

# Oxyhalogen-Sulfur Chemistry: The Bromate-(Aminoimino)methanesulfinic Acid Reaction in Acidic Medium<sup>1</sup>

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The reaction between (aminoimino)methanesulfinic acid, HO<sub>2</sub>SC(NH)NH<sub>2</sub> (AIMSA), and bromate has been studied in acidic medium. In excess AIMSA the stoichiometry of the reaction is 2BrO<sub>3</sub><sup>-</sup> + 3AIMSA + 3H<sub>2</sub>O → 3SO<sub>4</sub><sup>2-</sup> + 3CO(NH<sub>2</sub>)<sub>2</sub> + 2Br<sup>-</sup> + 6H<sup>+</sup>, and in excess bromate the stoichiometry is 4BrO<sub>3</sub><sup>-</sup> + 5AIMSA + 3H<sub>2</sub>O → 5SO<sub>4</sub><sup>2-</sup> + 5CO(NH<sub>2</sub>)<sub>2</sub> + 2Br<sub>2</sub> + 6H<sup>+</sup>. Br<sub>2</sub> is produced only when BrO<sub>3</sub><sup>-</sup> is in stoichiometric excess over AIMSA. It is produced from the reaction of the product, Br<sup>-</sup>, with excess BrO<sub>3</sub><sup>-</sup> after all the AIMSA has been consumed. The reaction has an initial induction period followed by formation of bromine. Although AIMSA is oxidized to SO<sub>4</sub><sup>2-</sup>, no SO<sub>4</sub><sup>2-</sup> formation is observed until Br<sub>2</sub> production commences. The reaction is autocatalyzed by bromide. The reactive oxidizing species in solution are HOBr and Br<sub>2</sub>. Bromide enhances their formation from bromate. A simple eight-reaction mechanism is used to describe the reaction. The reaction commences through a direct reaction between BrO<sub>3</sub><sup>-</sup> and AIMSA: BrO<sub>3</sub><sup>-</sup> + HO<sub>2</sub>SC(NH)NH<sub>2</sub> + H<sup>+</sup> → HBrO<sub>2</sub> + HO<sub>3</sub>SC(NH)NH<sub>2</sub> with  $k = 2.5 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ . The rate-determining step is the standard BrO<sub>3</sub><sup>-</sup> - Br<sup>-</sup> reaction which forms the reactive species HOBr: BrO<sub>3</sub><sup>-</sup> + Br<sup>-</sup> + 2H<sup>+</sup> → HBrO<sub>2</sub> + HOBr. A computer simulation analysis of the proposed mechanism gave good fit to the data.

## Introduction

Before 1980, all the known unconventional kinetics systems in chemistry were based on oxyhalogen oxidations.<sup>2</sup> With such a small select group of compounds exhibiting exotic dynamics, it took a long time to rationalize the origin of nonlinear dynamics in chemical systems. About 10 years ago, sulfur compounds were found to exhibit exotic dynamics in reactions which involved their oxidations by oxidants including, but not restricted to, oxyhalogens.<sup>3</sup> Oxidation of a sulfur compound can yield oscillatory behavior in a CSTR,<sup>4</sup> clock and crazy clock reactions,<sup>5</sup> stirring rate effects,<sup>6</sup> chemical chaos,<sup>7</sup> travelling waves,<sup>8</sup> gravity-induced anisotropies<sup>9</sup> in travelling waves, and spatiotemporal patterns.<sup>10</sup>

The combination of oxyhalogen compounds (e.g., bromate,<sup>11</sup> iodate,<sup>12</sup> and chlorite<sup>13</sup>) with sulfur compounds (hydrogen sulfide, thiocyanate, thiourea, etc.) has given us a wider range of nonlinear phenomena in chemistry. The study of nonlinear and/or oscillatory dynamics in these simple chemical systems is crucial if we are ever going to understand the more complex biochemical systems that sustain life.<sup>14</sup> The Belousov-Zhabotinskii (BZ) system is the most well-known chemical system which produces a wide range of nonlinear behavior.<sup>15</sup> The "drive" reaction for the BZ system (oxidation of malonic acid by acidified bromate in the presence of a metal ion) is well understood in terms of single-step mechanisms together with its thermodynamics and kinetics parameters.<sup>16</sup> The same cannot be said for the oxyhalogen-sulfur reactions. Without the relevant kinetics parameters for the oxyhalogen-sulfur reactions, any further studies of the attendant nonlinear phenomena will be impossible to effect.

