Chapter 6

Mass Spectrometric Detection of Oxidation Products and Intermediates of Aqueous Aerosol Iodide and/or Thiosulfate Reaction with Gaseous Ozone


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Abstract

The intermediates ISO₃⁻ (m/z = 207) and IS₂O₃⁻ (m/z = 239) generated in aqueous (NaI/Na₂S₂O₃) microdroplets traversing dilute O₃ gas plumes are detected via online electrospray mass spectrometry within ~ 1 ms, and their stabilities gauged by collisionally induced dissociation. The simultaneous detection of anionic reactants and the S₂O₆²⁻, HSO₄⁻, IO₃⁻, and I₃⁻ products, as a function of experimental conditions, provides evidence for air-water interfacial reactions, as compared to strictly bulk aqueous reactions. For example, O₃(aq) reacts ~ 3 times faster with I⁻ than with S₂O₃²⁻ in bulk solution; only S₂O₃²⁻ is significantly depleted in the interfacial layers of [I⁻]/[S₂O₃²⁻] = 10 microdroplets below [O₃(g)] ~ 50 ppm. This suggests that either interfacial kinetics are at variance with bulk aqueous kinetics and/or I⁻ mediates that ozone oxidation of S₂O₃²⁻.
Introduction

Atmospheric aerosols absorb and scatter solar radiation\textsuperscript{1} and mediate important chemical processes\textsuperscript{2,3,4,5}. For example, atmospheric SO\textsubscript{2} and NO\textsubscript{x} can be oxidized in the gas-phase, but acid rain results from their faster processing in aqueous aerosol droplets\textsuperscript{6,7,8}. However, the analysis of gas-aerosol reaction mechanisms and kinetics is assumed to follow concepts derived from studies performed in bulk aqueous solution\textsuperscript{9,10}. However, the possibility of unique reaction mechanisms and enhanced chemical kinetics of air-water interfacial reactions, as well as the reduced water activity in atmospheric aerosol particles, should prevent the simple extrapolation of bulk data to the aerosol phase. The minimal examination of reactions specific to the air-water interface is a result of the technical difficulties associated with producing radially small aerosol particles under atmospherically relevant conditions in the laboratory and probing their chemical transformations while suspended in reactive atmospheres. Most studies, with a few exceptions\textsuperscript{11,12,13}, have monitored the uptake of reactive gases by stationary trains of ~10–100 $\mu$m droplets\textsuperscript{14} that would have exceedingly large settling velocities (~1 km day\textsuperscript{-1}), short residence times (i.e., negligible number densities in the atmosphere), and relatively low surface-area-to-volume ratios\textsuperscript{15}.

Here, we report experiments in which the chemical composition of aqueous droplets ($r = 0.5$ to 3.0 microns) undergoing chemical reaction with a reactive gas is directly monitored by electrospray mass spectrometry (ES-MS) in ~1–10 ms time frames. The fast oxidations of $\Gamma$(aq) and $\text{S}_2\text{O}_3^{2-}$(aq) by O\textsubscript{3}(g), which proceed at nearly diffusionally controlled rates in bulk solution\textsuperscript{16}, are studied by spraying droplets across O\textsubscript{3}/air gas plumes. We detect and quantify anion reactants and products, as well as the previously
postulated short-lived reaction intermediates ISO$_3^-$ and IS$_2$O$_3^-$. Our results show that this technique is capable of tracking chemical reactions in the condensed phase during fast aerosol-gas reactions. ES-MS has been previously used for online monitoring of thermal, electrochemical and photochemical reactions$^{17,18,19,20,21,22,23,24,25,26,27,28}$.

