New and Surprising Experimental Results from the Oxidation of Sulfinic and Sulfonic Acids

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Thiourea, $(H_2N)_2C{=}S$, aminoiminomethanesulfinic acid, $H_2N(HN{=})CSO_2H$ (AIMSA), and aminoiminomethanesulfonic acid, $H_2N(HN{=})CSO_3H$ (AIMSOA) are all oxidized by mild oxidizing agents to a sulfate and an organic residue. AIMSA and AIMSOA are the postulated intermediates in the oxidation pathway of thiourea to sulfate. The oxidation of AIMSOA is accompanied by a cleavage of the C−S bond to form sulfate. Surprisingly, freshly prepared solutions of AIMSOA are oxidized by the common oxidants (oxyhalogens and halogens) at rates that are much slower than oxidation rates of AIMSA by the same oxidants. These results seem to suggest that AIMSOA may be structurally different from AIMSA and that the decomposition of AIMSOA to HSO_3^- is the prerequisite to its oxidation. The oxidation pathway of AIMSA to SO_4^{2-} also proceeds through the formation of HSO_3^- and not predominantly through AIMSOA.

Introduction

The ongoing process of improving sulfur-abatement procedures from industrial activity can only be improved if the reaction mechanisms of sulfur reactions are better elucidated. Furthermore, the physiological role of sulfur-based amino acids can also be rationalized if sulfur chemistry is more well-known.[2] We recently established a series of research studies that focused primarily on the kinetics and mechanisms of the oxidations of sulfur compounds by halogens, oxyhalogens, and transition metal ions in an effort to address this very problem.[3]

The compilation of our work resulted in a general mechanism that involves a sulfur center being oxidized, in excess oxidant, via a nonradical two-equivalent-transfer process that produces sulfate as a final product.[4−10] For small organic sulfur compounds, this process gives, successively, the sulfenic, sulfinic, and sulfonic acids. Further oxidation of the sulfonic acid will result in the cleavage of the C−S bond to give sulfate and a urea-type residue, $>C{=}O$.[4] The rate-determining step had been established as the initial oxidation of the thio compound to the unstable sulfenic acid. This general mechanism, applicable to a variety of these small organic sulfur compounds, can be illustrated by our proposed mechanism for the oxidation of thiourea by aqueous bromine:[8]

step 1: $$Br_2(aq) + (H_2N)_2C{=}S + H_2O \rightarrow H_2N(NH)CSOH + 2H^+ + 2Br^-$$

step 2: $$Br_2(aq) + H_2N(NH)CSOH + H_2O \rightarrow H_2N(NH)CSO_2H + 2H^+ + 2Br^-$$

step 3: $$Br_2(aq) + H_2N(NH)CSO_2H + H_2O \rightarrow H_2N(NH)CSO_3H + 2H^+ + 2Br^-$$

step 4: $$Br_2(aq) + H_2N(NH)CSO_3H + 2H_2O \rightarrow (H_2N)_2C{=}O + SO_4^{2-} + 4H^+ + 2Br^-$$

Step 1 forms the sulfenic acid, which is further oxidized in the second step to form the sulfinic acid. The sulfonic acid formed in step 3 is finally oxidized to form SO_4^{2-} in the last step, which is accompanied by a cleavage of the C−S bond.

Although this general mechanism can explain most experimental observations, there were some experimental results that could not be rationalized by this mechanism: (a) in a comparative study of the oxidation of a sulfide, sulfinic acid, and sulfonic acid the oxidation of the sulfinic acid was the fastest while the oxidation of the sulfonic acid was the slowest;[11] (b) the oxidation of thiourea by several oxyhalogens was bistable and produced sulfate in a clock reaction type oxidation to give a lateral instability that produced a traveling wave of acid and sulfate.[12]

Generally, the oxidation of a sulfur center has presented nonlinear and exotic dynamics that include clock reaction mechanisms,[13] chemical oscillations,[14] pH oscillations,[15] and pattern formation.[16] A good grasp of the oxidation mechanisms of a sulfur center is essential for the elucidation of the observed nonlinear dynamics.

The reaction of chlorite with thiourea and substituted thioureas is bistable and autocatalytic and can produce spatial inhomogeneities in acid concentrations in unstirred aqueous environments.[17] It had been accepted that the rapid formation of the acid is from the step that involves the cleavage of the C−S bond in the sulfonic acid intermediate, aminoiminomethanesulfonic acid (AIMSOA), to form sulfate:

$$NH_2(NH)CSO_3H + H_2O \rightarrow (NH_2)_2CO + SO_4^{2-} + 4H^+ + 2e^- \quad (R1)$$

Further experiments have shown that sulfonic acids, in general, are inert and slow-reacting. Organic aminosulfonic acids, especially, are so stable that the C−S bond cannot be cleaved to give sulfate even in the presence of very strong oxidizing agents.[18] The sulfinic acid, aminoiminomethanesulfinic acid (AIMSA, a precursor to AIMSOA in the oxidation chain), is extremely reactive. It is readily oxidized by very mild

