

## Chapter 7

# Mass Spectrometric Detection of Ozonation Products and Intermediates of Aqueous Aerosol Iodide and/or Sulfite: Implications for Interfacial Kinetics and Iodide-Mediated Sulfite Oxidation

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## Abstract

The oxidations of sulfite and iodide in the interfacial layers of aqueous droplets exposed for  $\sim 1$  to 10 ms to  $\text{O}_3(\text{g})$  are investigated by online mass spectrometry of electrostatically ejected anions. S(IV) oxidation losses in  $\text{Na}_2\text{SO}_3$  microdroplets are proportional to  $[\text{S(IV)}][\text{O}_3(\text{g})]$  up to  $\sim 90\%$  conversion. In contrast, although  $\text{I}^-$  is more abundant than  $\text{HSO}_3^-$  in the interfacial layers of equimolar ( $\text{Na}_2\text{SO}_3 + \text{NaI}$ ) microdroplets and  $\sim 3$  times more reactive than  $\text{HSO}_3^-$  toward  $\text{O}_3(\text{aq})$  in bulk solution, it is converted with minimal loss to  $\text{I}_3^-$  and  $\text{IO}_3^-$ , plus a persistent  $\text{ISO}_3^-$  intermediate. These observations reveal unanticipated interfacial gradients, reactivity patterns, and transport phenomena that had not been taken into account in previous treatments of fast gas-liquid reactions and may be of importance for gas-aerosol reactions in the Marine Boundary Layer.

## Introduction

The number density, size, and optical and chemical properties of atmospheric aerosols significantly impact the Earth's climate<sup>1</sup>. Aerosols absorb/scatter solar radiation<sup>2</sup>, but also support key chemical processes<sup>3,4,5</sup>. For example,  $\text{SO}_2(\text{g})$  is a pervasive anthropogenic contaminant, which largely partitions into aqueous aerosol droplets<sup>6,7</sup>, where it is assumed to be rapidly oxidized by the sparingly water-soluble  $\text{O}_3(\text{g})$ <sup>8</sup> in a process that mediates tropospheric sulfur chemistry<sup>9,10,11</sup>. The oxidation of  $\text{SO}_2$  by  $\text{O}_3$  has been thoroughly investigated in bulk water<sup>12,13</sup> and aqueous sulfuric acid<sup>14,15,16</sup>. Since  $\text{SO}_3^{2-}$  is far more reactive than  $\text{HSO}_3^-$  [ $\text{pK}_a(\text{HSO}_3^-) = 6.30$ ]<sup>17</sup>, overall reaction rates markedly increase above  $\text{pH} \sim 6$ .

Gas-liquid reactions have been previously investigated by monitoring the uptake of reactive gases by stationary trains of  $\sim 10$ – $100$   $\mu\text{m}$  droplets at relatively low pressures ( $\sim 10$ – $50$  Torr)<sup>18</sup> or on coated-wall Knudsen flow reactors<sup>19</sup>, and the results interpreted on the basis of continuous models parametrized with kinetic and transport data in bulk fluids<sup>20</sup>. However, there is now firm evidence that air/liquid interfaces are unique reaction media. Enhanced reactivity<sup>18,21</sup>, selective anion enrichment<sup>22</sup>, and higher acidity<sup>23</sup>, have been predicted for these interfaces. These predictions remain to be thoroughly evaluated<sup>24</sup>. Recently we reported experiments in which the composition of the interfaces of aqueous halide microdroplets undergoing chemical reaction with  $\text{O}_3(\text{g})$  was monitored by mass spectrometry with millisecond time resolution<sup>25,26</sup>. Here we report a kinetic and mechanistic study of interfacial  $\text{S(IV)/I}^- + \text{O}_3(\text{g})$  aerosol chemistry that further illustrates the peculiarities of these systems.