**Experimental**

The experimental setup is shown in Figures 6.1a and b. Aqueous solutions were pumped (50 μL min$^{-1}$) into the reaction chamber through a grounded stainless steel needle injector (~ 50 μM radius bore)$^{29}$ and pneumatically sprayed by means of coaxially flowing nebulizer gas. The difference between the exit velocities of the liquid jet (10.6 cm s$^{-1}$) and nebulizer gas (2.65 × 10$^4$ cm s$^{-1}$) is so large that the drag imposed on the liquid breaks it apart into micrometer size droplets. The terminal velocities of the microdroplets produced are ~ 10$^2$–10$^3$ cm s$^{-1}$, which lead to transit times around 1 to 10 ms across the ~ 0.5 cm wide ozone plume. The droplets are produced by fragmentation of electrically neutral solutions from a grounded injector, and are charged via statistical fluctuations that scale with (drop size)$^{-1/2}$.$^{31}$ The ensemble of spray droplets is on average neutral, but individual droplets carry charges that follow a Gaussian distribution, as expected for a random process. For example, this phenomenon is the basis of the classical oil drop experiment performed by Millikan to determine the magnitude of the elementary charge$^{32}$ and leads to the charge of sea-sprayed aerosols. The finer sea water aerosol droplets, which will remain airborne the longest after generation during bubble bursting, are reported to be negatively charged$^{33}$. It should be emphasized that charge separation during pneumatic nebulization of liquids does not produce highly charged droplets (10 to 100 charges per droplet vs. 10,000 charges per droplet) such as those created during
electrospray ionization using high-field nozzles\textsuperscript{34}. The spray droplets eventually contract through solvent evaporation, a process regulated by ambient temperature and relative humidity, thereby increasing electrostatic repulsion among excess surface charges. In highly charged droplets, Coulomb explosions may occur, producing a distribution of smaller, charged droplets. Once charged droplets near radii on the nm scale, ion evaporation may occur, yielding hydrated, gas-phase ions\textsuperscript{35}. Similar events will proceed in both sea-sprayed marine aerosols as they rise into the dry atmosphere, and our spray chamber as the droplets are electrostatically extracted into a high-temperature, high-flow-rate, dry-nitrogen gas stream. The drying events will generate smaller aerosols and eventually gas-phase ions whose chemical distribution is enriched in tensio- or surface active species. Thus, the ESMS technique effectively samples the interfacial layers of droplets.

Ozone was generated by flowing ultrapure O\textsubscript{2}(g) (0.1 L/min, Air Liquide) through a commercial ozonizer (Ozone Solution), diluted tenfold with ultrapure N\textsubscript{2}(g) (0.9 L/min) and quantified by UV absorption spectrophotometry (HP 8452) at 250 and 300 nm [absorption cross-sections $\sigma$(250 nm) = 1.1 x 10\textsuperscript{-17}, $\sigma$(300 nm) = 3.9 x 10\textsuperscript{-19} cm\textsuperscript{2} molecule\textsuperscript{-1} at 298 K]\textsuperscript{36} prior to entering the reaction chamber. In the text, the reported [O\textsubscript{3}(g)] values, which correspond to the concentrations actually sensed by droplets in the reaction chamber, are estimated to be $\sim$ 10 times smaller than the values determined from UV absorbances due to further dilution by the N\textsubscript{2} drying gas (Fig. 6.1a, 10 L/min). Gas flows were regulated by calibrated mass flow controllers (MKS). Typical instrumental parameters were as follows: drying gas temperature, 340 °C; Nebulizer pressure, 28 psi; collector capillary voltage, +3.5 kV; fragmentor voltage, 22 V. Solutions were prepared
with MilliQ water that had been previously purged with ultrapure N\textsubscript{2}(g) for at least 30 min. NaI (> 99 %), Na\textsubscript{2}SO\textsubscript{3} (> 98 %) and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (> 99.999 %) were obtained from Sigma-Aldrich. Solution pH was measured with a calibrated pH meter (VWR, SB21).

**Results and Discussion**

We have recently shown that I\textsuperscript{-} is rapidly oxidized to I\textsubscript{3}\textsuperscript{-} and IO\textsubscript{3}\textsuperscript{-} by O\textsubscript{3}(g) at ppm levels in this experimental setup\textsuperscript{37}. Thiosulfate is expected to react with O\textsubscript{3}(g) at similar rates\textsuperscript{38}. Since I\textsubscript{2}/I\textsubscript{3} also react rapidly with S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}, it should be possible to observe the transient intermediates I\textsubscript{2}S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} and IS\textsubscript{2}O\textsubscript{3}\textsuperscript{-} proposed by Raschig a century ago to account for their slow conversion into tetrathionate (see also Table 6.1)\textsuperscript{39,40,41,42,43}.

\[
\begin{align*}
I_2 + I^- & \rightleftharpoons I_3^- \quad (6.1, 6.1') \\
I_2 + S_2O_3^{2-} & \rightleftharpoons I_2S_2O_3^{2-} \quad (6.2, 6.2') \\
I_3^- + S_2O_3^{2-} & \rightleftharpoons I_2S_2O_3^{2-} + I^- \quad (6.3, 6.3') \\
I_2S_2O_3^{2-} & \rightleftharpoons IS_2O_3^- + I^- \quad (6.4, 6.4') \\
IS_2O_3^- + S_2O_3^{2-} & \rightarrow I^- + S_4O_6^{2-} \quad (6.5)
\end{align*}
\]