Sulfur oxidations are in general difficult to study because of poor reproducibility of experimental results. Irreproducibility can be traced to free-radical mechanisms<sup>17</sup> and extensive sulfur polymerizations in most reaction mixtures.<sup>18</sup> In oxidations of sulfide by bromate,<sup>18</sup> for example, it is very difficult to maintain experimental control as several S<sub>n</sub> (n = 1, 2, ..., 8) species are

formed during the course of the reaction. A possible method of studying sulfur oxidations is to use a sulfur-containing compound in which the sulfur-heteroatom bond is stronger than a sulfur-sulfur bond. Thus a number of studies have been done on the oxidation mechanisms of thiourea<sup>19</sup> and thiocyanate.<sup>20</sup>

The reaction of acidified bromate with thiourea gives oscillatory behavior in a CSTR.<sup>21</sup> The chlorite-thiourea reaction is also oscillatory in a CSTR<sup>22</sup> and gives spatiotemporal patterns in batch mode.<sup>10</sup> The kinetics and mechanisms of both reactions have been studied in acidic medium, and the mechanisms deduced implicate successive oxygen additions on the sulfur atom up to the sulfonic acid followed by cleavage of the S-C bond to form sulfate and urea. Of the postulated intermediate sulfur compounds, the sulfenyl acid, HOSC(NH)NH<sub>2</sub>, is very unstable and cannot be isolated.<sup>23</sup> The sulfinic acid, HO<sub>2</sub>SC(NH)NH<sub>2</sub> ((aminoimino)methanesulfinic acid, AIMSA) is a stable white crystalline substance at room temperature.

We undertook the study of the bromate-AIMSA reaction as a natural followup to our recent study of the bromate-thiourea reaction.<sup>19</sup> The kinetics and mechanism of the BrO<sub>3</sub><sup>-</sup>-AIMSA reaction should complement the mechanism postulated for the bromate-thiourea reaction.

The study of the oxidation mechanisms of sulfur compounds has been hampered by the fact that the kinetics can be studied only by observing the rate of formation of some intermediate or product. With the numerous possible intermediates in the oxidation of a sulfur center, the rate of formation of product is rarely related to the rate of consumption of reactants. AIMSA has, however, a very strong peak in the ultraviolet region at 270 nm which does not interfere with the bromate and bromine peaks. In this paper we report the kinetics of consumption of AIMSA, the reaction induction period, and kinetics of formation of Br<sub>2</sub>.

## Experimental Section

**Materials.** The following reagent grade chemicals were used without further purification: perchloric acid, 70-72%, sodium

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perchlorate (Fisher); potassium bromate (British Drug Houses); sodium bromide (Caledon Laboratories); (aminoimino)methanesulfonic acid (Kodak). AIMSA solutions were prepared just before use and not kept for more than 8 h.<sup>24</sup>

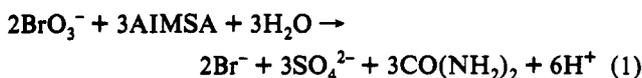
**Methods.** All experiments were carried out at 25 °C and at an ionic strength of 1.0 M (NaClO<sub>4</sub>). The reaction was monitored spectrophotometrically at  $\lambda = 270$  nm on a Hewlett-Packard 8452A UV-visible spectrophotometer. In excess BrO<sub>3</sub><sup>-</sup> the reaction was followed at  $\lambda = 390$  nm on a Hi-Tech Scientific SF-61AF stopped-flow spectrophotometer. The signal from the spectrophotometer was amplified and digitized on an Omega Engineering DAS-50/1 16-bit A/D board and interfaced to a Tandon 386SX computer for storage. Aqueous bromine has an absorption peak at 390 nm where we deduced an absorptivity coefficient of 161 M<sup>-1</sup> cm<sup>-1</sup>.

The stoichiometric determinations were performed in excess BrO<sub>3</sub><sup>-</sup> concentrations and in excess AIMSA. The stoichiometry was dependent on the ratio of the oxidant to reductant concentrations. In excess AIMSA conditions AIMSA was determined by its peak at 270 nm, where it has an absorptivity coefficient of 489 M<sup>-1</sup> cm<sup>-1</sup>. In excess BrO<sub>3</sub><sup>-</sup> conditions the Br<sub>2</sub>(aq) produced was determined by its absorbance at  $\lambda = 390$  nm. The total oxidizing power (BrO<sub>3</sub><sup>-</sup> + Br<sub>2</sub>(aq)) was determined iodometrically by adding excess acidified iodide and titrating the liberated iodine against standard thiosulfate with freshly prepared starch as indicator. A complimentary set of experiments was performed for excess AIMSA conditions in which the BrO<sub>3</sub><sup>-</sup> concentrations were gradually increased. The stoichiometric bromate equivalent was the maximum BrO<sub>3</sub><sup>-</sup> concentration at which no bromine is produced. The bromide produced was determined gravimetrically as AgBr and sulfate as BaSO<sub>4</sub>.

For the conventional Hewlett-Packard spectrophotometer experiments, bromate was added last, and time = 0 was defined as the point of complete delivery of bromate. The reaction mixture was vigorously stirred before being transferred to the spectrophotometer cuvette. There was a time lag of 20 s between mixing of reagent and commencement of experimental observations. In the stopped-flow experiments BrO<sub>3</sub><sup>-</sup>, H<sup>+</sup>, and Br<sup>-</sup> dependence experiments were performed in which the initial rates and induction periods (excess BrO<sub>3</sub><sup>-</sup> conditions only) were determined. The induction period is defined as the time the reaction takes to start producing bromine in excess BrO<sub>3</sub><sup>-</sup>. The induction period does not apply in excess AIMSA since no bromine is produced.