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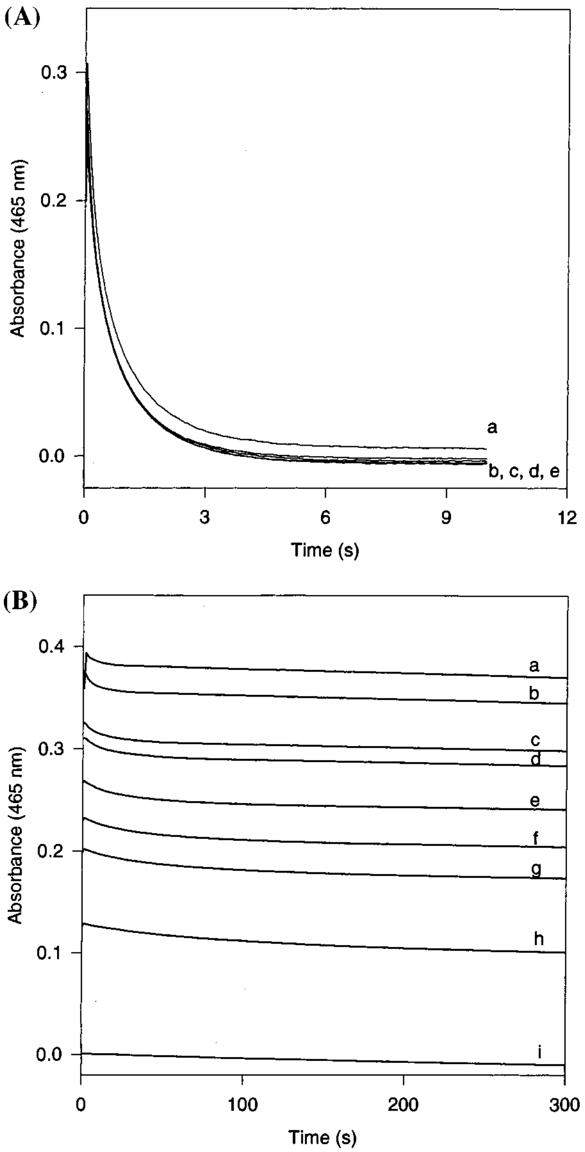


Figure 1. (A) Reaction of aminoiminomethanesulfinic acid, AIMSA, with iodine in excess of AIMSA. $[I_2]_0 = 5.5 \times 10^{-4}$ M; $[AIMSA]_0 = 6.65 \times 10^{-3}$ M. The solutions were aged for (a) 0, (b) 84, (c) 139, (d) 186, and (e) 227 min. (B) Oxidation of aminoiminomethanesulfonic acid, AIMSOA, with aqueous iodine. $[I_2]_0 = 1.1 \times 10^{-3}$ M; $[AIMSOA]_0 = 1.1 \times 10^{-2}$ M. The solutions were aged for (a) 2, (b) 14, (c) 34, (d) 45, (e) 70, (f) 118, (g) 138, (h) 168, and (i) 270 min.

oxidizing agents (e.g., I_2) to sulfate and urea.[3] AIMSOA has not yet been characterized and very little is known about its reactivity.

We present, in this manuscript, a series of experiments that suggest that there may be some fundamental differences in the bonding, structure, and reactivity of AIMSA and AIMSOA. By way of comparison, reactivities of hydroxymethanesulfinate (HMSA) and hydroxymethanesulfonate (HMSOA) are also discussed.

Experimental and Results

Bromine, iodine crystals, formaldehyde, aminoiminomethanesulfinic acid, sodium hydroxymethanesulfinate, and sodium hydroxymethanesulfonate (Aldrich) were used without further purification. Aminoiminomethanesulfonic acid (AIMSOA) was prepared from a standard literature procedure.[19] Conventional kinetics experiments were performed on a Lambda 2S UV−vis spectrophotometer, and faster reactions were followed on a Hi-Tech Scientific SF-DX2 stopped-flow spectrophotometer.

Reactions with Iodine. AIMSA reacts quite rapidly with aqueous iodine. In excess AIMSA the reaction is complete in less than 10 s (see Figure 1A). The stoichiometry of the reaction is

$$2I_2 + H_2N(HN{=})CSO_2H + 3H_2O \rightarrow (H_2N)_2C{=}O + SO_4^{2-} + 4I^- + 6H^+ \quad \text{(R2)}$$

The reaction is autoinhibitory, and iodide strongly inhibits the reaction.[3,20] In other reactions involving oxidation by iodine, the formation of the relatively inert electrophile I_3^- has been established as the autoinhibitory mechanism:[20]

$$I_2 + I^- \rightleftharpoons I_3^- \quad \text{(R3)}$$

On the other hand, the oxidation of AIMSOA by aqueous iodine is extremely slow (Figure 1B). In freshly prepared AIMSOA solutions the reaction quickly shuts down after a few minutes. The rate of the reaction is strongly affected by the age of the AIMSOA solutions used. Freshly prepared AIMSOA solutions produced the slowest rates (Figure 1B, trace a). Figure 1B shows a series of reactions performed with progressively aged solutions. Trace i shows a solution aged for 270 min. The reaction is now very fast. Most of the reaction is already complete by the time the stopped-flow spectrophotometer captures the absorbance trace.

