# Oxyhalogen-Sulfur Chemistry: Bromate Oxidation of 1-Methyl-2-thiourea in Acidic Medium<sup>1</sup>

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The reaction between bromate and 1-methyl-2-thiourea, CH<sub>3</sub>NH(NH<sub>2</sub>)C=S (MTU), has been studied in acidic medium. The stoichiometry of the reaction in excess MTU has been established as  $4\text{BrO}_3^- + 3\text{CH}_3\text{NH}(\text{NH}_2)\text{C}=\text{S} + 3\text{H}_2\text{O} \rightarrow 4\text{Br}^- + 3\text{SO}_4^{2^-} + 3\text{CH}_3\text{NH}(\text{NH}_2)\text{C}=\text{O} + 6\text{H}^+$  (A); and in excess bromate the stoichiometry is:  $8\text{BrO}_3^- + 5\text{CH}_3\text{NH}(\text{NH}_2)\text{C}=\text{S} + \text{H}_2\text{O} \rightarrow 4\text{Br}_2 + 5\text{SO}_4^{2^-} + 5\text{CH}_3\text{NH}(\text{NH}_2)\text{C}=\text{O} + 2\text{H}^+$  (B). Stoichiometry B includes the oxidation of MTU (stoichiometry A) and the oxidation of Br<sup>-</sup> by the excess BrO<sub>3</sub><sup>-</sup> : BrO<sub>3</sub><sup>-</sup> + 5Br<sup>-</sup> + 6H<sup>+</sup> \rightarrow 3Br\_2 + 3H\_2O. In excess BrO<sub>3</sub><sup>-</sup> the reaction is characterized by an induction period followed by formation of Br<sub>2</sub>. The reaction between Br<sub>2</sub> and MTU is very fast with a bimolecular lower limit rate constant of  $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  such that the formation of Br<sub>2</sub> is an indicator for the complete consumption of MTU. The reaction could be followed by monitoring the depletion of MTU through its absorbance at  $\lambda = 239$  nm or the formation of Br<sub>2</sub> at  $\lambda = 390$  nm. The rate of reaction was deduced as  $-d[\text{BrO}_3^-]/dt = k_0[\text{BrO}_3^-][\text{MTU}][\text{H}^+]^2$  with  $k_0 = 14.7 \pm 1.2 \text{ M}^{-3} \text{ s}^{-1}$ . A proposed 17-step reaction mechanism gives good agreement between experimental data and computer simulations.

# Introduction

The reactivity of the sulfur center is heavily dependent upon its environment and its oxidation state. In the free form as  $S^{2-}$ and HS<sup>-</sup> the sulfur center presents complex and exotic reaction characteristics especially with respect to its oxidation.<sup>2-6</sup> It is partly because of this complexity that a robust algorithm for the oxidation of a sulfur atom from an oxidation state of -2 to +6 has not yet been devised. Efficient environmental abatement procedures<sup>7</sup> cannot be devised until the mechanisms of sulfur oxidations in both aqueous and gaseous phases have been deduced.

It is generally accepted that although the sulfur center can attain several possible oxidation states between -2 to +6, a special stability is associated with oxidation states -2, 0, and +6. The 0 oxidation state is especially stabilized by polymerization, where S<sub>8</sub> is the most stable form of S(0).<sup>8</sup> Sulfur polymerizations will always distort oxidation mechanisms of the free S(-2) center<sup>2</sup> unless it is in the environment of a powerful oxidizing agent or in overwhelming excess of oxidant.

Sulfur chemistry is greatly simplified if the sulfur center is bonded to an organic molecule. Some of the reasons for subsequent simpler kinetics include the following: (a) the C–S bond is very strong and will not easily release a free sulfur atom, (b) the bulk of the organic moiety discourages extensive polymerizations past the dimer stage,<sup>9</sup> (c) the cleavage of the C–S bond can only occur when the sulfur atom is oxidatively and coordinatively saturated at oxidation state +6,<sup>10</sup> (d) oxidation steps are essentially irreversible (in excess oxidant), and (e) autooxidations and disproportionations, should they occur, serve only to ensure stoichiometric consistency, especially in excess of reductant.<sup>11</sup>

The removal of the major sources of irreproducibilities and complexities in sulfur chemistry makes it possible to study the kinetics and mechanisms of a sulfur center. The importance of sulfur chemistry in the environment,<sup>7</sup> biology,<sup>12</sup> and industry<sup>13</sup> made us recently embark on a series of research studies aimed specifically at kinetics and mechanisms of sulfur oxidations using, initially, sulfur atoms bonded to small organic molecules.<sup>14</sup>

Much insight into sulfur chemistry can be gained from a study of thiocarbonyl compounds,  $R_1R_2C=S$ . Small molecules such as thiourea, substituted thioureas, and thiosemicarbazides are moderately soluble in water, making it possible for the studies to be carried out in aqueous media.<sup>15</sup> The oxidation state of the sulfur center in thiocarbonyls is -2. Is it possible, then, to be able to oxidize such a sulfur atom to oxidation state +6 without the inherent complexities associated with sulfur chemistry? Would it be possible to cleave the C–S bond, and under what conditions? What role will the S(0) state play, if any?

Previous studies on the simplest thiocarbonyl, thiourea, had shown that the C=S double bond is extremely polar,<sup>16</sup> much more so than the corresponding C=O double bond due to the mismatch of size between the carbon and sulfur atoms which results in an incomplete  $\pi$ -bond overlap. Thus a permanent negative dipole resides on the sulfur atom, making it extremely vulnerable to electrophilic attack.<sup>17</sup>

We report in this paper on the oxidation of a substituted thiourea: 1-methyl-2-thiourea, MTU. The oxidation of thiourea by chlorite<sup>18</sup> and by bromate<sup>19</sup> exhibits sustained oscillations in a continuously stirred tank reactor (CSTR). The oxidation by chlorite further shows lateral instabilities in the form of a traveling acid wave front.<sup>20</sup> A good understanding of the mechanism of such exotic dynamics requires a good grasp of the kinetics and mechanism of the "drive" reaction. While focusing on the sulfur center, it is important to evaluate the effect of substitution on the rate of oxidation and the ease of the C–S bond cleavage to form  $SO_4^{2-}$ .