A similar mechanism has been proposed for the I\textsubscript{2}/I\textsubscript{3} + HSO\textsubscript{3}^-/SO\textsubscript{3}\textsuperscript{2-} reaction, which proceeds via the ISO\textsubscript{3}^- intermediate\textsuperscript{44,45,46,47}. The absorption spectra assigned by Packer and Anderson to the I\textsubscript{2}S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} and IS\textsubscript{2}O\textsubscript{3}\textsuperscript{-} intermediates detected in their pulse radiolysis experiments\textsuperscript{48}, were found to be blue-shifted relative to those of I\textsubscript{3}^- and I\textsubscript{2}.

**Identification of anion products and intermediates**

Figure 6.2 shows the mass spectra of aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} microdroplets in the absence and presence of O\textsubscript{3}(g). Signals at m/z = 112, 135, and 293, which are ascribed to S\textsubscript{2}O\textsubscript{3}^- , NaS\textsubscript{2}O\textsubscript{3}^- , and Na\textsubscript{3}(S\textsubscript{2}O\textsubscript{3})\textsubscript{2}^- , respectively, are observed in the absence of O\textsubscript{3}(g). We detect
the radical monoanion $S_2O_3^-$, rather than the closed-shell dianion $S_2O_3^{2-}$ (m/z = 56) in the ESMS of Na$_2$S$_2$O$_3$, in accord with previous reports$^{49,50}$. Apparently, $S_2O_3^{2-}$(g) has negative electron affinity due to electrostatic repulsion between vicinal localized charges in $S=S(O)(O^-)_2$. The ready detection of $S_2O_8^{2-}$, in which charges are localized farther apart, supports this interpretation. Therefore, field ejection of $S_2O_3^{2-}$ from charged droplets$^{51}$ likely involves concerted electron transfer to the solvent, i.e.: $S_2O_3(H_2O)_n^{2-} \rightarrow S_2O_3^{-} + (H_2O)_n^{-}$. Thus, we consider $S_2O_3^{-}$ to be a valid marker of $S_2O_3^{2-}$ under present conditions. In the presence of O$_3$(g), new signals at m/z = 80, 97, 119, and 261 appear, which correspond to $S_2O_6^{2-}$, HSO$_4^-$, NaSO$_4^-$, and Na$_3$(SO$_4$)$_2^-$, respectively.

Figure 6.3 shows a mass spectrum of NaI/Na$_2$S$_2$O$_3$ microdroplets reacting with O$_3$(g). The m/z = 175 and 381 signals correspond to IO$_3^-$ and I$_3^-$, while the signals at m/z = 207 and 239 are assigned to the I-S species ISO$_3^-$ and IS$_2$O$_3^-$, respectively. The m/z = 207 signal, accompanied by m/z = 97, 175, and 381 signals, is also produced in the reaction of NaI/Na$_2$SO$_3$ microdroplets with O$_3$(g). All product signals disappear at once upon discontinuing O$_3$(g) injection.

The identity of S-containing species was confirmed from the relative intensities of their M and M+2 signals. Intensity ratios: M/M+2 = 100/4.4, 100/8.8, and 100/17.6 are expected for natural $^{34}$S-abundance compounds containing one, two, and four S-atoms, respectively. The measured (112)/(114) = 100/9.9, (207)/(209) = 100/5.6, and (239)/(241) = 100/10.3 ratios are therefore consistent with species containing two, one, and two S-atom(s), respectively, and exclude $S_4O_6^{2-}$, I$_2$S$_2$O$_6^{2-}$ or I$_2$S$_4$O$_6^{2-}$ species. We infer that the m/z = 207 and 239 signals correspond to ISO$_3^-$ and IS$_2$O$_3^-$, respectively.
**Reaction Mechanism**