Reactions with Bromine. Aqueous bromine reacts quite rapidly with both AIMSA and AIMSOA (parts A and B of Figure 2). However, the reaction with AIMSA is so much faster and is over in about 0.01 s while the corresponding reaction with AIMSOA will take about 0.5 s. The reaction with AIMSA did not show any observable dependence on acid. On the other hand, acid strongly inhibits the Br_2−AIMSOA reaction (Figure 2B). The reaction does not proceed under conditions of $[H^+]_0 > 1.0$ M. The stoichiometries of the reactions are the same as those for the corresponding iodine reactions: 2:1 ratio for the AIMSA reaction and a 1:1 ratio for the AIMSOA reaction.

Reactions with Chlorite. AIMSA reacts very rapidly with chlorite over a very wide pH range.[21] The reaction is followed by the absorbance of chlorine dioxide at 360 nm. AIMSA is initially oxidized by chlorite to give HOCl:

$$H_2N(HN{=})CSO_2H + ClO_2^- + H^+ \rightarrow H_2N(HN{=})CSO_3H + HOCl \quad \text{(R4)}$$

The chlorine dioxide is formed from an extraneous oxyhalogen reaction[22] in which the HOCl produced in reaction R4 rapidly oxidizes ClO_2^- to produced ClO_2:

$$2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2(aq) + Cl^- + H_2O \quad \text{(R5)}$$

The rate of production of chlorine dioxide is proportional to the rate of reaction R4. Figure 3 shows the formation of chlorine dioxide whose oligooscillatory behavior in this reaction has been previously explained.[23] There was no visible reaction on a time scale of hours for the reaction of AIMSOA with chlorite. If the reported initial step of the chlorite−AIMSA reaction is reaction R4, we should expect similar rates for the two reactions.

Hydroxymethanesulfinic Acid (HMSA) and Hydroxymethanesulfonic Acid (HMSOA) Reactions. A comparison