Changing the substituents on the nitrogen may affect the rate

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of reaction but not the mechanism since the major reaction is at the sulfur center. The study of the kinetics and mechanism of the oxidation of 1-methyl-2-thiourea should provide support for the mechanism proposed for the oxidation of thiourea. A computer simulation of the proposed reaction scheme is also presented in the paper.

## **Experimental Section**

**Materials.** 1-Methyl-2-thiourea, MTU, (Aldrich), perchloric acid, 70–72%, sodium bromate, sodium bromide (Fisher), bromine, and p-(dimethylamino)benzaldehyde (Aldrich) were used without further purification. MTU solutions were prepared just before use and not kept for more than 24 h. Reaction solutions were prepared using singly distilled water.

**Methods.** Experiments were carried out at  $25 \pm 1.0$  °C. The ionic strength was maintained at 1.0 M (NaClO<sub>4</sub>) in all experiments with the exception of those run in high acid. The slower BrO<sub>3</sub><sup>--</sup>MTU reactions were monitored spectrophotometrically by following absorbance of MTU at  $\lambda = 239$  nm on a Perkin-Elmer Lambda 2S UV/vis spectrophotometer interfaced to a DEC 486-33DX computer. The reaction's progress could also be followed by monitoring the absorbance of Br<sub>2</sub> at  $\lambda =$ 390 nm. For the faster reactions, kinetics measurements were performed on a Hi-Tech Scientific SF-61AF stopped-flow spectrophotometer with an M300 monochromator and a spectrascan control unit. The signal from the spectrophotometer was amplified and digitized via an Omega Engineering DAS-50/1 16-bit A/D board interfaced to a computer for storage and analysis. The direct reactions between aqueous bromine and MTU were also monitored by following decrease in bromine absorbance at 390 nm on the stopped-flow spectrophotometer.

Stoichiometric Determinations. The stoichiometric determinations were performed both in excess  $BrO_3^-$  concentrations and excess MTU. In excess  $BrO_3^-$ , the total oxidizing power  $(BrO_3^- + HOBr + Br_2)$  was determined iodometrically. Sulfate was determined gravimetrically as  $BaSO_4$ . In these gravimetric determinations,  $BrO_3^-$  was first removed iodometrically since it forms slightly insoluble  $Ba(BrO_3)_2$  with  $BaCl_2$ , thus distorting the precipitation results. Bromine formed in excess  $BrO_3^-$  concentrations could be separately determined by its absorbance at 390 nm using the absorptivity coefficient of 142  $M^{-1}$  cm<sup>-1</sup>.  $Br^-$  was determined quantitatively by precipitation as AgBr using AgNO<sub>3</sub> (after removing  $SO_4^{2-}$  with measured amounts of  $BaCl_2$ ). The expected organic product, a substituted urea, was determined spectrophotometrically at  $\lambda = 430$  nm by using

p-(dimethylamino)benzaldehyde, which forms a pink complex<sup>21</sup> with any compound with an amide group (HN-C=O).

#### Results

**Stoichiometry.** The stoichiometry of the reaction in excess MTU was determined as

$$4BrO_3^- + 3CH_3NH(NH_2)C=S + 3H_2O \rightarrow 4Br^- + 3SO_4^{2-} + 3CH_3NH(NH_2)C=O + 6H^+ (R1)$$

The stoichiometric ratio of 4:3 was determined in two ways: (a) A series of experiments were performed at constant MTU while varying the  $[BrO_3^-]_0$ . These reaction solutions were capped and left overnight. After a 24 h incubation period they were analyzed for the presence of Br<sub>2</sub> ( $\lambda = 390$  nm). The stoichiometric equivalent of BrO<sub>3</sub><sup>-</sup> was the amount needed to just produce Br<sub>2</sub> as one of the products. (b) A series of experiments were also performed at constant  $[BrO_3^-]_0$  with variable  $[MTU]_0$ . Excess MTU was determined by reacting the



**Figure 1.** Stoichiometric data: Spectral scans of several reaction product solutions in which  $[MTU]_0$  was steadily increased at constant  $[BrO_3^-]_0$ . Absorbance at 430 nm indicates the amount of complex formed between the urea product and *p*-(dimethylamino)benzaldehyde. The maximum absorbance is obtained at a ratio of 4:3. Any further increase in  $[BrO_3^-]_0$  did not increase the amount of urea product formed.

product solution with *p*-(dimethylamino)benzaldehyde. The absorbance of the resulting solution at 430 nm indicated the amount of organic product formed. The stoichiometric equivalent was taken as the amount of MTU needed to give maximum absorbance at 430 nm. Any further increase in [MTU]<sub>0</sub> gave no additional increase in absorbance. Figure 1 shows the product spectral scans obtained from the reaction mixture, which show a maximum product formation when ratio  $R = [BrO_3^-]_0/[MTU]_0$  is 4:3.

In excess bromate the stoichiometry was determined as

$$8BrO_3^- + 5CH_3NH(NH_2)C=S + H_2O \rightarrow 4Br_2 + 5SO_4^{2-} + 5CH_3NH(NH_2)C=O + 2H^+$$
 (R2)

In overwhelming excess of  $\text{BrO}_3^-$ ,  $R \ge 5$ , the amount of  $\text{Br}_2$  formed,  $[\text{Br}_2]_{\text{f}}$ , was determined by the  $[\text{MTU}]_0$  and the ratio of  $([\text{MTU}]_0/[\text{Br}_2]_{\text{f}}) = 1.25$  was consistently maintained ( $\lambda = 390$  nm,  $\epsilon = 142 \text{ M}^{-1} \text{ cm}^{-1}$ ). One mole of MTU gave one mole of  $\text{SO}_4^{2-}$  (BaSO<sub>4</sub> precipitation). Working in high acid did not afford the opportunity to assess the amount of acid formed from either R1 or R2.

