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Kinetics and Mechanism of the Oxidation of Thiourea by Bromate in Acidic Solution[1]

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The reaction between bromate and thiourea has been studied in acidic medium. The stoichiometry of the reaction in excess thiourea is $4BrO_3^- + 3SC(NH_2)_2 + 3H_2O \rightarrow 3SO_4^{2-} + 3OC(NH_2)_2 + 4Br^- + 6H^+$; in excess bromate the stoichiometry is $8BrO_3^- + 5SC(NH_2)_2 + H_2O \rightarrow 5SO_4^{2-} + 5OC(NH_2)_2 + 4Br_2 + 2H^+$. No bromine is formed in excess thiourea. In excess bromate the reaction displays an initial induction period. At the end of the induction period, the redox potential of the reaction mixture rises sharply, sulfate appears (signaled by precipitation of $BaSO_4$ when $BaCl_2$ is initially added), and a yellow coloration (due to bromine) is first noticeable. Consequently, bromine is not formed until all thiourea is consumed. A 14-step mechanism is proposed and used to simulate the observed kinetics. The rate-determining step for bromine appearance is formation of HOBr from the BrO_3^-–Br^- reaction. The oxidation of thiourea proceeds via oxygen additions on sulfur, successively forming $HOSC(NH)NH_2$, $HO_2SC(NH)NH_2$, $HO_3SC(NH)NH_2)$, and SO_4^{2-}. The mechanism requires that cleavage of the X–C bond to form urea and SO_4^{2-} occur at the sulfonic acid level and not before, in agreement with experimental observation.

Introduction

Sulfur chemistry is closely linked with nonlinear in chemistry.[2] The oxidation of even such simple sulfur compounds as sulfide,[3] thiocyanate,[4,5] and thiourea[6] frequently produces nonlinear kinetics. Consequently, efforts at systematically designing chemical oscillators were greatly rewarded when sulfur compounds were reacted with oxyhalogen compounds such as sodium bromate or chlorite, especially in open (flow) reactors.[7] For example, the majority of pH-regulated oscillators so far dissolved involve the oxidation of some sulfur compound.[8]

Thiourea is one of the simplest and most reactive sulfur compounds and one that exhibits complex nonlinear behavior on being oxidized. With iodine it shows autoinhibition,[9] yet when oxidized by bromine it shows autocatalysis.[10] With iodate is shows oligooscillations,[9] and with bromate[11] and chlorite[12] it shows clock reaction characteristics. In an open reactor, oxidation of thiourea displays oscillatory behavior with bromate and chlorite. Fascinating, too, is the recent discovery that in a closed (batch) reactor, the chlorite–thiourea reaction gives a traveling wave of chlorine dioxide.[13]

Our interest in sulfur chemistry has been to understand the origin of the observed nonlinear behavior of sulfur compounds. A first step toward this goal is a search for full understanding of the kinetics and mechanism of the oxidation of sulfur compounds. Previous kinetics studies of elementary steps in prototype sulfur compound oxidations have revealed interesting reactivity patterns including sulfur–sulfur polymerizations,[14] free-radical formation,[15] halogenated sulfur intermediates,[16] and a pyrosulfate intermediate in the oxidation of HSO_3^- by HSO_5^-.[17]

Our related studies on the oxidation of thiocyanate by iodate[18] and by bromine[19] disclosed a consistent pattern of oxidation that proceeds via successive oxygen transfer to form sulfenyl, sulfinic, and sulfonic acids and, finally, sulfate ion. The reaction between chlorite and thiourea[20] also displays the same sequence. In this paper we report an experimental determination of the kinetics of the oxidation of thiourea by bromate in acidic solution and an analysis of the mechanism of this reaction by computer simulation.

Experimental Section

Materials. The following reagent grade chemicals were used without further purification: sodium bromide, thiourea, perchloric acid (60%), sodium bromide, sodium perchlorate (Fisher), bromine, silver nitrate, sodium bromate, and sodium hydroxide (Aldrich). Neither of the major reactants—sodium bromate and thiourea—was standardized; they were assumed to be of high enough purity. Perchloric acid was standardized by standard sodium hydroxide with methyl orange as indicator.