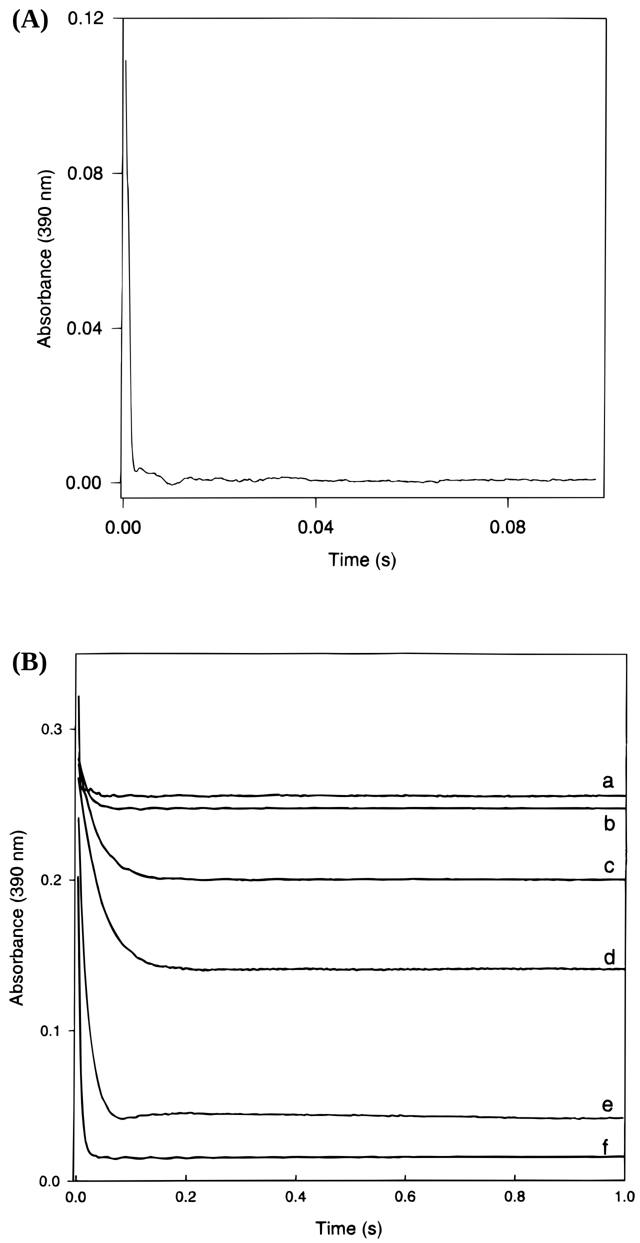


Figure 2. (A) Extremely rapid oxidation of AIMSA by aqueous bromine. Calculated initial bromine absorbance was 0.26. The reaction is too fast to be observed on the Hi-Tech DX2 stopped-flow spectrophotometer. $[Br_2]_0 = 1.8 \times 10^{-3}$ M; $[AIMSA]_0 = 3.25 \times 10^{-2}$ M. (B) Oxidation of AIMSOA with aqueous bromine at variable concentrations of acid. $[Br_2]_0 = 6.5 \times 10^{-3}$ M; $[AIMSOA]_0 = 5.0 \times 10^{-2}$ M. $[H^+]_0$ values are the following: (a) 4.0 M; (b) 0.5 M; (c) 0.3 M; (d) 0.125 M; (e) 0.01 M; (f) 0.

was also made between the reactions of HMSA and HMSOA. The relationship between HMSA and HMSOA is the same as that for AIMSA and AIMSOA. The oxidation of HMSA is very facile and rapid.[24,25] The products, in excess oxidants, are sulfate with either formaldehyde, formic acid, or carbon dioxide, depending on the strength and abundance of the oxidant. It has been postulated that the oxidation of HMSA passes through HMSOA as an intermediate before proceeding to give products.[24,25]

Reaction with Iodine. Oxidation of HMSOA by iodine is extremely slow (Figure 4A), but a corresponding oxidation of HMSA is complete within the dead-time of the instrument. The HMSOA−iodine reaction shown in Figure 4A had a half-life of over 1000 s. The reactions are even slower in reaction solutions with formaldehyde (Figure 4B). Figure 4B has an overwhelming excess of HMSOA (at least 10-fold excess), ensuring that all iodine would be consumed at the end of the reaction. The reaction had not reached its half-life even after 5 h. Figure 4B also shows that aged solutions with formaldehyde react faster than those solutions that are freshly made. The aged solutions gave a very fast initial reaction with the quantity of iodine consumed in this first step being proportional to the aging period.

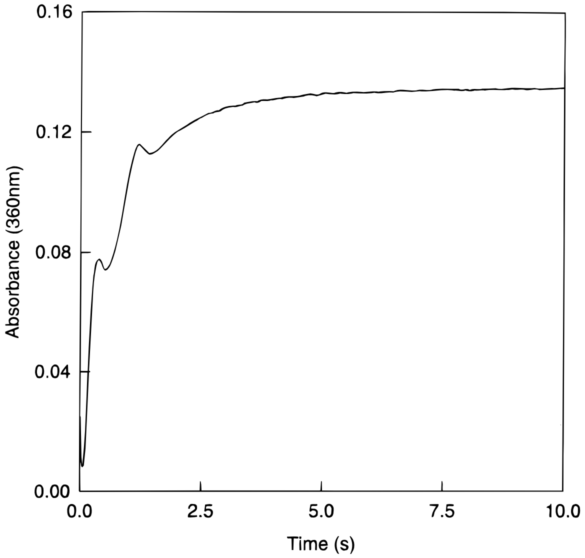


Figure 3. Reaction of chlorite and AIMSA showing the rapid and oligooscillatory production of chlorine dioxide. $[ClO_2^-]_0 = 5.0 \times 10^{-3}$ M; $[AIMSA]_0 = 5.0 \times 10^{-3}$ M. No observable reaction was detected with AIMSOA.

Reactions with Bromine. Reaction of HMSOA with bromine is slow, but a corresponding reaction with HMSA is very fast. Figure 5shows that the HMSA reaction is too fast to be captured on the time scale of the HMSOA reaction. The HMSA reaction, on a time scale of 0.02 s, is shown in the Figure 5 inset.

Reactions with Chlorite. The mechanism for the oxidation of HMSA by chlorite was recently reported.[24] The reaction is very fast and shows oligooscillatory behavior in the concentrations of chlorine dioxide (see Figure 6insert). The postulated first step of the oxidation is

$$ClO_2^- + HOCH_2SO_2H + H^+ \rightarrow HOCl + HOCH_2SO_3H \quad (R6)$$

This is then followed by the oxidation of $HOCH_2SO_3H$ to give sulfate and the organic residues:

$$ClO_2^- + HOCH_2SO_3H \rightarrow HOCl + SO_4^{2-} + HCHO + H^+ \quad (R7)$$

The oxyhalogen reaction, reaction R5, is also responsible for the production of chlorine dioxide, and thus, the formation of chlorine dioxide can be used as an indicator of the rate of reaction R4.

Figure 6 shows that the chlorite oxidation of HMSA is much faster than the oxidation of HMSOA. If reaction R6 is the rate-determining step (as has been assumed), then the rate of oxidation of HMSOA should be faster than that for HMSA. If reaction R7 is the rate-determining step, we should have a reverse situation.