The two stoichiometries are essentially the same in terms of the oxidation of MTU. The only difference lies in the further oxidation of  $Br^-$  by  $BrO_3^-$  to produce the bromine in stoichiometry R2.

**Reaction Kinetics.** Upon mixing acidic bromate and MTU solutions, no activity is observed in the leading reaction indicators: redox potential, absorbance, electrical conductivity, and pH for a measurable amount of time. With excess MTU over  $\text{BrO}_3^-$ , no activity is observed for an indefinite period, although all the  $\text{BrO}_3^-$  is consumed and some of the MTU is oxidized to  $\text{SO}_4^{2-}$  and urea according to stoichiometry R1. In excess  $\text{BrO}_3^-$ , however, the reaction starts out with a quiescent period in which the reaction indicators show no activity. After some induction period there is a sudden rise in the redox potential of the solution (Figure 2). Soon after the sudden increase in redox potential, the solution turns yellowish as



**Figure 2.** Typical redox potential trace for the  $\text{BrO}_3^--\text{MTU}$  reaction in excess  $\text{BrO}_3^-$ . The rapid increase in redox potential coincides with the formation of Br<sub>2</sub>. The final redox potential reading is essentially the  $\text{Br}^{-/1}_2\text{Br}_2$  couple. [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 0.023 M; [MTU]<sub>0</sub> = 0.0029 M; [H<sup>+</sup>]<sub>0</sub> = 0.143 M.

aqueous bromine is formed. The redox potential finally stabilizes at a value very close to the potential of the  $1/_2Br_2/Br^-$  couple (1.14 V > E > 1.00 V). The length of the induction period can be adjusted by changing the initial concentrations of the four major reactant species: acid, MTU, BrO<sub>3</sub><sup>-</sup>, and Br<sup>-</sup>. Thus the BrO<sub>3</sub><sup>-</sup>-MTU reaction can be regarded as a "clock reaction". The induction time, as defined in this paper, is the time taken by the reaction solution before it produces aqueous bromine.

We have divided the data presentation into four segments: (a) data collected at 239 nm, (b) data collected at 390 nm before the induction period, (c) data collected after the induction period, and (d) data collected on the effect of  $Br^-$ .

(a) Data Collected at  $\lambda = 239$  nm. The data at this wavelength were obtained using a conventional UV/vis spectrophotometer with a solution blank made up of acidic bromate in order to subtract the effect of bromate absorption in the UV range. UV spectral scans for the reaction solution show a peak at 239 nm, and this can be assigned to MTU. Reaction progress can be monitored in excess BrO<sub>3</sub><sup>-</sup> and in excess MTU by following the decay of the 239 nm peak. Figure 3 shows a series of UV spectra for the reaction solution, which show the decay of the 239 nm peak.

Acid Dependence. At constant  $[BrO_3^-]_0$  and  $[MTU]_0$ , the reaction is strongly catalyzed by acid (Figure 4a). Stoichiometries R1 and R2 show that acid is not a reactant, but a product. The catalytic effect of acid must be through the formation of a reactive intermediate either with  $BrO_3^-$  or with MTU. A plot of initial rate of consumption of MTU against  $[H^+]_0^2$  gives a straight line with an intercept kinetically indistinguishable from zero (see Figure 4b).

*Bromate Dependence.* There is a positive dependence between initial rate and  $[BrO_3^{-}]_0$ , although the catalytic effect is not as marked as with  $[H^+]_0$  (Figure 5a). The initial rate varies linearly with  $[BrO_3^{-}]_0$  (Figure 5b) with the expected intercept through the origin.

*MTU Dependence.* Varying initial MTU concentrations adjusts the initial MTU absorbance (Figure 6a). The reaction does show a first-order dependence in [MTU] since a plot of initial rate vs [MTU]<sub>0</sub> gives a straight line (Figure 6b).

(b) Data Collected at  $\lambda = 390$  nm. Data at  $\lambda = 390$  nm could only be collected in excess BrO<sub>3</sub><sup>-</sup> conditions. Bromine



**Figure 3.** Spectral scans in the UV region taken every 40 s showing absorbance activity at 239 nm and no activity anywhere else in the region. This peak is due to MTU, and its depletion can be monitored at this wavelength.  $[BrO_3^-]_0 = 0.0005 \text{ M}; [MTU]_0 = 0.000 25 \text{ M}; [H^+]_0 = 0.10 \text{ M}.$ 

formation ( $\lambda_{max} = 390$  nm) occurs only after all the MTU has been consumed. Thus the induction times monitored here indicate the relative rates of consumption of MTU.

Acid Dependence. The induction times obtained were much shorter in high acid concentrations (Figure 7a). The data collected at 390 nm show acid catalysis. Generally, the inverse of the induction time is a measure of the rate of reaction, and in this case a plot of reciprocal induction time vs  $[H^+]_0^2$  gives a straight line (Figure 7b).

*Bromate Dependence*. Bromate also decreases the induction period, and a plot of reciprocal induction time vs  $[BrO_3^-]_0$  gives a straight line (Figure 8).

*MTU Dependence.* In situations in which 3.0 > R > 1.3, increases in [MTU]<sub>0</sub> will increase the induction period, as it will take longer to consume MTU and to subsequently trigger formation of Br<sub>2</sub>. Figure 9 shows a situation in which *R* was maintained at a very high value (300 > R > 50). No change in the induction period is observed, although there is a change in the rate of formation of Br<sub>2</sub> after the induction period.