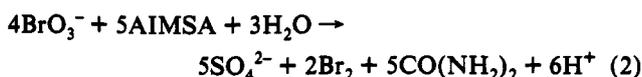
## Results

**Stoichiometry.** In excess AIMSA the measured stoichiometry is

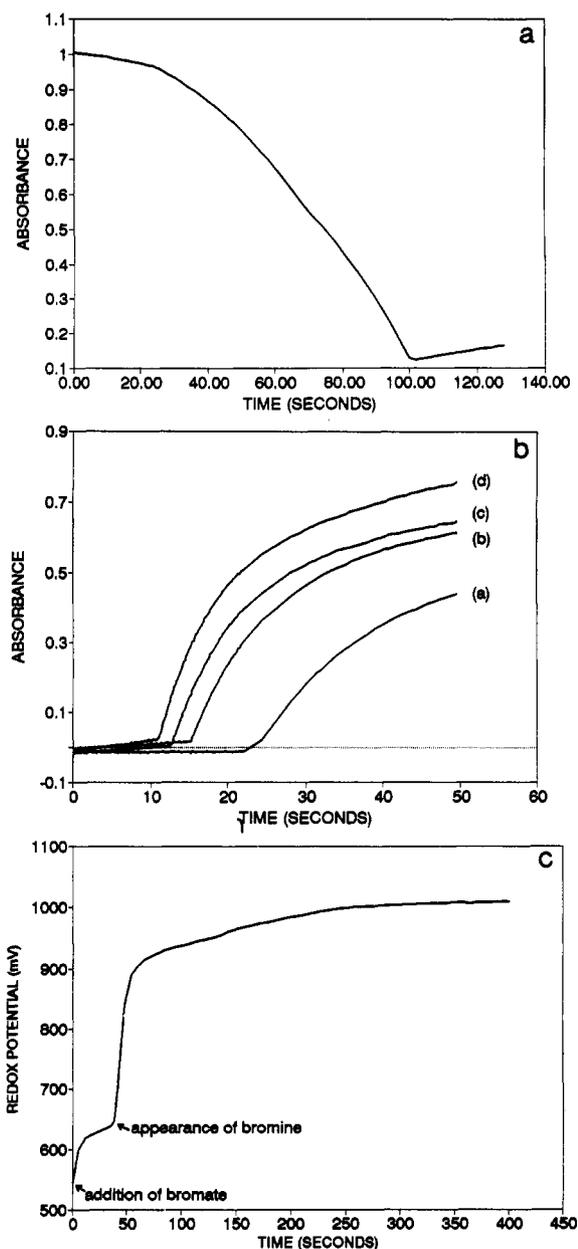


The ratio of BrO<sub>3</sub><sup>-</sup> to AIMSA was exactly 2:3 as determined by absorbance measurements (excess AIMSA determined by its peak at  $\lambda = 270$  nm) and by measuring the maximum [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> needed before Br<sub>2</sub> is produced. Gravimetric analysis showed that all the sulfur in AIMSA was obtained as SO<sub>4</sub><sup>2-</sup>. We did not measure H<sup>+</sup> ions produced in (1) but noted that qualitatively the pH dropped as the reaction proceeded in low acid (in high acid reaction was essentially buffered).

In excess bromate the measured stoichiometry is



The Br<sub>2</sub> produced was spectrophotometrically determined at  $\lambda = 390$  nm, and the results confirmed the ratio of AIMSA to Br<sub>2</sub>



**Figure 1.** (a) Typical absorbance trace at  $\lambda = 270$  nm showing the sigmoidal AIMSA consumption which denotes autocatalysis. [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 0.084 M, [AIMSA]<sub>0</sub> = 0.002 M, [H<sup>+</sup>]<sub>0</sub> = 0.125 M. (b) Absorbance trace in excess bromate at  $\lambda = 390$  nm. The induction period is the time taken before the production of bromine. [AIMSA]<sub>0</sub> = 0.01 M, [H<sup>+</sup>]<sub>0</sub> = 1.0 M, [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub>: (a) = 0.08 M, (b) = 0.12 M, (c) = 0.14 M, (d) = 0.16 M. (c) Redox potential trace in excess bromate. The rapid increase in potential coincides with bromine production. [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 0.0046 M, [AIMSA]<sub>0</sub> = 0.00029 M, [H<sup>+</sup>]<sub>0</sub> = 0.86 M.