Further information is gained by studying the dependence of signal intensities on \([\text{O}_3(\text{g})]\). Reactant anion signal intensities at \(m/z = 112 (\text{S}_2\text{O}_6^{2-})\), 127 (\(\Gamma\)) and 135 (\(\text{NaS}_2\text{O}_3^{-}\)) decline with increasing \([\text{O}_3(\text{g})]\), as shown in Figure 6.4a. Product and intermediate anion signal intensities at \(m/z = 80 (\text{S}_2\text{O}_6^{-})\), 97 (\(\text{HSO}_4^{-}\)), 119 (\(\text{NaSO}_4^{-}\)), 175 (\(\text{IO}_3^{-}\)), 381 (\(\text{I}_3^{-}\)), 207 (\(\text{ISO}_3^{-}\)), and 239 (\(\text{IS}_2\text{O}_3^{-}\)) are all enhanced upon increasing \([\text{O}_3(\text{g})]\), as shown in Figure 6.4b and c. Note the upward inflections observed at \(\sim 50 \text{ ppm O}_3(\text{g})\) in Figures 6.4b and c.

Figure 6.5 shows a plot of the \([\text{HSO}_4^{-}]/[\text{S}_2\text{O}_6^{2-}]\) ratio as function of \([\text{O}_3(\text{g})]\). A nonvanishing value below \(\sim 50 \text{ ppm O}_3(\text{g})\) is a direct indication that \(\text{S}_2\text{O}_6^{2-}\) and \(\text{HSO}_4^{-}\) are primary species produced in competing pathways, eqs. 6.10a and b in Table 6.152. The marked increase of this ratio at higher \([\text{O}_3(\text{g})]\), however, shows that further \(\text{HSO}_4^{-}\) is produced in the oxidation of reactive byproducts. This interpretation is confirmed by the inertness of 0.1 mM \(\text{S}_2\text{O}_6^{2-}\) toward \(\text{O}_3\), together with the lack of \(\text{HSO}_4^{-}\) \((m/z = 97)\) production below 420 ppm \(\text{O}_3(\text{g})\). Neither does a 0.25 mM \(\text{S}_4\text{O}_6^{2-}\) solution, prepared by titration of 0.5 mM \(\text{S}_2\text{O}_3^{2-}\) with \(\text{I}_3^{-}\):53

\[
\text{I}_3^{-} + 2\text{S}_2\text{O}_3^{2-} \rightarrow 3\Gamma + \text{S}_4\text{O}_6^{2-}
\]  

(6.6)

and subsequently sprayed in the reaction chamber, react with \(\text{O}_3(\text{g})\). The \(m/z = 112\) \((\text{S}_4\text{O}_6^{2-})\) and 97 \((\text{HSO}_4^{-})\) signal intensities remain constant below 520 ppm \(\text{O}_3(\text{g})\).

Figure 6.6 shows how \(\text{ISO}_3^{-}, \text{IS}_2\text{O}_3^{-}, \text{HSO}_4^{-},\) and \(\text{IO}_3^{-}\) signal intensities vary with \([\text{O}_3(\text{g})]\), and indicates that \(\text{HSO}_4^{-}, \text{IO}_3^{-}, \text{ISO}_3^{-},\) and \(\text{IS}_2\text{O}_3^{-}\) are later generation species whose rates of formation have a stronger, direct dependence on \([\text{O}_3(\text{g})]\) than those of \(\text{S}_2\text{O}_6^{2-}\) and \(\text{I}_3^{-}\).
We recently found that in this setup the oxidation of I by O\(_3\) (g) yields iodate, IO\(_3\)^{-}, and triiodide, I\(_3\)^{-} (R12-14). I\(_3\)^{-} is in equilibrium with I and I\(_2\)^{54,55,56,57} (R1). I\(_3\)^{-} and/or I\(_2\) can then react with HSO\(_3\)^{-} or S\(_2\)O\(_3\)^{2-} according to reactions R2-R3 and R7-R8\(^{28,32}\). The fact that we do not observe I\(_2\)SO\(_3\)^{2-} (m/z = 167) or I\(_2\)S\(_2\)O\(_3\)^{2-} (m/z = 183) in NaI/Na\(_2\)SO\(_3\) or NaI/Na\(_2\)S\(_2\)O\(_3\) droplets in contact with O\(_3\) (g) implies that their decomposition lifetimes are much shorter than \(\sim 1\) to 10 ms under present conditions (eqs. 6.4’ and 6.9); in accord with Margerum et al.\(^{32}\) I\(_2\)S\(_2\)O\(_3\)^{2-} is thermodynamically stable \((k_2/k_2 = K_2 = 3.2 \times 10^7 \text{ M}^{-1})\), but kinetically reactive \((k_4/k_4 = K_4 = 0.245 \text{ M})\). The dissociation equilibrium constant of I\(_2\)S\(_2\)O\(_3\)^{2-}, \(K_4 = 0.245 \text{ M}\), is \(\sim 100\) times larger than that of I\(_3\)^{-}, \(k_{-1}/k_1 = 1.39 \times 10^3 \text{ M}^{-1}\). Our results do not exclude, however, the participation of hypoiodous acid, HOI, which is considered to be more reactive than I\(_2\) or I\(_3\)^{-} as oxidant.