(c) Post-Induction Period Data. The majority of these experiments were performed in environments such that [BrO3-]0,  $[H^+]_0 \gg [MTU]_0$ . By the time the induction period ends, bromate and acid will still retain concentration values very close to their initial values. The concentration variables will now be limited to MTU concentrations and any reactive intermediates that might be formed. The observation of pseudo-first-order kinetics in the formation of Br<sub>2</sub> after the induction period is as expected. The data such as those in Figures 7a and 9 were analyzed for the apparent pseudo-first-order rate constant,  $k^{app}$ . Linear dependence was obtained between  $k^{app}$  and  $[H^+]_0^2$  (Figure 10a) and  $[BrO_3^-]_0$  (Figure 10b). In the case of [MTU] dependence, no relationship could be discerned between the pseudo-first-order rate constant and the initial MTU concentration. This is expected in a true pseudo-first-order kinetics environment. The rate constants obtained upon varying [MTU]<sub>0</sub> are shown in Table 1. There is a very slight increase in  $k^{app}$ , which can be considered insignificant.

(d) Effect of  $Br^-$ . The effect of bromide was difficult to assess. It is important to be able to deduce from experimental





**Figure 4.** (a, top) Absorbance traces at  $\lambda = 239$  nm showing the effect of acid. The first 20 s were not recorded, as they can be attributed to sample mixing and preparation.  $[BrO_3^-]_0 = 0.025$  M;  $[MTU]_0 = 0.000 25$  M.  $[H^+]_0 = (a) 0.15$  M; (b) 0.20 M; (c) 0.25 M. (b, bottom) Plot of initial rate of MTU depletion vs  $[H^+]_0^2$  from the data in part a. The intercept, as expected, is slightly negative (some threshold acid concentration is needed for the reaction to commence).

data whether Br<sup>-</sup> is acting as a general reagent or as a catalyst.  $Br^{-}$  reduced the induction time when  $[MTU]_0 > [Br^{-}]_0$ . However, when  $[Br^{-}]_{0} > [MTU]_{0}$  not only did the induction time decrease but the amount of Br2 formed also increased with  $[Br^{-}]_{0}$  (Figure 11a). The added  $Br^{-}$  ultimately ends up being converted to  $Br_2$ . The plot of reciprocal induction time vs  $[Br^-]_0$ showed a complex plot: below a certain threshold [Br<sup>-</sup>]<sub>0</sub> value, the induction time does not change. After the threshold value has been reached, there is a linear dependence. Due to the very widely spaced [Br<sup>-</sup>]<sub>0</sub> used, a semilog plot was used (Figure 11b) in order to plot all the initial Br<sup>-</sup> concentrations on the same plot. Figure 11b shows the catalytic effect of Br<sup>-</sup> as the induction period is greatly reduced in high [Br<sup>-</sup>]<sub>0</sub> conditions. The response of the pseudo-first-order rate constant was also complex (Figure 11c). The pseudo-first-order rate constant is unaffected by very low  $[Br^-]_0$  (e.g.  $10^{-6}-10^{-4}$  M Br<sup>-</sup>).

Direct  $Br_2$ -MTU Reaction. Figure 12 shows that this reaction is very fast: fast enough to test the limits of our

**Figure 5.** (a, top) Effect of  $[BrO_3^-]_0$  on the MTU depletion.  $[MTU]_0 = 0.000 25 \text{ M}$ .  $[H^+]_0 = 0.30 \text{ M}$ .  $[BrO_3^-]_0 = (a) 0.015 \text{ M}$ ; (b) 0.025 M. (b, bottom) Linear plot of initial rate of MTU consumption vs  $[BrO_3^-]_0$ . The plot also gives the expected zero intercept (reaction will not proceed without  $BrO_3^-$ ). Conditions are the same as in part a.

stopped-flow spectrophotometer. Figure 12 also shows that by the time this reaction is detected by the photomultiplier most of the Br<sub>2</sub> would have already been consumed. Attempts to slow the reaction by using Br<sub>3</sub><sup>-</sup> instead of Br<sub>2</sub> were unsuccessful. None of the standard dependence experiments could be performed on this reaction. The important information obtained from Figure 12 was that the reaction is too fast to be rate-determining in the BrO<sub>3</sub><sup>-</sup>-MTU reaction network. We managed to deduce a lower limit bimolecular rate constant for the Br<sub>2</sub>-MTU reaction of  $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

# Mechanism

1.6

The stoichiometric analysis results simplified the search for a plausible mechanism for this reaction: (a) the organic molecule is left intact, and the only activity in terms of oxidation (electron transfer and/or hydrolysis) is occurring at the sulfur center of the thiocarbonyl compound, MTU; (b) there is successive electron transfer from the sulfur center to the bromine center except when the oxidation state of the sulfur center is at



**Figure 6.** (a, top) Effect of varying  $[MTU]_0$  on the traces obtained at  $\lambda = 239$  nm (absorption peak for MTU). There is an expected decrease in initial absorbance as the initial MTU concentration is decreased.  $[H^+]_0 = 0.25$  M.  $[BrO_3^-]_0 = 0.025$  M.  $[MTU]_0 = (a) 0.000$  373 M; (b) 0.000 25 M; (c) 0.000 188 M; (d) 0.000 125 M. (b, bottom) Plot of initial reaction rate vs  $[MTU]_0$  for the data in part a.

+6 and that of the bromine center is at -1; and (c) the stoichiometry is so clean that it accounts for all the sulfur in the reaction mixture going to  $SO_4^{2-}$ , thus precluding the possibility of sulfur polymerizations and/or the formation of colloidal sulfur.

From the data presented in Figures 4b, 5b, and 6b, the rate of reaction is given by the equation

rate = 
$$k_0 [BrO_3^{-}] [H^+]^2 [MTU]$$
 (1)

From the experimental data the value of  $k_0$  was determined to be 14.7  $\pm$  1.2 M<sup>-3</sup> s<sup>-1</sup>. A rate-determining step that can support eq 1 is not easily deduced from the expected reaction initiation and subsequent reaction sequence. The reaction initiation can be presented through reaction R3:



**Figure 7.** (a, top) Absorbance traces at  $\lambda = 390$  nm in conditions of excess [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub>. Acid simultaneously reduces the induction time and accelerates rate of formation of Br<sub>2</sub>. [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 0.10 M; [MTU]<sub>0</sub> = 0.001 M. [H<sup>+</sup>]<sub>0</sub> = (a) 0.10 M; (b) 0.20 M; (c) 0.30 M; (d) 0.40 M; (e) 0.50 M. (b, bottom) Plot of reciprocal of induction time (equivalent to rate of reaction) vs [H<sup>+</sup>]<sub>0</sub><sup>2</sup> from the data shown in part a.