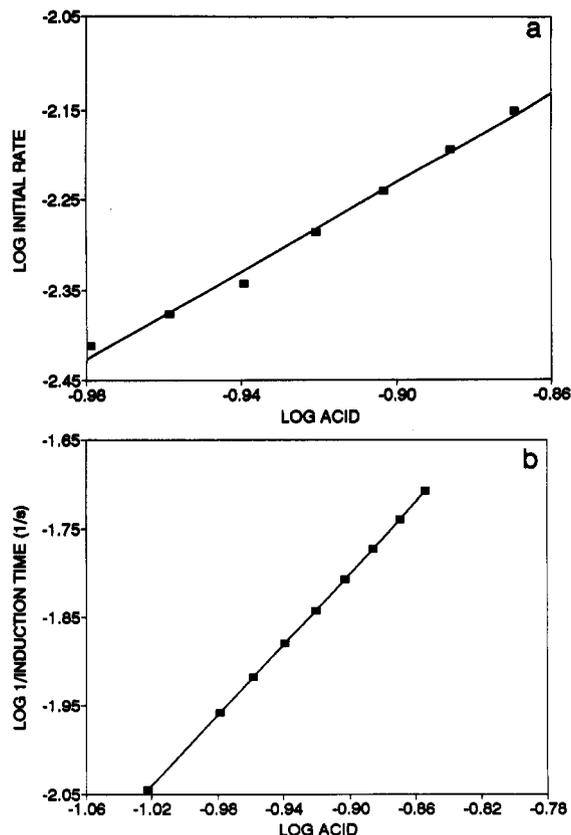
at 5:2. Iodometric determinations gave the BrO<sub>3</sub><sup>-</sup> to AIMSA ratio as 4:5. In high acid some of the urea is converted to NH<sub>4</sub><sup>+</sup> via NH<sub>3</sub>:



Qualitative tests gave a positive ammonium ion test in high acid.

The oxidation of AIMSA requires 4 equiv no matter which reactant is in excess. The variable stoichiometry depends on whether the bromine center in BrO<sub>3</sub><sup>-</sup> is reduced to Br<sup>-</sup> (eq 1) or to Br<sub>2</sub> (eq 2).

**Reaction Kinetics.** The absorbance change monitored at  $\lambda = 270$  nm, i.e., the depletion rate of AIMSA, was initially slow. The reaction then gradually picks up speed as in typical autocatalytic reactions. Such a plot is shown in Figure 1a. The absorbance



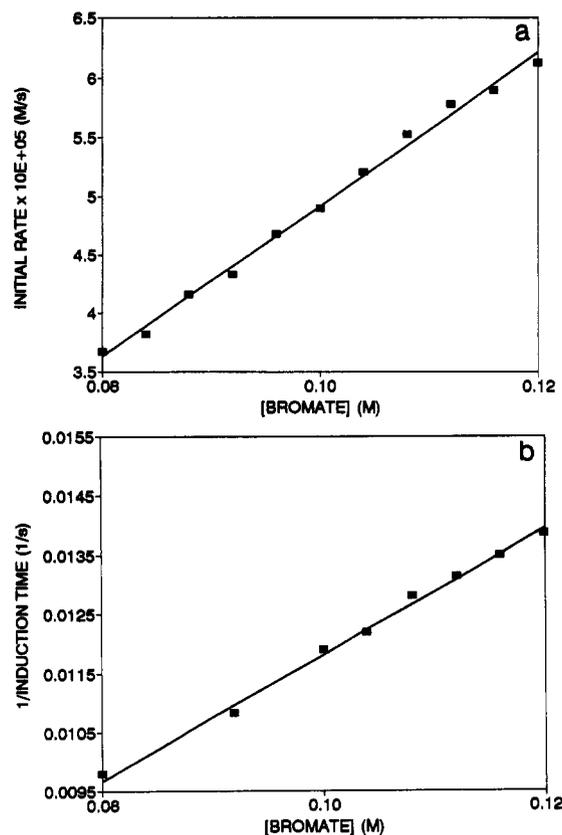
**Figure 2.** log-log plot of initial rate vs acid concentration. The slope is exactly 2, indicating a square dependence of the rate with the acid. The data was obtained by measuring the rate of consumption of AIMSAs at 270 nm.  $[\text{BrO}_3^-]_0 = 0.08 \text{ M}$ ,  $[\text{AIMSA}]_0 = 0.002 \text{ M}$ . (b) Effect of the acid on the inverse of the induction time in excess bromate conditions. This log-log plot also gave the value of slope as 2.  $[\text{BrO}_3^-]_0 = 0.08 \text{ M}$ ,  $[\text{AIMSA}]_0 = 0.002 \text{ M}$ .

increase observed in Figure 1a after total consumption of AIMSAs is due to  $\text{Br}_2$  which has a finite absorbance at 270 nm. In excess AIMSAs  $\text{Br}_2$  formation is not observed.