## Experimental

Experiments were performed in the spraying chamber of a commercial electrospray mass spectrometer (HP-1100). Sodium iodide and/or bisulfite solutions (10–100  $\mu\text{M}$ ) were directly infused (50  $\mu\text{L min}^{-1}$ ) into the chamber through a grounded stainless steel needle injector (100  $\mu\text{m}$  internal diameter, 150  $\mu\text{m}$  external diameter) surrounded by a coaxial sheath (250  $\mu\text{m}$  internal diameter) issuing 0.5  $\text{L min}^{-1}$  of nebulizer  $\text{N}_2$  gas. The difference between the exit velocities of the liquid jet (10.6  $\text{cm s}^{-1}$ ) and nebulizer gas ( $2.65 \times 10^4 \text{ cm s}^{-1}$ ) is so large that the drag imposed on the liquid breaks it apart into microdroplets. The terminal velocities reached by these microdroplets are between  $10^2$  and  $10^3 \text{ cm s}^{-1}$ <sup>27</sup>. The transit times of microdroplets across the  $\sim 0.5 \text{ cm}$  intersection with the ozone plume are  $1 \text{ ms} < \tau < 10 \text{ ms}$ . It should be emphasized that the pneumatically generated spray from the grounded nozzle injector is comprised of a normal distribution of weakly charged droplets centered at zero charge, as expected from statistical charge separation in the fragmentation of a neutral liquid jet<sup>25,26</sup>. This mechanism naturally discriminates against the production of highly charged droplets. Charged droplets of either sign can be electrostatically extracted into the mass spectrometer by applying a suitable bias ( $\pm 3\text{--}4 \text{ kV}$ ) at its inlet port.

After leaving the reaction zone, microdroplets rapidly evaporate, leading to sudden volume reduction and concomitant surface charge repulsion. Such droplets become mechanically unstable when Coulombic repulsive forces overtake liquid cohesive forces, causing the droplets to ‘explode’ by shedding their interfacial films to produce smaller droplets. This phenomenon repeats itself until nanometer droplets are formed. Ions will be field-ejected from the outer layers of these last-generation nanodroplets<sup>28</sup>. This

analytical technique therefore reports the composition of the nanodroplets produced from the outer interfacial layers of microdroplets that had reacted with  $\text{O}_3(\text{g})$ . Typical instrumental parameters were as follows: drying gas temperature,  $340^\circ\text{C}$ ; nebulizer pressure, 30 PSI; collector capillary voltage, +3.5 kV; fragmentor voltage, 19 V. Further experimental details and results were reported elsewhere<sup>25,29</sup>.

Ozone was generated by flowing  $\text{O}_2(\text{g})$  (0.1 L/min, Air Liquid America Co.) through a commercial ozonizer (Ozone Solutions), diluted tenfold with ultrapure  $\text{N}_2(\text{g})$  (0.9 L/min), and quantified by UV absorption spectrophotometry (HP 8452) [using absorption cross-sections  $\sigma(250\text{ nm}) = 1.1 \times 10^{-17}\text{ cm}^2\text{ molecule}^{-1}$ , and  $\sigma(300\text{ nm}) = 3.9 \times 10^{-19}\text{ cm}^2\text{ molecule}^{-1}$  at 298 K]<sup>30</sup> prior to being injected into the chamber. Actual  $[\text{O}_3(\text{g})]$  in the reaction chamber is about 10 times smaller than the values determined in this manner, due to further dilution by the hot ( $250^\circ\text{C}$ )  $\text{N}_2$  drying gas (10 L/min). Gas flows were regulated by mass flow controllers (MKS). Solutions were prepared with MilliQ water that had been previously purged with ultrapure  $\text{N}_2(\text{g})$  for at least 30 min to prevent reactant autooxidation. NaI (> 99 %) and  $\text{Na}_2\text{SO}_3$  (> 98 %) were obtained from Sigma-Aldrich. Solution pH was measured with a calibrated pH meter (VWR, SB21). Molecular formula assignments of S-containing species could be confirmed from the (M+2)/M ratios associated with natural abundance sulfur isotopes:  $^{34}\text{S}/^{32}\text{S} = 0.044$ .

## Results and Discussion

The typical data obtained from these experiments is shown in Figure 7.1, which displays the mass spectra of aqueous  $\text{Na}_2\text{SO}_3$  microdroplets in the absence and presence of ozone. Signals at  $m/z = 61$ , 81, and 97, which are ascribed to  $\text{HCO}_3^-$  (from atmospheric  $\text{CO}_2$ ),  $\text{HSO}_3^-$ , and  $\text{HSO}_4^-$  (a pervasive byproduct of S(IV) autooxidation), respectively, are observed in the absence of  $\text{O}_3(\text{g})$  (Figure 7.1, lower panel)<sup>31</sup>. Upon addition of  $\text{O}_3(\text{g})$ ,

$\text{HSO}_4^-$  is significantly enhanced, and new signals appear at  $m/z = 119$  ( $\text{NaSO}_4^-$ ) and  $m/z = 261$  [ $\text{Na}_3(\text{SO}_4)_2^-$ ] (Figure 7.1, upper panel), indicating extensive  $\text{S(IV)} \rightarrow \text{S(VI)}$  processing. The dependences of  $\text{HSO}_3^-$  and  $\text{HSO}_4^-$  interfacial concentrations on  $[\text{O}_3(\text{g})]$  in microdroplets that had been exposed to  $\text{O}_3(\text{g})$  for  $\sim 1$  to 10 ms are shown in Figure 7.2a.