Reaction R3 does not give the observed second-order dependence on acid concentration. The bromous acid formed in reaction R3 can further be reduced to form  $Br^-$ .

$$HBrO_{2} + CH_{3}NH(NH_{2})C=S →$$
  
CH<sub>3</sub>NH(NH)C-S-OH + HOBr (R4)

The  $Br^-$  produced in reaction R5 can then be used to form more reactive intermediates through the standard oxyhalogen reaction R6:<sup>22</sup>

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$$
 (R6)

The rate of reaction with reaction R6 as the rate-determining



**Figure 8.** Linear plot of reciprocal induction time vs  $[BrO_3^-]_0$  ( $\lambda = 390 \text{ nm}$ ).  $[MTU]_0 = 0.002 \text{ M}$ .  $[H^+]_0 = 0.030 \text{ M}$ . The positive intercept on the  $[BrO_3^-]_0$  axis is expected, as *R* has to be greater than 4/3 for any bromine to be formed.



**Figure 9.** "Peacock-tail type" traces derived from variation of  $[MTU]_0$ in large excess of  $[BrO_3]_0$  (R > 50). The induction period as well as the pseudo-first-order rate constant, stays the same. The rate of formation of Br<sub>2</sub>, however, varies.  $[BrO_3^-]_0 = 0.15$  M;  $[H^+]_0 = 0.030$ M;  $[MTU]_0 = (a) 0.0005$  M; (b) 0.001 M; (c) = 0.0015 M; (d) 0.002 M; (e) 0.0025 M; (f) 0.003 M.

step becomes

rate = 
$$k[BrO_3^{-}][H^+]^2[Br^-]$$
 (2)

After reaction R6, the most important reaction is R5, which is the rapid oxidation of MTU by HOBr.

Reaction R5 is the most important oxidation route of MTU and the other intermediate sulfur species.

The Br<sup>-</sup> formed in reaction R5 can be used in reaction R6 to produce more HOBr and HBrO<sub>2</sub>, but in the presence of HBrO<sub>2</sub> (from reaction R6), all the Br<sup>-</sup> will be converted to HOBr through the rapid equilibrium,  $R7^{:23}$ 

$$HBrO_2 + Br^- + H^+ \rightleftharpoons 2HOBr$$
 (R7)



**Figure 10.** (a, top) Effect of acid on the pseudo-first-order rate constant for the formation of bromine after the induction period: Linear plot of k' vs  $[H^+]_0$ .  $[BrO_3^-]_0 = 0.10 \text{ M}$ ;  $[MTU]_0 = 0.001 \text{ M}$ . (b, bottom) Effect of  $[BrO_3^-]_0$  on the pseudo-first-order rate constant, k'.  $[MTU]_0 = 0.002$ M;  $[H^+]_0 = 0.030 \text{ M}$ .

TABLE 1: Effect of Variation of  $[MTU]_0$  on the Pseudo-First-Order Rate Constant, k', for the Formation of Br<sub>2</sub> at the End of the Induction Period. In This Series  $[BrO_3^{-}]_0$ ,  $[H^+]_0 \gg [MTU]_0$ 

•	5 10/ 1 10	L 10		
	[MTU] <sub>0</sub> /M	$[H^+]_0/M$	$[BrO_3^-]_0/M$	$k^{\rm app}/{\rm s}^{-1}$
	0.0005	0.3	0.15	0.199
	0.001	0.3	0.15	0.204
	0.0015	0.3	0.15	0.203
	0.002	0.3	0.15	0.205
	0.0025	0.3	0.15	0.211
	0.003	0.3	0.15	0.210

HOBr will react further as in reaction R5 or any R5-type reactions (HOBr oxidation of the MTU and other intermediates) to produce  $Br^-$  and perpetuate the reaction. If reactions R5 and R7 are rapid enough, it is easy to see how eqs 1 and 2 will become equivalent.

**Further Oxidations.** A mechanism that invokes bromous acid and hypobromous acid as the reactive species requires the oxidation processes to proceed through a series of 2-electron



**Figure 11.** (a, top) Effect of  $[Br^-]_0$  on the absorbance traces at 390 nm. Low  $Br^-$  concentrations do not affect the rate of reaction nor the induction time.  $[BrO_3^-]_0 = 0.15$  M;  $[MTU]_0 = 0.002$  M;  $[H^+]_0 = 0.30$  M.  $[Br^-]_0 = (a) 0.000$  01 M; (b) 0.0001 M; (c) 0.0005 M. (d) 0.001 M; Addition of  $Br^-$  up to  $1 \times 10^{-5}$  M gave the same trace (a). These low  $Br^-$  concentrations did not affect the reaction kinetics. (b, middle) Semilog plot of  $[Br^-]_0$  vs the induction time. The data used are from Figure 11a. (c, bottom) Semilog plot of  $[Br^-]_0$  vs the pseudo-first-order rate constant for the formation of bromine. Low  $[Br^-]_0$  do not affect the rate constant.



**Figure 12.** Direct reaction of  $Br_2$  vs MTU monitored at 390 nm. The reaction is so fast that it is nearly over by the time it is detected by the stopped-flow spectrophotometer. [MTU]<sub>0</sub> = 0.002 M. [Br<sub>2</sub>]<sub>0</sub> = (a) 0.0053 M; (b) 0.0035 M; (c) 0.0018 M.

reactions. We expect the sulfur center, as well, to be oxidized via two-electron transfer transitions. The first step in the oxidation of the sulfur center is reaction R5 which forms the sulfenyl acid,  $CH_3NH(NH)C-S-OH$ . The sulfenyl acid can further be oxidized to form the sulfinic acid:

Further oxidation of the sulfinic acid yields the sulfonic acid:

Subsequent oxidation of the sulfonic acid should concurrently occur with the cleavage of the C–S bond to form a urea and  $SO_4^{2-}$ .