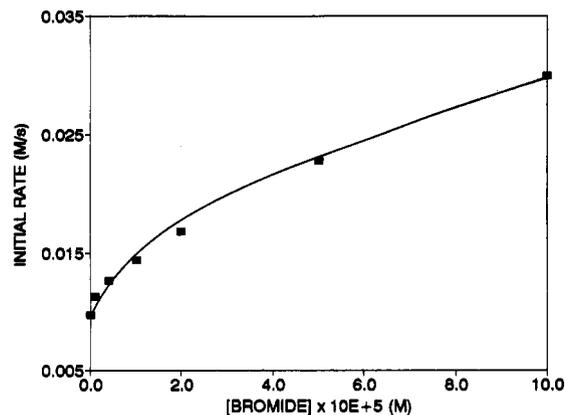
At  $\lambda = 390 \text{ nm}$  and in excess  $\text{BrO}_3^-$  the reaction possesses an initial quiescent period in which no change in the absorbance is observed. After this induction period bromine is slowly formed (Figure 1b). The length of the induction period is controlled by the initial reactant concentrations. Figure 1b also shows the effect of bromate concentrations on the induction period. Higher  $[\text{BrO}_3^-]_0$  decreases the length of the induction period. The redox potential traces mimic the absorbance traces. There is a sharp increase in redox potential at the point of bromine production (Figure 1c). After bromine production the redox potential is dominated by the bromine/bromide couple.

**Effect of Acid.** Acid has a very strong catalytic effect on the reaction, although according to our stoichiometry it is a product and not a reactant. The order of the reaction as determined from the rate of consumption of AIMSAs was evaluated from initial rates. A log-log plot of initial rate vs acid concentrations gave a straight line of slope = 2 (Figure 2a). A plot of  $[\text{H}^+]^2$  vs initial rate also gave a straight line confirming the order of 2 derived from the log-log plots. In excess  $[\text{BrO}_3^-]$  conditions the inverse of the induction time is proportional to the rate of reaction. This can be justified from Figure 1a, which shows that bromine production does not commence until all the AIMSAs has been consumed. The induction period is thus the time needed for complete consumption of AIMSAs. Our data give a square dependence of the inverse of the induction period with respect to acid. log-log plots of inverse induction period vs  $[\text{H}^+]$  gave a straight line of slope = 2 (Figure 2b).

**Effect of Bromate.** Higher bromate concentrations enhance the rate of reaction (see Figure 1b). The rate of consumption of



**Figure 3.** (a) Dependence of the initial rate ( $\lambda = 270 \text{ nm}$ ) on the initial bromate concentrations.  $[\text{AIMSA}]_0 = 0.002 \text{ M}$ ,  $[\text{H}^+]_0 = 0.125 \text{ M}$ . (b) Effect of bromate on the inverse of the induction period ( $\lambda = 390 \text{ nm}$ ).  $[\text{AIMSA}]_0 = 0.002 \text{ M}$ ,  $[\text{H}^+]_0 = 0.125 \text{ M}$ .



**Figure 4.** Effect of bromide on the initial rate of the reaction showing the observed saturation as  $[\text{Br}^-]_0$  increases.  $[\text{BrO}_3^-]_0 = 0.088 \text{ M}$ ,  $[\text{AIMSA}]_0 = 0.002 \text{ M}$ ,  $[\text{H}^+]_0 = 0.1 \text{ M}$ .

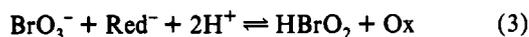
AIMSAs ( $\lambda = 270 \text{ nm}$ ) was directly proportional to the initial bromate concentrations (Figure 3a). The inverse of the induction period was also directly proportional to the initial bromate concentrations (Figure 3b). The results from Figures 3a and b solidly established the order of the reaction with respect to  $[\text{BrO}_3^-]$  as unity.

**Effect of Bromide.** Bromide was a very effective catalyst for this reaction. Its effect was larger at low concentrations. As higher  $\text{Br}^-$  concentrations are used, the catalytic effect tails off. A plot of initial rate vs  $[\text{Br}^-]$  gives direct proportionality with a saturation (Figure 4).

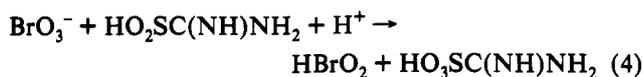
#### Mechanism

The reaction kinetics strongly implicates the standard oxyhalogen reduction mechanisms are being dominant. When

bromate is reduced to bromide or bromine, the initial step of such a reduction can be summarized as<sup>25</sup>

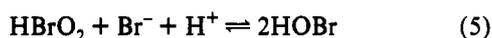


where Red is any two-electron reductant. In our proposed mechanism the first step of the reaction should be the direct reaction of bromate and AIMSAs:

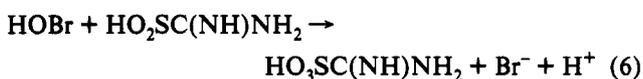


Reaction 4 is the initiation reaction. It starts the chain in the production of the reactive species HBrO<sub>2</sub>, HOBr, and Br<sup>-</sup>. Reaction 4 is very important at the beginning of the reaction but becomes ineffective as the reaction commences due to the autocatalytic nature of the reaction. The important species that should accumulate to accelerate the rate of reaction is Br<sup>-</sup>. Bromate solutions contain trace amounts of Br<sup>-</sup> up to 5 × 10<sup>-6</sup> M<sup>26</sup>. These trace amounts of bromide are sufficient to sustain the reaction.