The reactant conversion vs.  $[\text{O}_3(\text{g})]$  data of Figure 7.2a cannot be analyzed using integrated kinetic equations for constant volume batch reactors, such as those employed in conventional studies, in which concentrations are expressed as explicit functions of time.<sup>32</sup> The chemical events probed in present experiments actually occur in a few-nm-thick open films that exchange ionic solutes with the droplets interior and  $\text{O}_3(\text{g})$  with the gas-phase, in  $\sim 1$  to 10 ms time frames. The analysis of gas-liquid reactions has been conventionally carried out via coupled partial differential equations associated with diffusional transport in homogeneous media separated by sharp boundaries<sup>33</sup>. Such methodology may not be appropriate to our films, because diffusional transport applies to large molecular assemblies spread over lengths much longer than mean free paths, and the medium in which transport takes place is no longer homogeneous or isotropic close to the interface, where compositional gradients arise even in the absence of chemical reaction.<sup>29</sup> Therefore, the issue of whether our findings correspond to surface or bulk reactive transformations should be decided by an in-depth evaluation of the data rather than by strict compliance with previously established models<sup>33</sup>.

By assuming that the interfacial liquid films are in solubility or collisional equilibrium with  $\text{O}_3(\text{g})$  (i.e.,  $[\text{O}_3(\text{int})] \propto [\text{O}_3(\text{g})]$ ), we can tentatively treat them as unidimensional flow reactors where reactive losses are offset by reactant inflow from the underlying layers.

$$d[S(IV)]/dt = \{[S(IV)] - [S(IV)]_0\} \tau^{-1} = -k_R [S(IV)]^n [O_3(g)] + \{[S(IV)]_0 - [S(IV)]\} \tau_t^{-1} \quad (7.1)$$

In eq. 7.1,  $\tau$  is the average contact time between microdroplets and  $O_3(g)$ ,  $\tau_t$  is the average time for bulk  $S(IV)$  to replenish a partially depleted film,  $k_R$  is an effective reaction rate constant, and  $n$  is a phenomenological kinetic order that reflects the influence of mass transport over a particular range of experimental conditions<sup>24,34</sup> Figure 7.2b shows that  $\gamma = [HSO_3^-]/[HSO_3^-]_0$  closely follows a single exponential decay to a nonzero limiting value:  $\gamma = \gamma_\infty + \gamma_0 \exp\{-\beta [O_3(g)]\}$ , which is consistent with an interfacial chemical reaction largely unperturbed by  $S(IV)$  transport from the droplets core below  $\sim 500$  ppm  $O_3(g)$ . However, the fact that  $\gamma_\infty \sim 0.1$  at  $\sim 1200$  ppm  $O_3(g)$  indicates that conversion is ultimately limited by mass transfer. Accordingly, a  $[S(IV)]_0 - [S(IV)]/[S(IV)]^n$  vs.  $k_R [\tau/(1 + \tau \tau_t^{-1})] [O_3(g)]$  plot (from eq. 7.1) is linearized with  $n = 1.0 \pm 0.1$  ( $r^2 = 0.998$ ) independent of  $[S(IV)]_0$  (Figure 7.2c). A kinetic order  $n$  significantly smaller than 1 would have indicated that the interfacial film is competitively replenished by intradroplet transport. The oxidation of  $I^-$  under similar conditions yields, for example:  $n = 0.67 \pm 0.03$ .<sup>25</sup> These results are quite reproducible under various experimental conditions, although we have no direct control of the droplet size distribution.

Figure 7.3 shows the mass spectra of  $NaI/Na_2SO_3$  microdroplets in the absence (Figure 7.3, lower panel) and presence (Figure 7.3, upper panel) of  $O_3(g)$ . The  $m/z = 175$  and  $381$  product signals correspond to  $IO_3^-$  and  $I_3^-$ , whereas the dominant  $m/z = 207$  signal is assigned to the  $ISO_3^-$  intermediate.  $HSO_4^-$ ,  $IO_3^-$ , and  $ISO_3^-$  signal intensities monotonically increase at higher  $[O_3(g)]$  (Figure 7.4). In contrast,  $I_3^-$  displays a broad