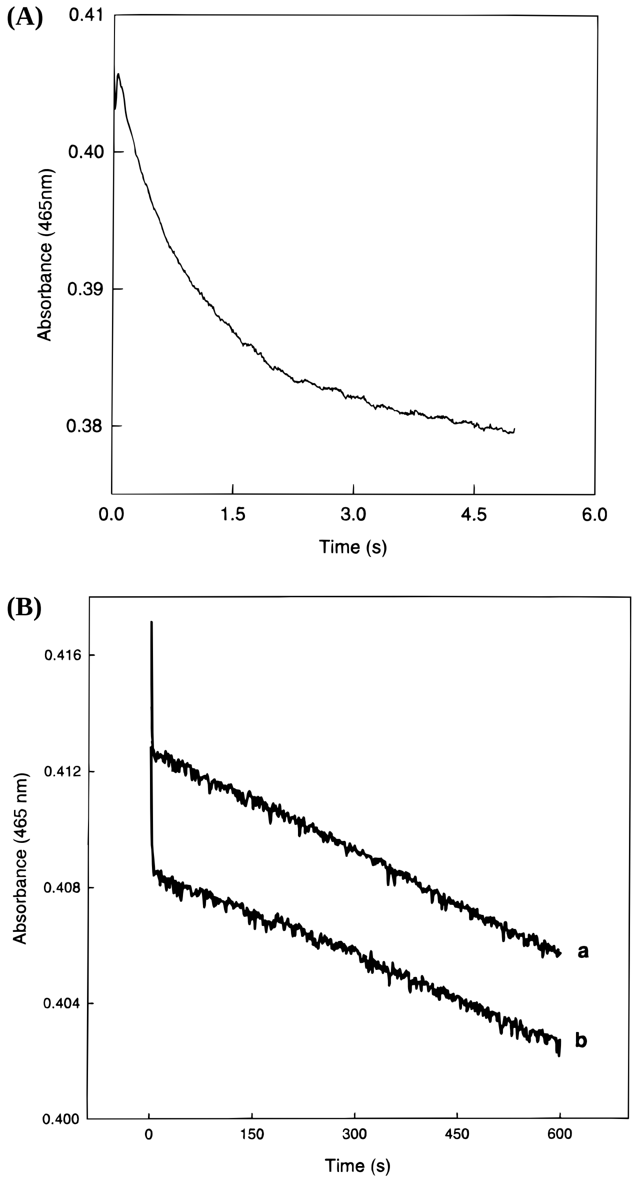


Figure 4. (A) Reaction of HMSOA with aqueous iodine. $[I_2]_0 = 5.0 \times 10^{-4}$ M; $[\text{HMSOA}]_0 = 5.0 \times 10^{-4}$ M. (B) Effect of formaldehyde in the iodine HMSOA reaction. $[I_2]_0 = 1.1 \times 10^{-3}$ M; $[\text{HMSOA}]_0 = 1.1 \times 10^{-2}$ M. Trace a is from fresh solution of HMSOA, and trace b is from solutions aged for 180 min.

The data shown in Figures 1−6 indicate that either (a) the oxidation of sulfinic acids does not pass through a sulfonic acid intermediate or (b) there is a fundamental difference in the bonding and structure of sulfinic and sulfonic acids.

Further Experimental Data: Effect of Formaldehyde. Only the iodine oxidations were tested for the effects of formaldehyde. The substrates used were AIMSA and AIMSOA. The rapid oxidation of formaldehyde by aqueous bromine did not allow the same set of experiments to be set up for bromine oxidations. Figure 7A shows a series of experiments run with 0.01 M formaldehyde. This concentration is comparable to the concentration of AIMSOA in solution (0.011 M). The aged solutions reacted more rapidly. The effect of aging is not as large as in the case with solutions without formaldehyde.

Figure 7B shows another series of experiments run with overwhelming excess of formaldehyde (12.3 M). In this case, aging the reaction solutions does not seem to have any effect on the rate of reaction.

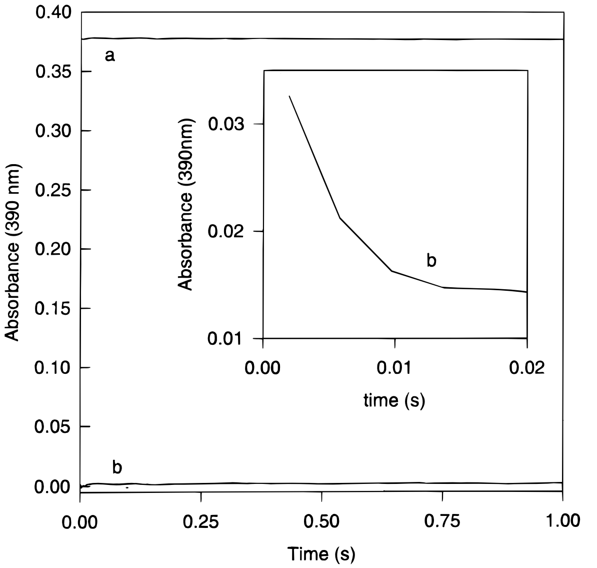


Figure 5. Reactions of HMSOA and HMSA with aqueous bromine. The reaction of HMSA is so fast that it cannot be captured by the Hi-Tech DX2 stopped-flow spectrophotometer on the 1 s time scale. The inset shows the HMSA reaction on a 0.02 s time scale. $[Br_2]_0 = 5.0 \times 10^{-4}$ M; $[\text{HMSA}]_0 = 1.1 \times 10^{-4}$ M.