The next step will be to form the reactive species, HOBr, from HBrO<sub>2</sub>:



HOBr can oxidize AIMSAs or the sulfonic acid formed in eq 4:



Sequence (5)–(6) shows that only trace amounts of Br<sup>-</sup> will be needed to initiate the reaction since Br<sup>-</sup> used in eq 5 will be regenerated in eq 6. The autocatalytic species in this reaction network is HOBr, and this can be seen from adding (5) + (6) in which 1 mol of HOBr produces 2 mol of HOBr. The rate-determining step (of type eq 3) is the reaction that produces HOBr from BrO<sub>3</sub><sup>-</sup>:



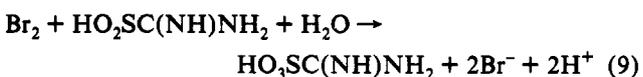
The Br<sup>-</sup> comes from the (4) + (5) + (6) sequence or is deliberately added to the reaction mixture as in Figure 4. The amount of bromide will determine the initial rate of reaction, e.g., eq 1:

$$d[\text{HOBr}]/dt = k_0[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 \quad (1)$$

A competitive reaction in the presence of HOBr and Br<sup>-</sup> is the formation of Br<sub>2</sub>:<sup>27</sup>



The reaction of Br<sub>2</sub> with AIMSAs is so fast that it is near diffusion control.<sup>28</sup> Thus no Br<sub>2</sub> will accumulate until all the AIMSAs have been consumed:



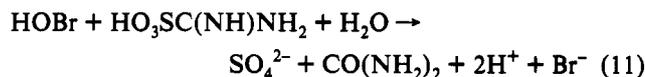
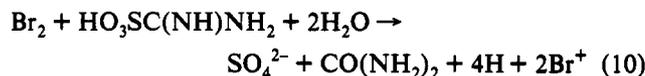
Reaction 9 produces more Br<sup>-</sup>; enhancing reactions 5 and 7 which produce the reactive species.

Further oxidation of the sulfonic acid to sulfate is generally slower than the oxidation of AIMSAs to the sulfonic acid. This assertion can be justified from previous experiments that have shown that sulfate production commences simultaneously with bromine production and not before.<sup>19</sup> Our proposed mechanism has a period in which the sulfonic acid will accumulate to a maximum before being oxidized to sulfate. The oxidation can

**TABLE 1: Rate Laws and Rate Constants Used in Computer Simulations**

	forward reaction	reverse reaction
4	$2.5 \times 10^{-2}[\text{BrO}_3^-][\text{AIMSA}][\text{H}^+]$	0
5	$2.5 \times 10^6[\text{HBrO}_2][\text{Br}^-][\text{H}^+]$	$2.0 \times 10^{-5}[\text{HOBr}]^2$
6	$1.05 \times 10^3[\text{HOBr}][\text{AIMSA}]$	0
7	$2.1[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$	$1.0 \times 10^4[\text{HBrO}_2][\text{HOBr}]$
8	$8.9 \times 10^8[\text{HOBr}][\text{Br}^-][\text{H}^+]$	$1.10 \times 10^2[\text{Br}_2]$
9	$5.0 \times 10^6[\text{Br}_2][\text{AIMSA}]$	0
10	$1.5 \times 10^2[\text{Br}_2][\text{RSO}_3]$	0
11	$2.05 \times 10^3[\text{HOBr}][\text{RSO}_3]$	0

be via Br<sub>2</sub> or HOBr:



The species BrO<sub>3</sub><sup>-</sup>, HBrO<sub>2</sub>, HOBr, and Br<sub>2</sub> are oxidizing and HO<sub>2</sub>SC(NH)NH<sub>2</sub>, HO<sub>3</sub>SC(NH)NH<sub>2</sub>, and Br<sup>-</sup> represent the total reducing agents in solution. A complete reaction network that represents the full mechanism for the oxidation of AIMSAs by bromate would require a permutation of the four oxidizing agents with the three reducing agents. Bromate oxidations are usually very slow, and after initiation reaction 4 the reactive species subsequently formed become more important as oxidizing agents. Although HBrO<sub>2</sub> is a stronger oxidizing agent than BrO<sub>3</sub><sup>-</sup>, HOBr is much stronger than HBrO<sub>2</sub> such that by using reaction 5, HOBr can be substituted for HBrO<sub>2</sub>. The BrO<sub>3</sub><sup>-</sup>-AIMSAs reaction is strongly autocatalytic; suggesting that (5) is a very important reaction in this mechanism. Direct oxidation by HBrO<sub>2</sub> can thus be assumed to be negligible in our proposed mechanism.

**Computer Simulations.** The bromate-AIMSAs reaction was simulated using the simple eight-step mechanism denoted by reactions 4–11. The kinetics parameters and rate laws used in the simulations are shown in Table 1. Two different methods were used to simulate the reaction: the Livermore solver of ordinary differential equations (LSODE) integrator<sup>29</sup> and the semiimplicit Runge-Kutta method devised by Kaps and Rentrop.<sup>30</sup> Both methods gave identical simulations. Of the eight reactions used for the simulations, three are standard oxybromine reactions whose kinetics parameters are well-known. The remaining five reactions are oxybromine-sulfur reactions in which the bromine center is reduced while the sulfur center is oxidized. The simulations were greatly simplified by assuming that the oxybromine-sulfur reactions are essentially irreversible.