\[
\text{HOI} + \text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightarrow \text{IS}_2\text{O}_3^{-} + \text{H}_2\text{O} \tag{6.15}
\]

The dependence of IS\(_2\)O\(_3\)^{-} (m/z = 239) signal intensity in 30 \(\mu\)M Na\(_2\)S\(_2\)O\(_3\) droplets as a function of [NaI] in the range of 1–300 \(\mu\)M, at constant [O\(_3\) (g)] = 300 ppm, is shown in Figure 6.7a. The observed exponential growth to a maximum is qualitatively consistent with the proposed mechanism of formation. Figure 6.7b shows the dependence of IS\(_2\)O\(_3\)^{-} (m/z = 239) signal intensity in 30 \(\mu\)M NaI droplets as a function of [Na\(_2\)S\(_2\)O\(_3\)] in the range of 1–300 \(\mu\)M, at constant [O\(_3\) (g)] = 350 ppm. In contrast with the behavior observed in Figure 6.7a, IS\(_2\)O\(_3\)^{-} peaks at [Na\(_2\)S\(_2\)O\(_3\)] \(\sim 100\) \(\mu\)M. This response implies that S\(_2\)O\(_3\)^{2-} participates both in the formation and destruction of IS\(_2\)O\(_3\)^{-}, and is consistent with the increasing role of eq. 6.5 at higher [Na\(_2\)S\(_2\)O\(_3\)]\(^{32}\). From the reported value of \(k_5 = 1.29 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}\), we estimate that the half-life of IS\(_2\)O\(_3\)^{-} in eq. 6.5 is \(\sim 5\) ms at [Na\(_2\)S\(_2\)O\(_3\)] \(\sim 100\) \(\mu\)M, which provides a direct measure of our temporal window. The rapid hydrolysis of
ISO$_3^-$, eq. 6.16, regenerates $\Gamma$, and may be responsible for the results shown in Figure 6.8a.

**Interfacial Reaction Kinetics**

Figure 6.8 shows the dependence of [$\Gamma$] and [S$_2$O$_3^{2-}$] vs. [O$_3$(g)] in three different solutions: [NaI]$_0$ = [Na$_2$S$_2$O$_3$]$_0$ = 30 μM (a), [NaI]$_0$ = 10 × [Na$_2$S$_2$O$_3$]$_0$ = 300 μM (b), and [Na$_2$S$_2$O$_3$]$_0$ = 10 × [NaI]$_0$ = 300 μM (c). S$_2$O$_3^{2-}$ undergoes significant oxidation in all cases over the entire [O$_3$(g)] range covered in these experiments. In contrast, $\Gamma$ oxidation begins above [O$_3$(g)] ~ 50 ppm in the a and b mixtures, and is fully inhibited in c. Since O$_3$(aq) reacts ~ 3 times faster with $\Gamma$ than with S$_2$O$_3^{2-}$ in the bulk (see Table 6.1) these observations imply that the interfacial layers of the droplets are predominantly populated by S$_2$O$_3^{2-}$ and/or that reactivities at the air-water interface are significantly different than in the bulk. Considering that the ratio of signal intensities, I(S$_2$O$_3^{2-}$)/I(Γ) = 1.2 ± 0.1, in equimolar Na$_2$S$_2$O$_3$/NaI solutions is a direct measure of the relative affinities of S$_2$O$_3^{2-}$ and $\Gamma$ for the interfacial layers of microdroplets, we must conclude that their relative reactivities toward O$_3$(g) are indeed reversed relative to the bulk. Note that decrease of $\Gamma$ at [O$_3$(g)] ≥ 50 ppm in Figure 6.8a coincides with the onset of the IS$_2$O$_3^-$ and ISO$_3^-$ in Figure 6.4c, supporting the proposed involvement of the products of $\Gamma$ oxidation in their mechanism of formation.