maximum at  $\sim 80$  ppm  $O_3(g)$ . These processes likely proceed via the set of reactions shown in Table 7.1. The fact that  $I_3^-$  signals peak and then decline with  $[O_3(g)]$ , while  $IO_3^-$  signals keep increasing, follows from  $I^-$  and  $O_3$  competition for the HOI precursor, eqs. 7.1, 7.10, and 7.11 in Table 7.1 (Scheme 7.1). We found that  $I^-$  signals are larger than those of  $HSO_3^-$  in an equimolar NaI/Na<sub>2</sub>SO<sub>3</sub> solution, and also larger than in a NaI solution of the same concentration. In other words,  $I^-$  competes favorably with  $HSO_3^-$  for the air/water interface, even at sub-millimolar bulk concentrations and in the absence of  $O_3(g)$ . Thus,  $I^-$  is enriched near the air-water interface proper, while  $HSO_3^-$  lies behind in the deeper layers under stationary conditions. The differential affinity of the various anions for the interfacial region is a phenomenon that has not been taken into account in previous work on gas-liquid reactions.

Considering that S(IV) mixtures at pH 6.6 (which consist of  $0.7 HSO_3^- + 0.3 SO_3^{2-}$ ) react with a composite second-order rate constant:  $k^{II}[S(IV) + O_3] \sim 4 \times 10^8 M^{-1} s^{-1}$ , that is  $\sim 3$  times smaller than  $k^{II}(I^- + O_3) = 1.2 \times 10^9 M^{-1} s^{-1}$  in bulk solution, the fact that  $I^-$  is oxidized to  $IO_3^-$ ,  $I_3^-$ , and  $ISO_3^-$  without apparent loss of interfacial  $I^-$  is an unexpected result (Figure 7.4b). The  $IO_3^-$  and  $I_3^-$  yields:  $Y(X) = [S(X^-) f_x^{-1}] / [S(I^-)_0 - S(I^-)]$ , measured in NaI/Na<sub>2</sub>SO<sub>3</sub> solutions at  $[O_3(g)] = 210$  ppm,  $[NaI] = 10 \mu M$ , are also anomalous because they increase with  $[Na_2SO_3]$ , eventually exceeding unity (Figure 7.5).  $S(X)$ s are ESMS signal intensities, and  $f_x$ s the relative response factors ( $f_{IO_3^-} = S(IO_3^-)/S(I^-) = 0.80$ , and  $f_{I_3^-} = S(I_3^-)/S(I^-) = 0.76$ ) determined under present experimental conditions.

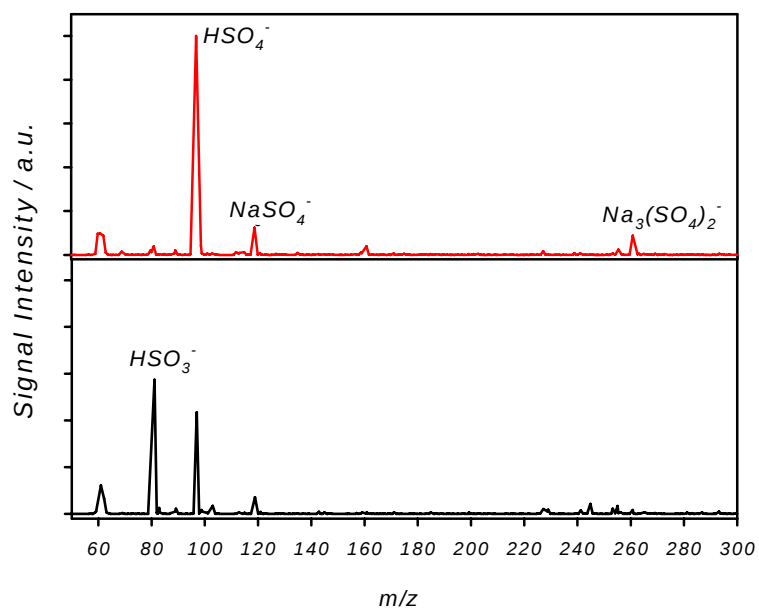
It is apparent that the interfacial layers are efficiently replenished with  $I^-$  from the droplet's core during reaction with  $O_3(g)$ , and that this process is enhanced in the presence of S(IV). This phenomenon arises from interfacial anion fractionation. As  $O_3$

penetrates the droplets, it largely reacts with  $\text{I}^-$  first, but increasingly so with  $\text{HSO}_3^-$  further inside, thereby minimizing  $\text{I}^-$  depletion from the underlying region that eventually resupplies the outermost layers.  $[\text{S(IV)}] \times [\text{I}^-]$  also peaks in this region, maximizing  $\text{ISO}_3^-$  production, whose hydrolysis, eq. 7.6, regenerates  $\text{I}^-$  and contributes to buffering interfacial  $\text{I}^-$  concentrations (Scheme 7.1). The  $\text{ISO}_3^-$  intermediate may derive from  $\text{I}_2/\text{I}_3^-$  via reactions R2-R5<sup>35,36,37,38</sup>, but more likely from HOI via eq. 7.12. The fact that  $\text{ISO}_3^-$  signals are  $\sim 20$  times more intense than those of  $\text{IO}_3^-$  and  $\text{I}_3^-$  under most conditions supports the efficient scavenging of HOI, the initial precursor of  $\text{IO}_3^-$  and  $\text{I}_3^-$  by S(IV), reactions R10–R12.