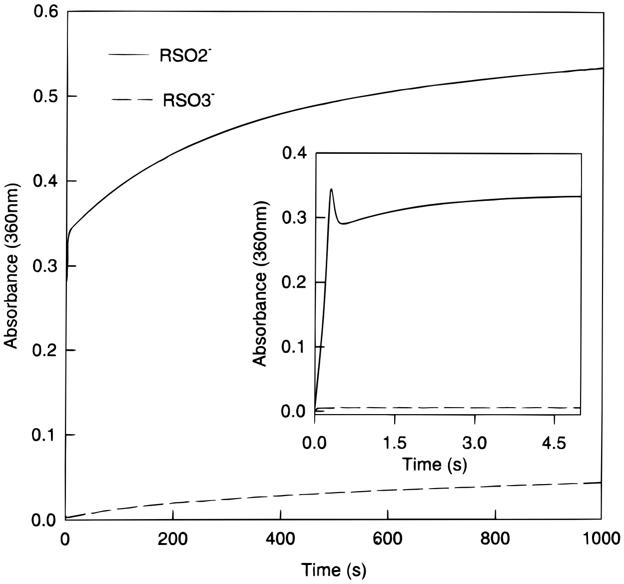


Figure 6. Comparison between the reactions of chlorite with HMSOA and with HMSA. The reaction with HMSA is so fast that it is not possible to catch the first stage of the reaction on the time scale of the HMSOA reaction. This detail is shown in the inset. $[\text{ClO}_2^-]_0 = 1.1 \times 10^{-3}$ M; $[\text{HMSOA}]_0 = [\text{HMSA}]_0 = 1.1 \times 10^{-3}$ M.

Discussion

HMSA is a well-known industrial chemical that is used in the textile industry. HMSOA has been implicated in atmospheric chemistry as a pathway for the stabilization of sulfur dioxide.[26] It is prepared from the reaction of formaldehyde and sodium bisulfite[27] and not from the oxidation of a sulfinic acid.

$$\text{CH}_2(\text{OH})_2 + \text{HSO}_3^- \rightleftharpoons \text{CH}_2(\text{OH})\text{SO}_3^- + \text{H}_2\text{O} \quad \text{(R8)}$$

The adduct HMSOA is much more stable in acidic conditions and quickly decomposes when above pH 7. The equilibrium constant of this reaction has been established as 7.82×10^6 M^{-1} at pH 6.[27] The rate of attainment of equilibrium when