**Intermediate Stability**

We probed the thermal stability of the ISO$_3^-$, IS$_2$O$_3^-$, and I$_3^-$ in the gas-phase via collisional-induced dissociation experiments, in which the variation of ion signal intensities were recorded as function of fragmentor voltage (FV). FV is the electrical potential difference between the capillary exit and the first skimmer, a region where ions
are accelerated up to excess kinetic energies given by: \( KE = FE \times q_i = \frac{1}{2} m_i v_i^2 \) (\( q_i \) is the charge, \( m_i \) the mass, and \( v_i \) the excess velocity of ion \( i \), respectively). Molecular ions convert their excess KE into internal (vibrational/rotational) excitation during impact with (N\(_2\)) bath gas molecules prior to undergoing collisionally induced dissociation (CID)\(^{59}\). Figure 6.9a shows the dependence of m/z = 127 (I\(^-\)), 207 (ISO\(_3\)^-), 239 (IS\(_2\)O\(_3\)^-) and 381 (I\(_3\)^-) signal intensities on FV. The monotonous increase of the I\(^-\) signal reveals that ion collection efficiencies generally increase with FV. The maxima observed in the case of ISO\(_3\)^-, IS\(_2\)O\(_3\)^-, and I\(_3\)^- indicates, therefore, the onset of fragmentation. Curve deconvolution into two sigmoids, followed by the conversion of laboratory (KE) to center-of-mass (CEM) kinetic energies—\( CEM = m/(m + M) \) KE, where \( m = 28 \) is the molecular mass of the N\(_2\) collider gas and \( M = 207, 239, \) or 381, the molecular masses of the various anions—leads to the fragmentation curves shown in Figure 6.9b. Threshold CEM energies are consistent with the reported values for BDE(I\(^-\)–I\(_2\)) = 1.31 eV\(^{60}\), and BDE(I\(^-\)–SO\(_3\)) = 1.67 eV\(^{61}\). The fact that IS\(_2\)O\(_3\)^- and ISO\(_3\)^- have similar stabilities in the gas-phase suggests the presence of weak I-S bonds in both species\(^{32}\).
**Figures**

**Figure 6.1.** Diagram of electrospray and overall reactor setup. A) Schematic diagram of electrospraying chamber and O$_3$(g) injection system. B) An overview of the experimental setup. MFC stands for mass flow controller.
**Figure 6.2.** ESI-MS of aqueous Na$_2$S$_2$O$_3$ and gaseous O$_3$ reaction products. (100 μM Na$_2$S$_2$O$_3$, pH 6.2) droplets in the presence of 640 ppm O$_3$(g) (─), and in its absence (—). A) m/z = 112 (S$_2$O$_3^-$); B) 135 (NaS$_2$O$_3^-$); C) 293 [Na$_3$(S$_2$O$_3$)$_2$]; P) 80 (S$_2$O$_6^{2-}$); Q) 97 (HSO$_4^-$); R) 119 (NaSO$_4^-$); S) 261 [Na$_3$(SO$_4$)$_2$]

![ESI-MS of Na$_2$S$_2$O$_3$ and O$_3$](image)

**Figure 6.3.** ESI-MS of aqueous Na$_2$S$_2$O$_3$-NaI droplets and gaseous O$_3$ reaction products. (100 μM Na$_2$S$_2$O$_3$ + 100 μM NaI, pH 6.2) microdroplets in the presence of 760 ppm O$_3$(g) (─), and in its absence (—). D) m/z = 127 (I$^-$); E) 277 (NaI$_2^-$); U) 159 (IO$_2^-$), V) 175 (IO$_3^-$), W) 381 (I$_3^-$), X) 207 (ISO$_3^-$), Y) 239 (IS$_2$O$_3^-$), Z) 255 (IS$_2$O$_4^-$)