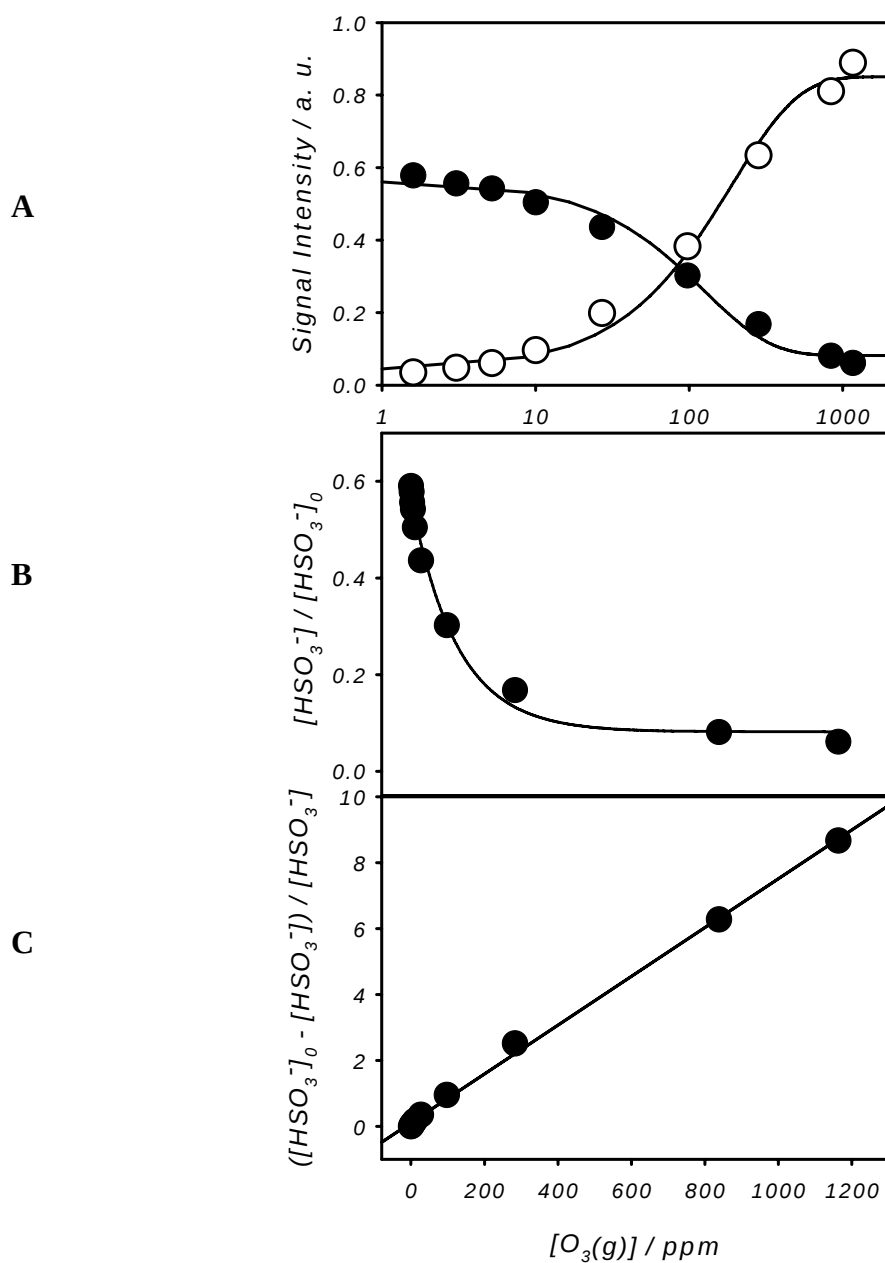
In summary, we have shown that it is possible to monitor fast reactions in the interfacial layers of aqueous microdroplets during exposure to a reactive gas by mass spectrometry. The larger propensity of  $\text{I}^-$  vs.  $\text{HSO}_3^-$  for the air-water interface influences their reactions with  $\text{O}_3(\text{g})$  via a combination of physical and chemical processes. Mutually inert solutes can compete for reactive gases in ways that are beginning to be understood.