**Possible Sulfur–Sulfur Interactions.** Reactions R3–R5 and R8–R10 represent oxybromine–sulfur compound interactions. Some sulfur-sulfur interactions may be necessary in this system to maintain stoichiometric consistency especially in conditions of excess MTU. Since no colloidal sulfur was observed when MTU is in excess, there must be some fast rearrangements that leave the sulfur center at either oxidation state -2 (as in MTU) or at oxidation state +6 (as in SO<sub>4</sub><sup>2–</sup>). The other possible oxidation state, 0, will not be stable in this environment as a sulfenyl acid. Sulfenyl acids can either dimerize or autooxidize:

$$2CH_3NH(NH)C-SOH \Rightarrow$$
  
 $CH_3NH(NH_2)C=S + CH_3NH(NH)C-SO_2H$  (R11)

The sulfinic acid, in the absence of further oxidant, can also

TABLE 2: Mechanism of the Oxidation of 1-Methyl-2-thiourea by Bromate in Acidic Medium

reaction		
no.	reaction	
M1	$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HBrO_2 + HOBr$	2.1[]
M2	$HBrO_2 + Br^- + H^+ \rightleftharpoons 2HOBr$	2.5
M3	$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$	8.9 >
M4	$BrO_3^- + SC(NH_2)(NH)CH_3 + H^+ \rightleftharpoons HBrO_2 + HOSC(NH)(NH)CH_3$	5.3 >
		5.
M5	$HBrO_2 + SC(NH_2)(NH)CH_3 \rightarrow HOSC(NH)(NH)CH_3 + HOBr$	1.0 >
M6	$HOBr + SC(NH_2)(NH)CH_3 \rightarrow HOSC(NH)(NH)CH_3 + Br^- + H^+$	1.0 >
M7	$Br_2 + SC(NH_2)(NH)CH_3 + H_2O \rightarrow HOSC(NH)(NH)CH_3 + 2Br^- + 2H^+$	1.0 >
M8	$Br_2 + HOSC(NH)(NH)CH_3 + H_2O \rightarrow HO_2SC(NH)(NH)CH_3 + 2Br^- + 2H^+$	2.7 >
M9	$Br_2 + HO_2SC(NH)(NH)CH_3 + H_2O \rightarrow HO_3SC(NH)(NH)CH_3 + 2Br^- + 2H^+$	1.5 >
M10	$Br_2 + HO_3SC(NH)(NH)CH_3 + 2H_2O \rightarrow SO_4^{2-} + OC(NH_2)(NH)CH_3 + 2Br^- + 4H^+$	1.0 >
M11	$HOBr + HOSC(NH)(NH)CH_3 \rightarrow HO_2SC(NH)(NH)CH_3 + Br^- + H^+$	4.0 >
M12	$HOBr + HO_2SC(NH)(NH)CH_3 \rightarrow HO_3SC(NH)(NH)CH_3 + Br^- + H^+$	5.0 >
M13	$HOBr + HO_3SC(NH)(NH)CH_3 + H_2O \rightarrow SO_4^{2-} + OC(NH_2)(NH)CH_3 + Br^- + H^+$	1.0 >
M14	$BrO_3^- + HOSC(NH)(NH)CH_3 + H^+ \rightarrow HO_2SC(NH)(NH)CH_3 + HBrO_2$	1.03
M15	$BrO_3^- + HO_2SC(NH)(NH)CH_3 + H^+ \rightarrow HO_3SC(NH)(NH)CH_3 + HBrO_2$	9.0[1
M16	$HBrO_2 + HOSC(NH)(NH)CH_3 \rightarrow HO_2SC(NH)(NH)CH_3 + HOBr$	2.5 >
M17	$HBrO_2 + HO_2SC(NH)(NH)CH_3 \rightarrow HO_3SC(NH)(NH)CH_3 + HOBr$	1.5 >

autooxidize:

$$2CH_3NH(NH)C-SO_2H \rightleftharpoons CH_3NH(NH)C-SOH + CH_3NH(NH)C-SO_3H$$
 (R12)

Further reactions analogous to R12 will finally produce MTU and  $SO_4^{2-}$ .

**The Induction Period.** There is only one reaction that forms bromine, and it is the reverse of the bromine hydrolysis reaction:<sup>24</sup>

$$HOBr + Br^{-} + H^{+} \rightleftharpoons Br_{2} + H_{2}O \qquad (R13)$$

Reaction R13 is known to be a very fast reaction. While  $Br_2$  is being formed through reaction R13, it will be concurrently consumed via reaction R14,<sup>25</sup>

$$Br_2 + CH_3NH(NH_2)C = S + H_2O \rightarrow CH_3NH(NH)C -$$
  
SOH + 2Br<sup>-</sup> + 2H<sup>+</sup> (R14)

as well as in other reduction reactions that  $Br_2$  can undergo with other sulfur compound intermediates. In general, these reactions can be grouped as

$$Br_2 + S(X) + H_2O \rightarrow 2Br^- + S(X+2) + 2H^+$$
 (R15)

The two-electron oxidation occurs by means of an oxygen transfer onto the sulfur atom.