**Reaction 4:** The simulations were most sensitive to  $k_4$ . (4) could, however, be eliminated if there was a large enough initial [Br<sup>-</sup>]. Thus the importance of this reaction was only to initiate the reaction by producing enough Br<sup>-</sup> to sustain the reaction.

**Reaction 5:** The kinetics parameters used were taken from the revised values of Field and Forsterling.<sup>31</sup> This reaction is very important in maintaining autocatalysis by HOBr.

**Reaction 6:** The reaction of HOBr with AIMSAs should be a rapid oxygen-transfer process. This oxidation pathway is dominant during the induction period, and the simulations were sensitive to the value of  $k_6$  chosen. A low value of  $k_6$  would give Br<sub>2</sub> before the end of the induction period.

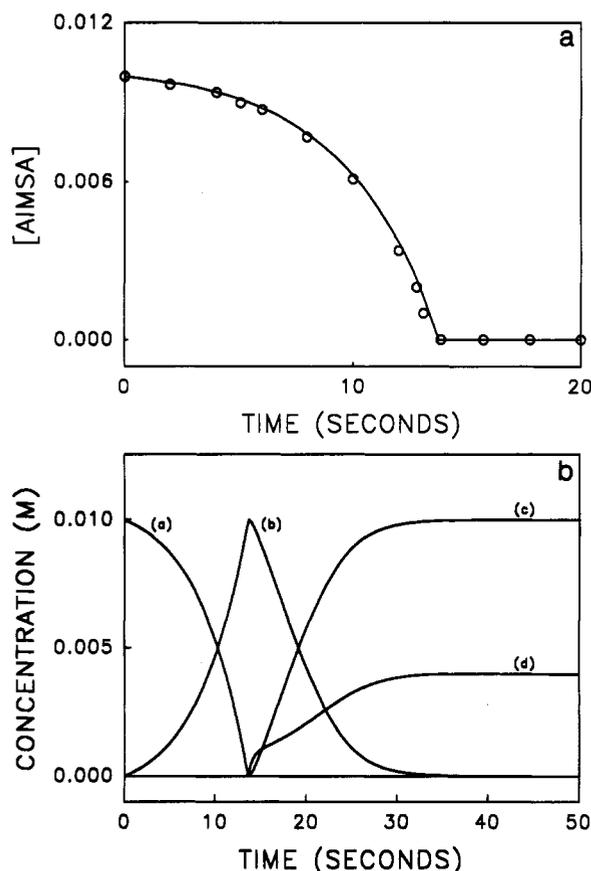
**Reaction 7:** This is a standard oxyhalogen reaction which gives rise to the [H<sup>+</sup>]<sup>2</sup> term in oxyhalogen reactions.<sup>32</sup>

**Reaction 8:** The hydrolysis of bromine was studied by Eigen and Kustin using relaxation techniques.<sup>27</sup> We have used unmodified the values they deduced for the forward and reverse reactions.

**Reactions 9:** Our preliminary experiments have shown that this reaction is very fast.<sup>28</sup> The simulations were insensitive to

TABLE 2

no.	reaction	status
M1	$\text{BrO}_3^- + 2\text{H}^+ + \text{Br}^- \rightleftharpoons \text{HBrO}_2 + \text{HOBr}$	eq 7
M2	$\text{HBrO}_2 + \text{H}^+ + \text{Br}^- \rightleftharpoons 2\text{HOBr}$	eq 5
M3	$\text{HOBr} + \text{H}^+ + \text{Br}^- \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O}$	eq 8
M4	$\text{Br}_2 + \text{SC}(\text{NH}_2)_2 + \text{H}_2\text{O} \rightarrow \text{NH}_2(\text{NH})\text{CSOH} + 2\text{Br}^- + 2\text{H}^+$	not used
M5	$\text{Br}_2 + \text{NH}_2(\text{NH})\text{CSOH} + \text{H}_2\text{O} \rightarrow \text{NH}_2(\text{NH})\text{CSO}_2\text{H} + 2\text{Br}^- + 2\text{H}^+$	not used
M6	$\text{Br}_2 + \text{NH}_2(\text{NH})\text{CSO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{NH}_2(\text{NH})\text{CSO}_3\text{H} + 2\text{Br}^- + 2\text{H}^+$	eq 9
M7	$\text{Br}_2 + \text{NH}_2(\text{NH})\text{CSO}_3\text{H} + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{CO}(\text{NH}_2)_2 + 2\text{Br}^- + 4\text{H}^+$	eq 10
M8	$\text{HOBr} + \text{SC}(\text{NH}_2)_2 \rightarrow \text{NH}_2(\text{NH})\text{CSOH} + \text{Br}^- + \text{H}^+$	not used
M9	$\text{HOBr} + \text{NH}_2(\text{NH})\text{CSOH} \rightarrow \text{NH}_2(\text{NH})\text{CSO}_2\text{H} + \text{Br}^- + \text{H}^+$	not used
M10	$\text{HOBr} + \text{NH}_2(\text{NH})\text{CSO}_2\text{H} \rightarrow \text{NH}_2(\text{NH})\text{CSO}_3\text{H} + \text{Br}^- + \text{H}^+$	eq 6
M11	$\text{HOBr} + \text{NH}_2(\text{NH})\text{CSO}_3\text{H} \rightarrow \text{SO}_4^{2-} + \text{CO}(\text{NH}_2)_2 + \text{Br}^- + 3\text{H}^+$	eq 11
M12	$\text{BrO}_3^- + \text{SC}(\text{NH}_2)_2 + \text{H}^+ \rightleftharpoons \text{NH}_2(\text{NH})\text{CSOH} + \text{HBrO}_2$	equivalent to eq 4
M13	$2\text{NH}_2(\text{NH})\text{CSOH} \rightleftharpoons \text{HO}_2(\text{NH})\text{CSOH} + \text{SC}(\text{NH}_2)_2$	not used
M14	$\text{NH}_2(\text{NH})\text{CSO}_3\text{H} + \text{NH}_2(\text{NH})\text{CSOH} \rightleftharpoons 2\text{NH}_2(\text{NH})\text{CSO}_2\text{H}$	not used