![ESI-MS of Na$_2$S$_2$O$_3$-NaI and O$_3$](image)
Figure 6.4. Na$_2$S$_2$O$_3$-NaI$_{(aq,drop)}$ and O$_3$(g) reaction products vs. [O$_3$(g)]. (100 µM Na$_2$S$_2$O$_3$ + 100 µM NaI, pH 6.2) A) ESMS signal intensities at m/z = 112 (S$_2$O$_3^-$, ●), 127 (I$^-$, ○), and 135 (NaS$_2$O$_3^-$, ▲) vs. [O$_3$(g)]. B) ESMS signal intensities at m/z = 80 (S$_2$O$_6^{2-}$, △), 97 (HSO$_4^-$, ○), 175 (IO$_3^-$, ■), and 381 (I$_3^-$, □) vs. [O$_3$(g)]. C) ESMS signal intensities at m/z = 207 (ISO$_3^-$, ◊), 239 (IS$_2$O$_3^-$, ♦) vs. [O$_3$(g)]
**Figure 6.5.** ESI-MS HSO\(_4^-\)/S\(_2\)O\(_6^{2-}\) signal ratio vs. [O\(_3\)(g)]. Ratio of signal intensities at m/z = 97 and 80: I(HSO\(_4^-\))/I(S\(_2\)O\(_6^{2-}\)) vs. [O\(_3\)(g)] in (100 μM Na\(_2\)S\(_2\)O\(_3\) + 100 μM NaI, pH 6.2) microdroplets

![Graph showing the relationship between HSO\(_4^-\)/S\(_2\)O\(_6^{2-}\) signal ratio and [O\(_3\)] ppm.](image)

**Figure 6.6.** Na\(_2\)S\(_2\)O\(_3\)-NaI\(_{aq\_drop}\) and O\(_3\)(g) reaction products vs. [O\(_3\)(g)]. Normalized ESI-MS signal intensities I at m/z = 97 (HSO\(_4^-\)), 175 (IO\(_3^-\)), 207 (ISO\(_3^-\)), and 239 (IS\(_2\)O\(_3^-\)) vs. [O\(_3\)(g)] in (100 μM Na\(_2\)S\(_2\)O\(_3\) + 100 μM NaI, pH 6.2) microdroplets

![Graph showing the relationship between normalized signal intensities and [O\(_3\)] ppm.](image)
**Figure 6.7.** IS$_2$O$_3^-$ signal intensities vs. [Na$_2$S$_2$O$_3$] and [NaI]. A) [Na$_2$S$_2$O$_3$]$_0$ in (Na$_2$S$_2$O$_3$ + 30 μM NaI, pH 6.2) microdroplets at [O$_3$(g)] = 350 ppm, and B) [NaI]$_0$ in (30 μM Na$_2$S$_2$O$_3$ + NaI, pH 6.2) microdroplets at [O$_3$(g)] = 300 ppm

![Graph A](image1.png)

![Graph B](image2.png)
Figure 6.8. Normalized I and S$_{2}$O$_3^-$ ESI-MS signal intensities vs. [O$_3$$_{(g)}$]. A) m/z = 127 (I) ([NaI]$_0$ = [Na$_2$S$_2$O$_3$]$_0$ = 30 μM) (Δ), ([NaI]$_0$ = 300, [Na$_2$S$_2$O$_3$]$_0$ = 30 μM) (○), and ([NaI]$_0$ = 30, [Na$_2$S$_2$O$_3$]$_0$ = 300 μM) (●), and B) m/z = 112 (S$_2$O$_3^-$) in: ([NaI]$_0$ = [Na$_2$S$_2$O$_3$]$_0$ = 30 μM) (▽), ([NaI]$_0$ = 300, [Na$_2$S$_2$O$_3$]$_0$ = 30 μM) (□), and ([NaI]$_0$ = 30, [Na$_2$S$_2$O$_3$]$_0$ = 300 μM) (■)
Figure 6.9. Collision-induced dissociation of Na$_2$S$_2$O$_3$-NaI$_{\text{aq}}$ and O$_3$(g) products. A) ([NaI]$_0$ = [Na$_2$S$_2$O$_3$]$_0$ = 100 μM) microdroplets at [O$_3$(g)] = 410 ppm. I$^-$ (○); ISO$_3^-$ (▼); IS$_2$O$_3^-$ (▲); I$_3^-$ (◊). B) ESI-MS signal intensities vs. center of mass energy. I$_3^-$ (◊); ISO$_3^-$ (▼); IS$_2$O$_3^-$ (▲)
# Tables