## Figures

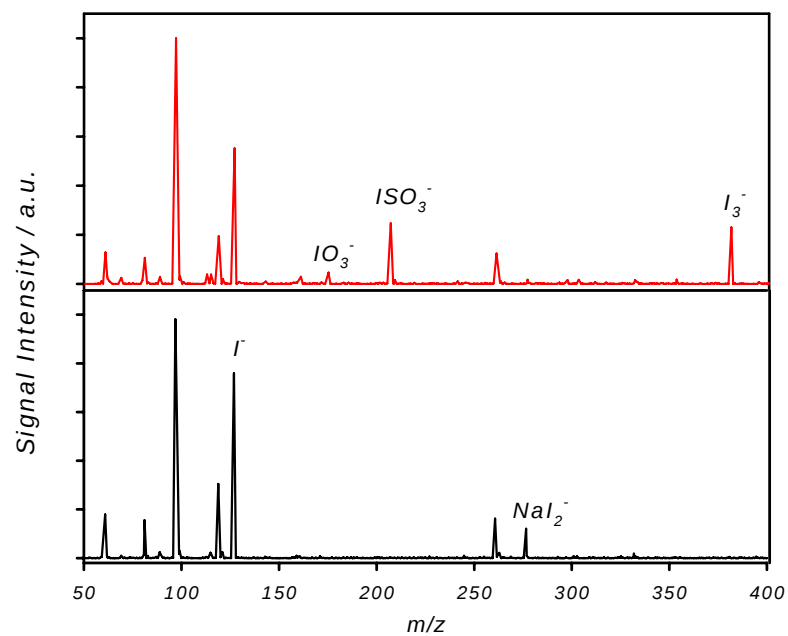
**Figure 7.1.** ESI-MS of aqueous  $\text{Na}_2\text{SO}_3$  droplets and gaseous  $\text{O}_3$  reaction products. 0.1 mM  $\text{Na}_2\text{SO}_3(\text{aq})$  solutions at pH 6.8 in the presence of 670 ppm  $\text{O}_3(\text{g})$  (—), and in the absence of  $\text{O}_3(\text{g})$  (—)



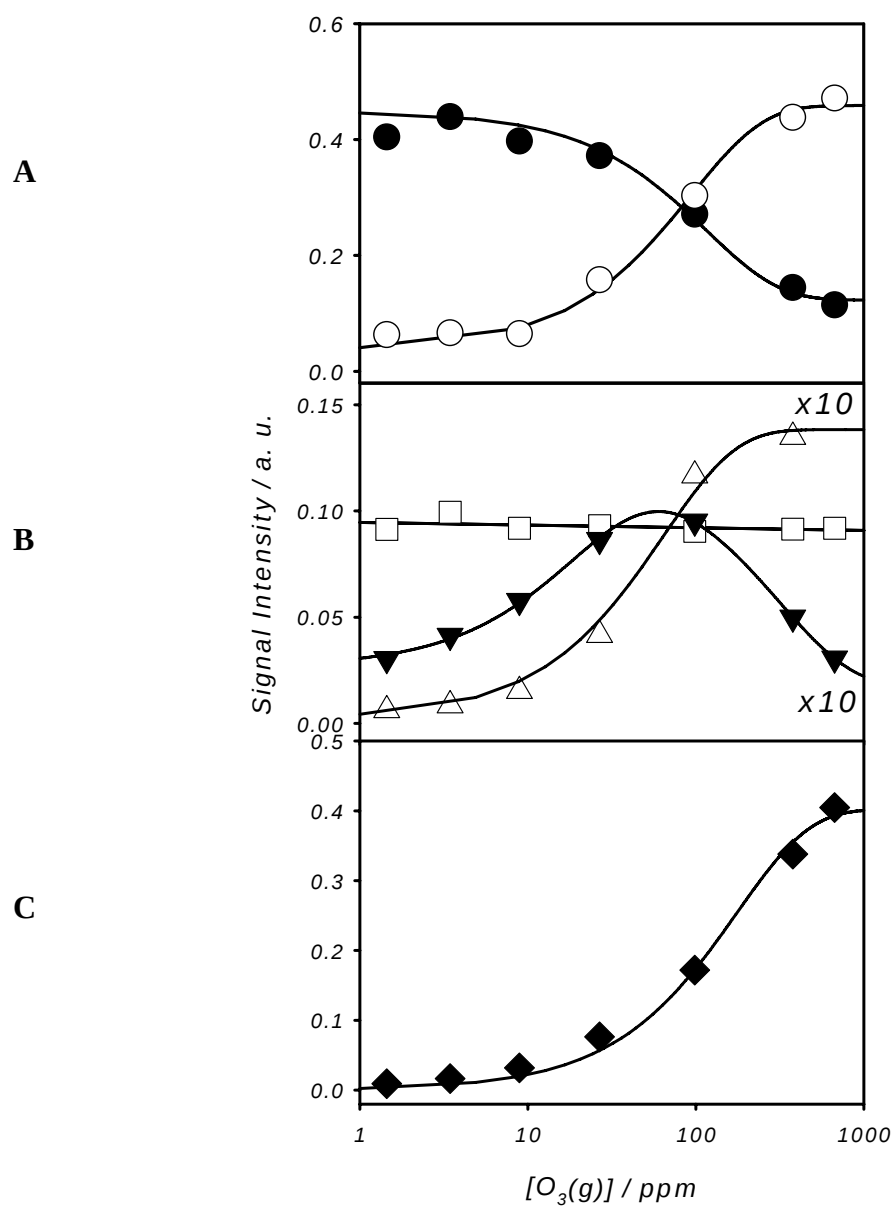
**Figure 7.2.**  $\text{HSO}_3^-$  and  $\text{HSO}_4^-$  absolute and relative ESI-MS signals vs.  $[\text{O}_3(\text{g})]$ . A) Mass spectral signal intensities:  $\text{HSO}_3^-$  (●),  $\text{HSO}_4^-$  (○) versus  $[\text{O}_3(\text{g})]$  in microdroplets produced by spraying 0.1 mM  $\text{Na}_2\text{SO}_3$  aqueous solutions at pH 6.8. B) Single exponential plot of  $\text{HSO}_3^-$  losses. C) Linearized kinetic plot of  $\text{HSO}_3^-$  losses



