \qquad (1\text{-}5)$$

would produce the free radicals and molecular products,

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (1\text{-}9)$$

$$BH + \cdot OH \rightarrow B\cdot + H_2O \qquad (5\text{-}19)$$

$$BH + HO_2\cdot \rightarrow B\cdot + H_2O_2 \qquad (6\text{-}1)$$

where B• would be any of the three dehydrogenated radicals, and

$$B\cdot + \cdot OH \rightarrow BOH \qquad (6\text{-}2)$$

would produce the enols. These reactions had been anticipated in Chapter 2. The reaction

$$PhSO_3^- + HO_2\cdot \rightarrow PhO\cdot + HSO_4^- \qquad (5\text{-}15)$$

would account for the desulfonation, where PhO• would represent any one of the homologs after desulfonation, and

$$PhO\cdot + HO_2\cdot \rightarrow QO_2 + H_2O \qquad (6\text{-}3)$$

where the QO_2 would represent any of the quinones formed from the

three compounds. This mechanism was not anticipated originally, however, the facts that desulfonation was not observed in deaerated solutions, that phenols were not in evidence and that sulfate production was pH sensitive would indicate that these reactions are occurring.

As the oxygen concentration decreases, reduction in the rate of hydrogen peroxide production indicated that

$$H^{\bullet} + H_2O_2 \rightarrow H_2O + \bullet OH \qquad (1\text{-}8)$$

becomes important.

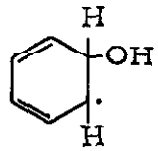
Reaction (1-9) alone cannot account for the losses in oxygen that have been observed, nor do reactions (5-19) and (6-2) account for all the hydroxyl radicals that have been produced as primary decomposition products of water. However, some of these hydroxyl radicals will combine to form peroxides via reaction (5-24)

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \qquad (5\text{-}24)$$

some will react with hydrogen peroxide by

$$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet \qquad (1\text{-}7)$$

and others may be eliminated via a reaction equivalent to reaction (1-23).

2  $\rightarrow C_6H_5OH + H_2O + C_6H_6$ (1-23)

The facts that a significant amount of oxygen has not been accounted for by free radical reactions, that carbon dioxide was observed in irradiated benzenesulfonic acid solutions, and that larger oxygen depletions were observed to occur in p-toluene- rather than in benzenesulfonic acid, indicate the possibility of oxidation of a small quantity of the solute. This oxidation would occur as a result of a small number of direct interactions of the radiation with the solute, rather than with the water or after ring opening by the free radicals. Thus, benzenesulfonic acid could experience oxidation via

$$C_6H_5SO_3^- + 7O_2 \rightarrow 6CO_2 + H_2SO_4 + H_2O + H^+ \quad (6\text{-}4)$$

while the p-toluenesulfonic acid would be oxidized by

$$CH_3C_6H_4SO_3^- + \frac{17}{2}\ O_2 \rightarrow 7CO_2 + H_2SO_4 + 2H_2O + H^+ \quad (6\text{-}5)$$

Reactions (6-4) and (6-5) would indicate that a small number of molecules undergoing these reactions would consume a much larger amount of oxygen even though any one molecule may never be completely oxidized. The reactions would also account for the larger depletions observed in the p-toluenesulfonic acid solutions. If it is assumed that the 12-carbon alkyl chain is not degraded when the ring is oxidized, the lower initial rate of oxygen consumption observed in the irradiated ABS solutions would be explained.

In deaerated solutions enols were still produced by reactions (5-17) and (6-2), although no sulfate was formed. Decreases in the ultraviolet absorbance peaks of the three compounds were accelerated

in deaerated solutions. This decrease was interpreted to indicate the formation of dimers and polymers by

$$B\bullet + B\bullet \rightarrow BB \qquad (5\text{-}21)$$

These compounds were not actually observed since analytical methods were not available for the dimers that were expected.

6-2 Environmental Engineering Significance

If irradiation is to be considered as a method of treating water and wastewater, prior to its introduction into a potable water supply, or the environment, as the case may be, the purpose of the irradiation must be considered. The bactericidal aspects were discussed in Chapter 1, along with the effects of irradiation on the settling properties of sewage. This study, however, was concerned with another facet of the water and waste treatment problem, that is, to determine the factors which will effect the degradation of organic molecules that may appear in the water environment.