**Table 6.1.** Kinetic data for Na$_2$S$_2$O$_3$-NaI(aq) and O$_3$(g) reactions at 298 K

<table>
<thead>
<tr>
<th>eq#</th>
<th>Reaction</th>
<th>Rate or equilibrium constants (M, s units)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>$I_2 + I^- \rightleftharpoons I_3^-$</td>
<td>721 M$^{-1}$</td>
<td>56</td>
</tr>
<tr>
<td>6.2</td>
<td>$I_2 + S_2O_3^{2-} \rightleftharpoons I_2S_2O_3^{2-}$</td>
<td>$7.8 \times 10^9$ M$^{-1}$s$^{-1}$</td>
<td>41</td>
</tr>
<tr>
<td>6.2'</td>
<td>$I_3^- + S_2O_3^{2-} \rightleftharpoons I_2S_2O_3^{2-} + I^-$</td>
<td>$2.5 \times 10^7$ s$^{-1}$</td>
<td>41</td>
</tr>
<tr>
<td>6.3</td>
<td>$I_3^- + S_2O_3^{2-} \rightleftharpoons I_2S_2O_3^{2-} + I^-$</td>
<td>$4.2 \times 10^8$ M$^{-1}$s$^{-1}$</td>
<td>41</td>
</tr>
<tr>
<td>6.3'</td>
<td>$I_2S_2O_3^{2-} \rightleftharpoons IS_2O_3^- + I^-$</td>
<td>0.245 M</td>
<td>41</td>
</tr>
<tr>
<td>6.4</td>
<td>$I_3^- + S_2O_3^{2-} \rightleftharpoons I_2S_2O_3^{2-} + I^-$</td>
<td>$9.5 \times 10^3$ s$^{-1}$</td>
<td>41</td>
</tr>
<tr>
<td>6.4'</td>
<td>$I_2S_2O_3^{2-} \rightleftharpoons IS_2O_3^- + I^-$</td>
<td>N/A</td>
<td>41</td>
</tr>
<tr>
<td>6.5</td>
<td>$IS_2O_3^- + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$</td>
<td>$1.3 \times 10^6$ M$^{-1}$s$^{-1}$</td>
<td>41</td>
</tr>
<tr>
<td>6.6</td>
<td>$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$</td>
<td>N/A</td>
<td>41</td>
</tr>
<tr>
<td>6.7</td>
<td>$I_2 + HSO_3^- \rightarrow I_2SO_3^{2-} + H^+$</td>
<td>$1.7 \times 10^9$ M$^{-1}$s$^{-1}$</td>
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</tr>
<tr>
<td>6.8</td>
<td>$I_3^- + HSO_3^- \rightarrow I^- + I_2SO_3^{2-} + H^+$</td>
<td>$1.5 \times 10^7$ M$^{-1}$s$^{-1}$</td>
<td>44</td>
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<td>6.9</td>
<td>$I_2SO_3^{2-} \rightarrow ISO_3^- + H^+$</td>
<td>N/A</td>
<td>44</td>
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<td>6.10a</td>
<td>$S_2O_3^{2-} + O_3 \rightarrow S_2O_6^{2-}$</td>
<td>$3.7 \times 10^8$ M$^{-1}$s$^{-1}$</td>
<td>38</td>
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<tr>
<td>6.10b</td>
<td>$\rightarrow SO_4^{2-} + SO_2$</td>
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<tr>
<td>6.11</td>
<td>$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+$</td>
<td>$1.3 \times 10^{-2}$ M</td>
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<tr>
<td>6.12</td>
<td>$I^- + O_3 + H^+ \rightarrow HOI + O_2$</td>
<td>$1.2 \times 10^9$ M$^{-1}$s$^{-1}$</td>
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<tr>
<td>6.13</td>
<td>$HOI + 2O_3 \rightarrow IO_3^- + 2O_2 + H^+$</td>
<td>$3.6 \times 10^4$ M$^{-1}$s$^{-1}$</td>
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</tr>
<tr>
<td>6.14</td>
<td>$HOI + I^- + H^+ \rightarrow I_2 + H_2O$</td>
<td>$4.4 \times 10^{12}$ M$^{-2}$s$^{-1}$</td>
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</tr>
<tr>
<td>6.15</td>
<td>$HOI + S_2O_3^{2-} + H^+ \rightarrow IS_2O_3^- + H_2O$</td>
<td>N/A</td>
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<tr>
<td>6.16</td>
<td>$ISO_3^- + H_2O \rightarrow I^- + SO_4^{2-} + 2H^+$</td>
<td>$298$ s$^{-1}$</td>
<td>44</td>
</tr>
</tbody>
</table>
References


(52) Gmelins Handbuch der anorganischen Chemie, Schwefel, Teil B, Lieferung 2;


(56) McIndoe, J. S.; Tuck, D. G. Dalton Trans. 2003, 2, 244.


(64) Eigen, M.; Kustin, K. J. Am. Chem. Soc. 1962, 84, 1355.