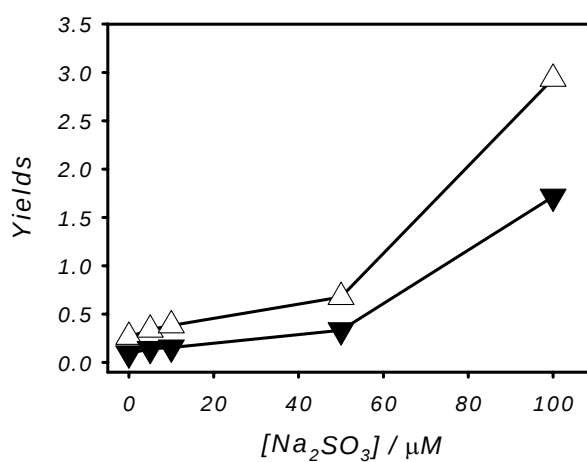
**Figure 7.3.** ESI-MS of aqueous  $\text{Na}_2\text{SO}_3$ -NaI droplets and gaseous  $\text{O}_3$  reaction products. (0.1 mM  $\text{Na}_2\text{SO}_3$  + 0.1 mM NaI) aqueous solutions at pH 6.6 in the presence of 50 ppm  $\text{O}_3(\text{g})$  (—), and in the absence of  $\text{O}_3(\text{g})$  (—). See also Figure 7.1 for further spectral assignments



**Figure 7.4.** A) Mass spectral intensities of  $\text{HSO}_3^-$  ( $\circ$ ),  $\text{HSO}_4^-$  ( $\bullet$ ). B)  $\text{I}^-$  ( $\square$ ),  $\text{IO}_3^-$  ( $\times 10$ ,  $\Delta$ ),  $\text{I}_3^-$  ( $\times 10$ ,  $\blacktriangledown$ ). C)  $\text{ISO}_3^-$  ( $\blacklozenge$ ) signals vs.  $[\text{O}_3(\text{g})]$  in microdroplets produced by spraying (0.1 mM  $\text{Na}_2\text{SO}_3$  + 0.01 mM  $\text{NaI}$ ) aqueous solutions at pH 6.6