**Figure 5.** Computer simulation of the rate of consumption of AIMSAs. The data points represent simulation data and the solid line represents experimental data.  $[\text{BrO}_3^-]_0 = 0.12 \text{ M}$ ,  $[\text{H}^+]_0 = 1.0 \text{ M}$ ,  $[\text{AIMSA}]_0 = 0.01 \text{ M}$ . (b) Simulation profiles of some of the species in solution. Bromine and sulfate production does not commence until all the AIMSAs has been consumed. The sulfonic acid goes through a transient peak before being oxidized to sulfate. (a) =  $[\text{AIMSA}]$ , (b) =  $[\text{HO}_2\text{SC}(\text{NH})\text{NH}_2]$ , (c) =  $[\text{SO}_4^{2-}]$ , (d) =  $[\text{Br}_2]_0$ .

the value of  $k_9$  as long as it was over  $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . Below this value  $\text{Br}_2$  would be formed before AIMSAs had been totally consumed.

**Reactions 10 and 11:** The oxidation of the sulfonic acid was very important in determining the rate of production of  $\text{Br}_2$  at the end of the induction period. If both (10) and (11) were too fast, the  $\text{Br}^-$  formed would react with  $\text{BrO}_3^-$  (7) to form more  $\text{HOBr}$  which would quickly form  $\text{Br}_2$  (8).

The computer simulations gave an excellent fit to the experimental data. They correctly fit the sigmoidal AIMSAs consumption trace (Figure 5a) as well as the length of the induction period (Figure 5b). The simulations also show the delayed  $\text{SO}_4^{2-}$  production which commences simultaneously with  $\text{Br}_2$  production. The sulfonic acid, as predicted, goes through a maximum before

falling to produce  $\text{SO}_4^{2-}$ . These simulation data are superimposed on Figure 5b.

## Discussion

By using AIMSAs as the reductant instead of thiourea,<sup>19</sup> the mechanism is simplified quite considerably with the reaction network being reduced from 14 to 8 reactions. Most importantly, sulfur-sulfur interactions are reduced since the only intermediate possible before sulfate formation is sulfonic acid. The mechanism we have postulated complements the original  $\text{BrO}_3^-$ -thiourea reaction. No new reactions have been used in this mechanism; rather six reactions have been removed from the  $\text{BrO}_3^-$ -thiourea reaction. The conjecture that the oxidation of thiourea passes through the sulfenyl, sulfinic, and sulfonic acids before attaining the +6 oxidation state in  $\text{SO}_4^{2-}$  has been proved by using the reduced  $\text{BrO}_3^-$ -thiourea mechanism for the  $\text{BrO}_3^-$ -AIMSAs reaction.

The mechanism we have postulated does not implicate a free-radical mechanisms. We feel this is justified. The sulfur atom in AIMSAs is at oxidation state +2; passage to  $\text{SO}_4^{2-}$  can be achieved by two two-electron jumps. Use of the free-radical  $\text{BrO}_2$  species can be justified in one-electron oxidation processes in which  $\text{HBrO}_2$  becomes the autocatalytic species. Our data have shown strong bromide catalysis which, through reaction 5, implicates  $\text{HOBr}$  as the autocatalytic species.

The mechanism postulated here easily explains the important features of the reaction: induction period, acid and bromate dependences of the induction period, catalysis by bromide, and delayed sulfate production.

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## Appendix

Table 2 shows the mechanism for the bromate-thiourea reaction. This bromate-AIMSAs mechanism was derived from this mechanism by omitting six reactions that involve thiourea and the sulfenyl acid,  $\text{NH}_2(\text{NH})\text{CSOH}$ .

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