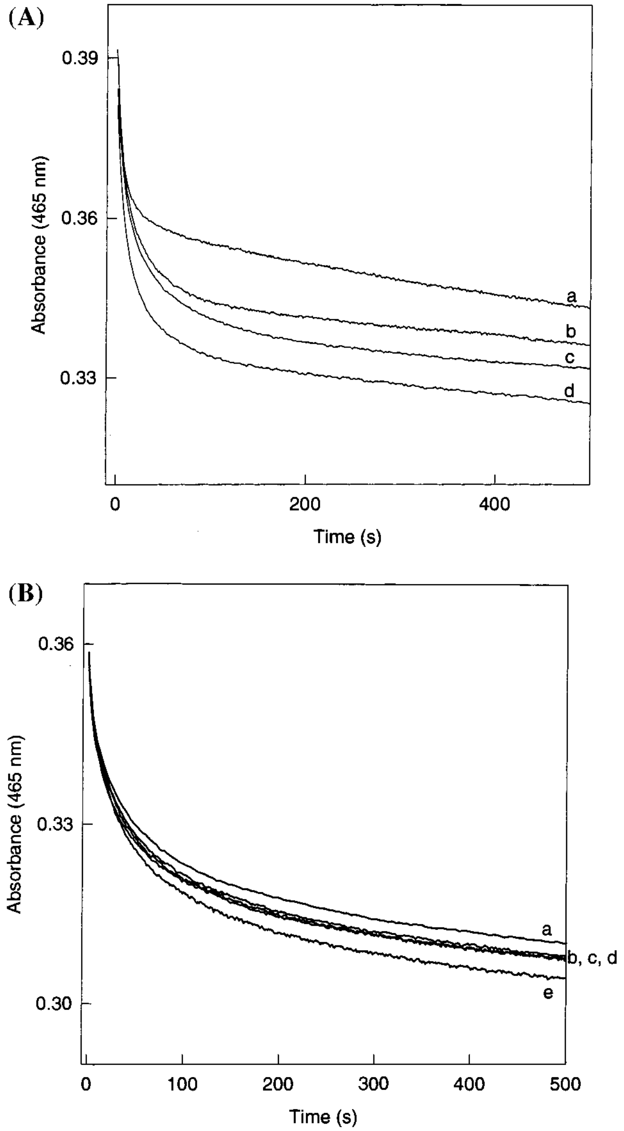


Figure 7. (A) Reaction traces at 465 nm of the oxidation of AIMSOA by iodine in the presence of 1.1×10^{-2} M HCHO. $[I_2]_0 = 1.1 \times 10^{-3}$ M; $[\text{AIMSOA}]_0 = 1.1 \times 10^{-2}$ M. The age of the solutions is as follows: (a) 2 min; (b) 40 min; (c) 260 min; (d) 363 min. (B) Reaction traces with overwhelming excess of formaldehyde, 12.3 M. $[I_2]_0 = 1.1 \times 10^{-3}$ M; $[\text{AIMSOA}]_0 = 1.1 \times 10^{-2}$ M. The age of the solutions is as follows: (a) 2 min; (b) 30 min; (c) 70 min; (d) 120 min; (e) 300 min.

starting with pure HMSOA is about 45−75 min at this pH.[27] Upon dissolving HMSOA in water, we expect a slow equilibrium process to occur in which formaldehyde and bisulfite are formed. The oxidation of bisulfite to sulfate is fast:

$$HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3H^+ + 2e^- \qquad (R9)$$

If all the HMSOA decomposed to give the bisulfite, then the observed oxidation rate upon addition of oxidant would be fast. If, however, HMSOA remained in the adduct form, then it will be oxidized at a slower rate. The effect of aging our reagent solutions is to increase the bisulfite and formaldehyde concentrations in solution. The longer-aged solutions attain a higher concentration of free bisulfite. Figure 7A clearly shows the effect of aging on our solutions.

Effect of Formaldehyde. Formaldehyde is involved in the equilibrium R8 that determines the formation of the adduct HMSOA. Addition of formaldehyde suppresses the dissociation of HMSOA to give HSO_3^-. The reaction is expected to be retarded by formaldehyde. This retardation has been observed in our experiments (see Figure 4).

Reactions of AIMSA and AIMSOA. The solid-state structure of AIMSA is well-known.[28] The structure of AIMSOA was recently obtained in our laboratory.[29] In its zwitterionic form AIMSOA is strictly planar with a tetrahedral sulfur atom with three nearly equivalent S−O bonds. Because of its efficient packing, the density of AIMSOA is 1.948 g cm^{-3}. Both structures of AIMSA and AIMSOA show extensive hydrogen bonding.[28,29] The biggest difference between the structures of AIMSA and AIMSOA lies in the C−S bond lengths. AIMSA's C−S bond length is anomalously long at 0.1867 nm, while that of AIMSOA is 0.1815 nm. The geometry around the sulfur atom in AIMSA is planar, while that in AIMSOA is tetrahedral.

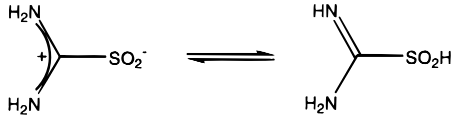
It is expected that in aqueous solution the AIMSOA zwitterion will be more stable than the corresponding zwitterion from AIMSA. The stronger electron-withdrawing properties of the $-SO_3^-$ group over the $-SO_2^-$ group as well as the lower basicity of the $-SO_3^-$ oxygens on AIMSOA make the AIMSOA zwitterion more preferable in solution over the AIMSA zwitterion. The zwitterion is susceptible to nucleophilic attack from the solvent because of the formally positive charge resident on the carbon atom. This very small difference in the sulfinic and sulfonic acids imparts a vast difference in their reactivities.

Effect of Acid. Acid stabilizes the zwitterion of AIMSOA. We could not detect products of AIMSOA decomposition (NH_4^+ and HSO_3^-) under conditions of pH less than 1.00 even after incubating the AIMSOA solutions for more than 2 days.[29] Production of HSO_3^- will increase the rate of consumption of Br_2 in the AIMSOA−Br_2 reaction (see Figure 2B). This especially holds under conditions where $[\text{AIMSOA}]_0 \gg [Br_2]_0$. Under these conditions, complete decomposition of the AIMSOA is not necessary for the generation of sufficient HSO_3^- to consume bromine. Initial bromine absorbances were the same for all reaction solutions shown in Figure 2B. The amount of bromine rapidly consumed at the beginning of the reaction is proportional to the amount of HSO_3^- in solution.

$$HSO_3^- + Br_2(aq) + H_2O \rightarrow SO_4^{2-} + 2Br^- + 3H^+ \quad [\text{fast}] \quad (R10)$$

The trace with no acid, trace f, has enough HSO_3^- to consume all the bromine during the initial very fast reaction phase.