Our experimental data show that the group of reactions indicated in reaction R15 is very fast and that  $Br_2$  will not coexist with MTU nor with any of its intermediate oxidation products.<sup>25</sup> Thus as long as there is reductant in the reaction solution,  $Br_2$  will not accumulate, and the reaction will remain in the "induction period" step. Three major competing reactions are of importance during the induction period. The first is the general oxidation of the sulfur compound by  $BrO_3^-$  to produce  $Br^-$ :

$$BrO_3^- + [- - S(-2)] + ... \rightarrow Br^- + SO_4^{2-} + ...$$
(R16)

Secondly, there is the  $BrO_3^- - Br^-$  reaction which produces  $Br_2{:}^{22}$ 

$$BrO_{3}^{-} + 5Br^{-} + 6H^{+} \rightarrow 3Br_{2} + 3H_{2}O$$
 (R17)

Thirdly is the general R15-type group of reactions which consume Br<sub>2</sub>. Among these three processes, R16 is the slowest

V (forward rate), V (reverse rate)  $BrO_3^{-}][Br^{-}][H^{+}]^2$ ,  $1.0 \times 10^4[HBrO_2][HOBr]$  $\times 10^{6}$ [HBrO<sub>2</sub>][Br<sup>-</sup>][H<sup>+</sup>], 2.0  $\times 10^{-5}$ [HOBr]<sup>2</sup>  $\times 10^{8}$ [HOBr][Br<sup>-</sup>][H<sup>+</sup>], 1.10  $\times 10^{2}$ [Br<sub>2</sub>]  $\times 10^{1}$ [BrO<sub>3</sub><sup>-</sup>][SC(NH<sub>2</sub>)(NH)CH<sub>3</sub>][H<sup>+</sup>],  $.0 \times 10^{-6}$ [HBrO<sub>2</sub>][HOSC(NH)(NH)CH<sub>3</sub>]  $\times 10^{4}$ [HBrO<sub>2</sub>][SC(NH<sub>2</sub>)(NH)CH<sub>3</sub>] × 10<sup>4</sup>[HOBr][SC(NH<sub>2</sub>)(NH)CH<sub>3</sub>  $\times 10^{3}[Br_{2}][SC(NH_{2})(NH)CH_{3}]$  $\times 10^{7}[Br_{2}][HOSC(NH)(NH)CH_{3}]$  $\times 10^{7}[Br_{2}][HO_{2}SC(NH)(NH)CH_{3}]$  $\times 10^{2}[Br_{2}][HO_{3}SC(NH)(NH)CH_{3}]$  $\times 10^{4}$ [HOBr][HOSC(NH)(NH)CH<sub>3</sub>]  $\times 10^{4}$ [HOBr][HO<sub>2</sub>SC(NH)(NH)CH<sub>3</sub>]  $\times 10^{4}$ [HOBr][HO<sub>3</sub>SC(NH)(NH)CH<sub>3</sub>]  $\times 10^{1}$ [BrO<sub>3</sub><sup>-</sup>] [HOSC(NH)(NH)CH<sub>3</sub>][H<sup>+</sup>]  $BrO_3^{-}[HO_2SC(NH)(NH)CH_3][H^+]$ × 10<sup>4</sup>[HBrO<sub>2</sub>][HOSC(NH)(NH)CH<sub>3</sub>]  $1.5 \times 10^{4}$ [HBrO<sub>2</sub>][HO<sub>2</sub>SC(NH)(NH)CH<sub>3</sub>]

and rate-determining group. Thus the global reaction dynamics will be determined by reaction R16.

**Post-Induction Period.** The rate of consumption of MTU, the length of the induction period, and the formation of bromine all appear to follow the same rate law, which has the term  $k[BrO_3^-][H^+]^2$ . Thus these three events would appear to be controlled by reaction R6. At the end of the induction period, with all the reductant consumed, the  $BrO_3^--Br^-$  reaction will dominate. Bromine is formed via reaction R13, but since R13 is fast, it is not rate-determining, and the rate of  $Br_2$  formation will be controlled by the rate of formation of HOBr (reaction R6):

$$d[Br_2]/dt = d[HOBr]/dt = k[BrO_3^{-}][H^+]^2[Br^-]$$
 (3)

After considering the relative concentrations of the reactive species,

$$d[Br_2]/dt = k^{app}[Br^-]$$
(4)

where

$$k^{app} = k[BrO_3^{-}][H^{+}]^2$$

With the amount and rate of formation of  $Br^-$  being proportional to [MTU];  $Br^-$  in eqs 3 and 4 can be replaced by MTU ( $[Br^-]_{formed} = 1.33[MTU]_0$ ). The data in Figure 10a,b support the form of eq 3.

Effect of Br<sup>-</sup>. Br<sup>-</sup> is a major reactant/intermediate/product within the reaction network. Equation 3 explains why Br<sup>-</sup> shortens the length of the induction period. Very low concentrations of Br<sup>-</sup> will have no effect on the rate of reaction (see Figure 11b,c) because normal BrO<sub>3</sub><sup>-</sup> solutions contain an equilibrium amount of Br<sup>-</sup> ions that cannot be totally eliminated.<sup>26</sup> Generally, the Br<sup>-</sup> concentrations are on the order of  $10^{-6}-10^{-5}$  M. This explains why a threshold value is needed before bromide can exert any catalytic effect. The catalytic effect of Br<sup>-</sup> is through the enhancement of reaction R17 at the start of the reaction. The Br<sub>2</sub> formed in R17 will participate in R15-type reactions to accelerate the rate of consumption of MTU. Thus the induction period will be reduced (see Figure 11a).

#### **Computer Simulations**

A simplified mechanism that accounts for the observed features of the reactions was used for the simulations. The simulations reported here are for the situation with excess  $BrO_3^-$ . Excess  $BrO_3^-$  conditions give  $Br_2$  formation after an induction period. To support the mechanism, the simulations needed to correctly predict the induction time, the rate of formation of  $Br_2$ , and the mass balance in terms of the bromine and oxybromine species. Such features are not observed in conditions of excess MTU. Excess  $BrO_3^-$  conditions allowed us to ignore the sulfur–sulfur reactions, which simplified the mechanism greatly. The simulation reactions are divided into three groups: the oxybromine reactions, the initiation reactions, and the oxybromine–sulfur compound reactions. These reaction are shown in Table 2.

**Oxybromine Reactions.** Only three oxybromine reactions were considered relevant for this reaction system: reactions R6, R7, and R13 (these have been renumbered in Table 2 as reactions M1, M2, and M3, respectively).