In the case of the sulfonated compounds studied, the reactions which are of the most interest are those leading to desulfonation of the molecule. There is no immediately obvious reason for the formation of enols or dimers to have any significant effect on the treatability of the compounds studied or on those formed. Opening of the benzene ring could be important in biological treatment since this action would overcome the stability associated with the benzene ring. Desulfonation, however, converts these molecules from non-volatile organic ions to volatile organic molecules which,

as quinones, have lost the stability of the benzene ring.

The fact that desulfonation, or removal of other substituent groups, will not occur in deaerated solutions would limit the location of an irradiator, in a sewage treatment facility, to an aeration tank, where oxygen can be provided. Even though Figure 5-25 indicates a higher rate of ABS reduction in deaerated solutions, this rate probably results from the dimers not reacting with methylene blue. The fact that oxygen is consumed so quickly would affect the economics of the plant, since additional aeration would require larger physical and mechanical facilities. If irradiation were to be used as a wastewater treatment process, it would be more economical to use a fission product such as cesium-137 as opposed to cobalt-60. In addition to being cheaper, since it is a waste product, cesium-137 has a longer half-life, 26.6 years, as compared to the 5.2 year half-life of cobalt-60. This difference would allow the material to remain in place for a much longer period, probably for the life of the treatment plant.

Installation of the radioactive material on the bottom of an aeration tank would have several advantages in addition to the availability of oxygen. The nine to fifteen foot sewage depths common to aeration tanks are sufficient to reduce the radiation intensities by factors of from 10^{-11} to 10^{-18} considering the floor of the tank as an infinite plane source. This attenuation would protect the plant worker while absorbing essentially all of the radiation. Also, the circulation set up by the diffused-air aerators enables the entire system to come into close contact with the

radioactive source during detention in the tank. A further advantage would be that the process is readily adaptable to existing treatment facilities since no additional equipment is required.

If a ten-foot-deep tank contained a cesium-137 base having a source strength of one curie per square foot, the sewage would be absorbing a dose of approximately 4×10^{22} ev per liter per minute. The dose per unit volume would be determined from the detention time in the aerator.

Use of an irradiator in a water treatment plant could result in a more economical operation. Fresh water initially contains a higher oxygen concentration than does wastewater, and may even be saturated. The treated water is usually placed in a reservoir after treatment. This retention would allow the oxygen concentration to return to its original level without the aid of artificial reaeration. Another benefit that would accrue from the use of the irradiator would be the bactericidal effects, discussed earlier. Use of radiation could reduce or eliminate the necessity of chlorination since X-rays have been shown to be an effective means of reducing a bacterial population.

The use of radiation might be further complicated by the presence of bicarbonates and carbonates, although not in the quantities that are usually found in natural waters. Here a typical value for bicarbonate concentration of about 120 mg/l or 0.002M should exhibit little effect during irradiation. However, this may not be the case in wastewater which may contain significant amounts of industrial wastes. Bicarbonates and other ions which react with

free radicals could minimize the effectiveness of the ionizing radiation, if present in high concentrations.

6-3 Areas for Further Study

A most interesting question, raised by this and similar studies where oxygen concentrations have been measured, regards the fate of the oxygen utilized during irradiation by what appears to be direct, rather than indirect, degradation mechanisms. Utilizing stable isotopes of oxygen, it should be possible to determine if the oxygen has been reduced to water and in what quantity this has occurred. This question could be answered by distilling the water after irradiation and then determining the concentration of the heavier oxygen in the water using a mass spectrometer. Distillation would de-gas the water while concentrating the salts. The use of organics, tagged with radioactive carbon-14, would enable the measurement of changes in solutes by measuring the radioactivity of an alkaline solution after de-gassing an irradiated sample into that solution. This method would indicate the amount of carbon dioxide formed by the amount of radioactive carbonate resulting from this procedure.

Another interesting study would be an examination of the degradation of organics and possibly bacterial populations in natural waters, rather than in the high purity distilled water usually used. These results would indicate what protective effects, if any, would be afforded to the bacteria and organic solutes by the scavenging action of the salts present in natural waters.

Since bicarbonates and carbonates are common to natural waters, a study of the radiation chemistry of these anions would provide additional data as to the economic feasibility of radiation as a means of providing a high degree of water treatment.

Finally, if equipment were available, the effect of dose rate on degradation should be studied, since, in aqueous solutions, higher rates of degradation are usually observed at lower dose rates. This type of study would provide the data required for optimizing the size of structures providing detention times for water being irradiated, since construction and isotope costs must be considered in this case.

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