Data in Figure 1B can also be explained by evoking the decomposition of the AIMSOA zwitterion. Longer-aged solutions contain more HSO_3^- and hence consume iodine much more rapidly. Figure 1A shows that aging the AIMSA solution has no significant effect on the rate of reaction. AIMSA, upon being dissolved, will predominantly exist in neutral form with a C=N double bond:



(R11)

Effect of Formaldehyde. Formaldehyde is involved in the decomposition of the AIMSOA zwitterion through a secondary reaction. Addition of HCHO decreases the amount of free bisulfite (see reaction R8), and thus, we expect a retardation of the reaction. This is indeed the case with the data in Figure 7A, which can be compared with data in Figure 1A. In these data, the amount of HCHO added is not in overwhelming excess over the AIMSOA. The rate of reaction is, however, reduced by a factor of 100 because of the addition of formaldehyde. However, the age of the solution still affects the rate of reaction, with the aged solutions reacting faster because of decomposition of AIMSOA.

In Figure 7B the reaction had an overwhelming excess of HCHO; $[HCHO]_0/[AIMSOA]_0 > 1000$. Thus, all the HSO_3^- produced is consumed by the added HCHO. The age of the reaction no longer becomes a factor, and the reaction ceases to respond to it. This is the observation in Figure 7B.

Possible Reaction Pathway for the Oxidation of AIMSA. The following simple experiment was performed. A 1:1 mole ratio of AIMSA to bromine was mixed and allowed to stand for more than 2 h. The expected result was the oxidation of AIMSA to AIMSOA only as expected from the following stoichiometry:

$$(NH_2)_2CSO_2 + Br_2 + H_2O \rightarrow (NH_2)_2CSO_3 + 2Br^- + 2H^+ \quad (R12)$$

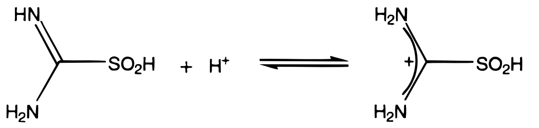
If the oxidation of AIMSA forms AIMSOA as an intermediate, then we expect very little or no sulfate production at all. A test for sulfate proved that there was nearly quantitative sulfate production based on the stoichiometry

$$2Br_2 + (NH_2)_2CSO_2 + 3H_2O \rightarrow (H_2N)_2C{=}O + SO_4^{2-} + 4Br^- + 6H^+ \quad (R13)$$

with the bromine concentrations being limiting. This experiment indicates that the oxidation of AIMSA proceeds through more than one possible pathway with one of them not involving AIMSOA.

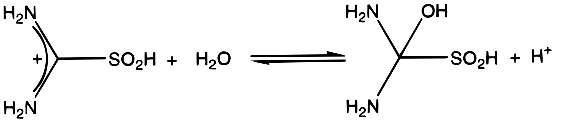
The preparation of AIMSOA, however, had been affected by the use of a mild oxidizing agent peracetic acid.[19] This oxidation was also carried out in chilled solutions to slow the reaction and to obtain a quantitative yield of AIMSOA. Product dependency on the strength of the oxidizing agent is very common. For example, peracetic acid can oxidize cysteine to cysteine sulfinic acid while aqueous bromine produces cysteine sulfonic acid and hydrogen peroxide produces the cysteine dimer cystine.[30]

Our proposed oxidation pathway involves an initial protonation of the imine nitrogen atom:



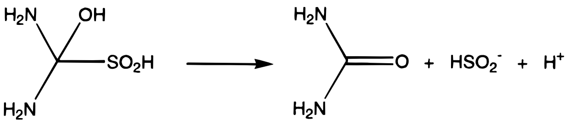
(R14)

The positive charge is delocalized around the two nitrogen atoms and the carbon atom. This activates the carbon atom for nucleophilic attack from the solvent:



(R15)

The cleavage of the C−S bond gives urea and an unstable sulfur species HSO_2^-:



(R16)

The HSO_2^- species is readily oxidized to bisulfite:

$$HSO_2^- + H_2O \rightarrow HSO_3^- + 2H^+ + 2e^- \quad (R17)$$

HSO_3^- is next also easily oxidized to sulfate (reaction R9).

Conclusion

In the crystalline form, small organic sulfinic and sulfonic acids have nearly the same structure and exist in their zwitterionic forms. However, upon dissolving in polar solvents, the sulfinic acid zwitterion loses its stability to its neutral form. The sulfonic acid zwitterion decomposes to form HSO_3^-, which can be quickly oxidized to sulfate. The experimental data presented in this manuscript show that sulfonic acids are very stable in solution and decompose only very slowly (cf. half-life of approximately 3 days). Their decomposition can give an anomalous rate of oxidation depending upon the length of time the solutions have been aged. The differences in the rates of reaction, however, need further attention. The accepted general mechanism of a sulfinic acid being oxidized to the sulfonic acid before formation of sulfate may need to be revised. It does appear that the oxidation of a sulfinic acid may be proceeding through the HSO_2^- and HSO_3^-, which then are oxidized to sulfate. There is need for more extensive experimental data and analysis.

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