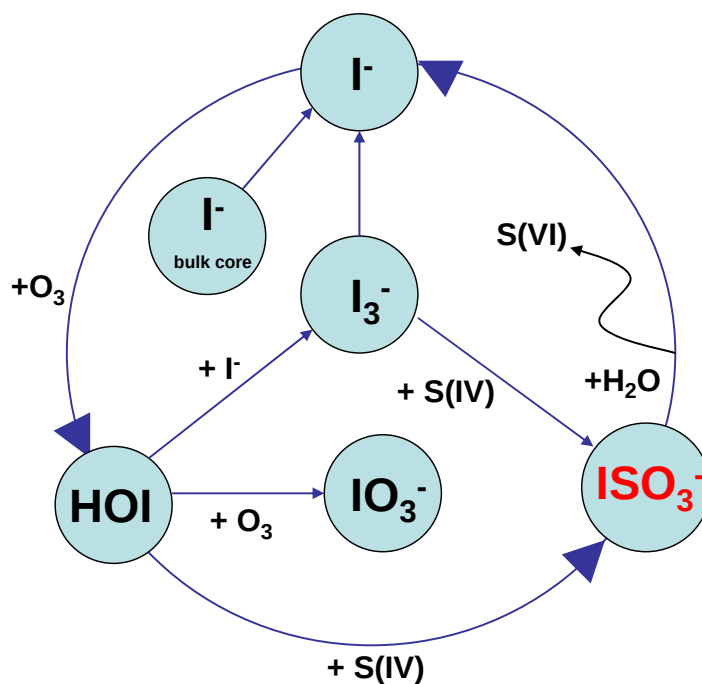


**Figure 7.5.**  $\text{IO}_3^-$  and  $\text{I}_3^-$  iodide-normalized yields vs.  $[\text{Na}_2\text{SO}_3]$ .  $\text{IO}_3^-$  ( $\Delta$ ) and  $\text{I}_3^-$  ( $\blacktriangledown$ ) yields based on interfacial  $\text{I}^-$  losses (see text for definition of yield) vs.  $[\text{Na}_2\text{SO}_3]$  in microdroplets produced by spraying ( $\text{Na}_2\text{SO}_3 + 0.01 \text{ mM NaI}$ ) aqueous solutions at pH 6.6 in 210 ppm  $\text{O}_3(\text{g})$



## Schemes

**Scheme 7.1.** Catalytic cycle for iodide-mediated ozone oxidation of sulfite



## Tables

**Table 7.1.** Kinetic data for  $\text{Na}_2\text{SO}_3\text{-NaI}_{(\text{aq})}$  and  $\text{O}_{3(\text{g})}$  reactions at 298 K

| eq#  | Reaction                                                                                      | Rate, equilibrium constants in M, s units          | Ref. |
|------|-----------------------------------------------------------------------------------------------|----------------------------------------------------|------|
| 7.1  | $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$                                     | $721 \text{ M}^{-1}$                               | 39   |
| 7.2  | $\text{I}_2 + \text{SO}_3^{2-} \rightarrow \text{ISO}_3^- + \text{I}^-$                       | $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$    | 35   |
| 7.3  | $\text{I}_3^- + \text{SO}_3^{2-} \rightarrow \text{ISO}_3^- + 2\text{I}^-$                    | $2.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$    | 35   |
| 7.4  | $\text{I}_2 + \text{HSO}_3^- \rightarrow \text{I}^- + \text{ISO}_3^- + \text{H}^+$            | $1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$    | 35   |
| 7.5  | $\text{I}_3^- + \text{HSO}_3^- \rightarrow 2\text{I}^- + \text{ISO}_3^- + \text{H}^+$         | $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$    | 35   |
| 7.6  | $\text{ISO}_3^- + \text{H}_2\text{O} \rightarrow \text{I}^- + \text{SO}_4^{2-} + 2\text{H}^+$ | $298 \text{ s}^{-1}$                               | 35   |
| 7.7  | $\text{SO}_3^{2-} + \text{O}_3 \rightarrow \text{SO}_4^{2-} + \text{O}_2$                     | $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$    | 9    |
| 7.8  | $\text{HSO}_3^- + \text{O}_3 \rightarrow \text{HSO}_4^- + \text{O}_2$                         | $3.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$    | 9    |
| 7.9  | $\text{I}^- + \text{O}_3 + \text{H}^+ \rightarrow \text{HOI} + \text{O}_2$                    | $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$    | 40   |
| 7.10 | $\text{HOI} + 2\text{O}_3 \rightarrow \text{IO}_3^- + 2\text{O}_2 + \text{H}^+$               | $3.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$    | 41   |
| 7.11 | $\text{HOI} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$            | $4.4 \times 10^{12} \text{ M}^{-2} \text{ s}^{-1}$ | 42   |
| 7.12 | $\text{HOI} + \text{SO}_3^{2-} + \text{H}^+ \rightarrow \text{ISO}_3^- + \text{H}_2\text{O}$  | N/A                                                | N/A  |

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