*Reaction R6.* This is the most important reaction in this mechanism. This reaction has been extensively studied, and the kinetics parameters are well-known. The values used for the simulations were obtained from the FKN mechanism of Field *et al.*<sup>27</sup>

*Reaction R7.* This reaction controls the bromous acid concentrations. It is essential in generating the reactive species HOBr. It is a very rapid reaction, which proceeds as written with an equilibrium constant of  $4 \times 10^{13}$  M<sup>-1</sup>. The kinetics parameters adopted for simulations were from the work of Noyes.<sup>28</sup>

*Reaction R13.* The hydrolysis of Br<sub>2</sub> was studied by Eigen and Kustin using temperature-jump spectrophotometry. The forward rate constant of  $8 \times 10^9$  M<sup>-2</sup> s<sup>-1</sup> was derived from their work.<sup>24</sup>

**Initiation Reactions.** These reactions were unnecessary if one assumed a high enough initial  $Br^-$  concentration in the reaction mixture (about  $10^{-4}$  M). The relevance of these reactions was to produce enough  $Br^-$  to permit the reaction to start producing its own  $Br^-$  and other oxyhalogen intermediates. Reaction R3 is the initiator reaction when coupled with further reduction of the HBrO<sub>2</sub> (reactions R4 and R5). The three initiator reactions were irrelevant when  $Br^-$  was initially added to the reaction mixture (see Figure 11a). The initiation reactions are labeled as M4–M6 in Table 2. They also did not influence the overall global reaction kinetics. The simulations were also not very sensitive to the kinetics constants used for reaction R3 when  $Br^-$  was initially added as a reactant. The value of  $k_{M4}$  used of 53.0 M<sup>-2</sup> s<sup>-1</sup> was chosen from the best simulations fit.

**Oxybromine–Sulfur Compound Reactions.** For these sets of reactions, two major oxidants were assumed:  $Br_2$  and HOBr. HBrO<sub>2</sub> was important as one of the initiation reactions (reaction M5), and by assuming a rapid reaction R7, HBrO<sub>2</sub> was also the most important precursor to the formation of HOBr. Four reductants were assumed: MTU and the sulfenyl, sulfinic, and sulfonic acids. Thus eight reactions were needed to produce an exhaustive list of oxybromine–sulfur compound reactions (M6–M13). Since the basic assumption was that such reactions were fast, the kinetics constants chosen did not affect the simulations results as long as they were fast enough so as not to be rate-determining.

Additional Oxybromine–Sulfur Compound Reactions. Though  $BrO_3^-$  is a very poor oxidizing agent compared with  $Br_2$  and HOBr, two extra reactions were added: M14 and M15. This was necessary because, despite its slow rate of oxidation,  $BrO_3^-$  is in overwhelming excess over the reactive intermediates and, through pure mass action kinetics, ends up being a significant oxidation pathway. Use of HBrO<sub>2</sub> oxidations in the



**Figure 13.** (a, top) Comparison between experimental (solid line) and simulations (dotted line) for the induction period and formation of  $Br_2$  in conditions of excess  $[BrO_3^{-}]_0$  using the mechanism shown in Table 2. There is good agreement in terms of the induction period, the rate of formation of bromine, and the material balance.  $[BrO_3^{-}]_0 = 0.15$  M;  $[MTU]_0 = 0.002$  M;  $[H^+]_0 = 0.30$  M. (b, bottom) Simulation results on other relevant species in the reaction. The simulations accurately predict that the formation of bromine commences after the MTU has been consumed (in these conditions this is about 2 s). Sulfate is formed at about the same rate as bromine, and the sulfonic acid initially accumulates before falling as sulfate is formed.

simulations (reactions M16, M17) allowed the simulations to converge much faster in terms of stoichiometric consistency but were not significant in terms of rate of reaction due to the rapid reversibility of reaction R7.

The 17 rate equations in Table 2 were numerically integrated using the semiimplicit Runge–Kutta method devised by Kaps and Rentrop.<sup>29</sup> The results of the simulations are shown in Figure 13a,b. There appears to be very good agreement between experimental data and the simulations. Figure 13b also proves earlier observations that showed that sulfate formation occurs after the induction period and at about the same rate as bromine formation.

## Conclusion

The mechanism reported here shows that the previous mechanism suggested for the bromate oxidation of the unsubstituted thiourea was correct.<sup>15</sup> More experimental data have been presented here than in previous studies of oxidation mechanisms of sulfur compounds. The data that show the depletion of the substrate at  $\lambda = 239$  nm have been especially useful in confirming the proposed mechanism. The reaction with thiourea is faster than the reaction with MTU. The studies with MTU provide experimental evidence that shows that bromine formation takes place only after all the sulfur compound is consumed. Bromide shows the same effect in both reactions, i.e., a linear dependence at low concentrations, which becomes nonlinear at high concentrations.<sup>15</sup> A 14-step mechanism was proposed for the bromate-thiourea reaction.<sup>15</sup> The mechanism proposed for the bromate-MTU system has 17-steps, which include the formation and oxidation of the intermediate HO2-SC(NH)NHCH<sub>3</sub>, a sulfinic acid. This is supported by previous studies of the kinetics and mechanism of the oxidation of aminoiminomethanesulfinic acid by oxyhalogens.<sup>25</sup> Disproportionation reactions of the oxidized sulfur compound intermediates were included in the mechanism of the bromatethiourea system. These have been omitted from the bromate-MTU mechanism, as new experimental data show that sulfursulfur interactions are insignificant in conditions of excess oxidant. Computer simulations of the mechanisms for both systems show that once the sulfonic acid, HO<sub>3</sub>SC<, is formed, its consumption is relatively slow. This is the stage where the C-S bond is cleaved to give sulfate. The study reported in this paper thus supports the general mechanism proposed for the oxidation of the sulfur center in thiocarbonyl compounds by oxyhalogens and shows that substitution at the nitrogen affects only the rate of reaction.

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