Stoichiometric determinations were performed by analyzing for sulfate, bromate, and bromine. Sulfate was analyzed gravimetrically as $BaSO_4$ only in excess thiourea, because $Ba(BrO_3)_2$ is not very soluble in water, and thus gravimetric analysis of solutions with excess bromate gave anomalously high values.[21] Although barium bromite also forms a precipitate, it is sufficiently soluble that it does not precipitate in millimolar quantities. Generally, for quantitative determinations of sulfate, the reaction solutions were allowed to sit for at least 24 h before addition of barium chloride. Subsequently, the precipitate was allowed to settle for another 24 h before any analyses were performed. Excess bromate was acidified and mixed with excess iodide, and the liberated iodine was titrated against standard sodium thiosulate with starch as indicator. Bromine was evaluated from its absorbance at 390 nm (absorptivity coefficient 142 M^{-1} cm^{-1}). There was no direct method of independently determining bromide concentrations. The bromide ion specific electrode was ineffective in the presence of sulfur compounds; almost instantly upon using it, its surface was coated with a black film of some sulfur compound, and the potential reading started to drift.

Methods. The reaction was followed by monitoring changes in redox potential and optical absorbance of bromine. Redox potential measurements were carried out with platinum and Radiometer K601 $Hg|Hg_2SO_4|K_2SO_4$ electrodes. The use of mercury/mercuric sulfate as reference instead of the normal calomel electrode was to avoid possible interference by chloride ions from the electrode. Absorbance measurements were carried out on a Varian DMS 200 UV/visible spectrophotometer and on a Pye Unicam SP1750 spectrophotometer. The reaction was performed with high initial acid and bromate concentrations such

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that initial concentrations $[H^+]_0$, $[BrO_3^-]_0 \gg [SC(NH_2)_2]_0$. As a result, no fluctuations in pH were observed during the course of the reaction.

Both slow and fast reactions were carried out in a thermostated Hi-Tech SF-3L stopped-flow spectrophotometer. No difference in absorbance between stirred and unstirred solutions was observed, and all absorbance readings were made in unstirred solutions. The ionic strength was maintained at 1.0 M ($NaClO_4$) and the reaction temperature was kept at 25 ± 0.1 °C.

Results

Stoichiometry. The stoichiometry found in excess bromate was

$$8BrO_3^- + 5SC(NH_2)_2 + H_2O \rightarrow 5SO_4^{2-} + 5OC(NH_2)_2 + 2H^+ + 4Br_2 \quad (R1)$$

There was quantitative formation of sulfate as predicted by R1. Gravimetric determinations of sulfate were successful in excess thiourea conditions or at the exact stoichiometric ratio of 8:5. Using absorbance measurements, over 97% of expected bromine was detected. The 3% loss could be attributed to the volatility of the bromine or the hydrolysis of bromine. Iodometric titration gave a titer that included both the excess bromate and the bromine produced. Urea can hydrolyze to give NH_4^+ and CO_2 in strongly acidic media:

$$OC(NH_2)_2 + H_2O + 2H^+ \rightarrow CO_2 + 2NH_4^+ \quad (R2)$$

However, we did not observe any gas evolution in our reaction mixtures at pH 2.

In excess thiourea no bromine was produced, and the stoichiometric ratio of bromate to thiourea became 4:3:

$$4BrO_3^- + 3SC(NH_2)_2 + 3H_2O \rightarrow 3SO_4^{2-} + 3OC(NH_2)_2 + 4Br^- + 6H^+ \quad (R3)$$

confirming results obtained in an earlier study.[22]

The 4:3 ratio was arrived at by running several experiments in which the bromate concentrations were varied for a fixed amount of thiourea. The required stoichiometric bromate concentration was the highest possible before bromine is evolved. Bromide was determined by running two identical experiments: in one the amount of sulfate was determined ($BaSO_4$), and in the other the amount of sulfate plus bromide (Ag_2SO_4 + AgBr) was determined.

Reaction Dynamics. Upon mixing excess bromate and thiourea, there is initially no activity in either the redox potential or the absorbance of bromine at 390 nm. After a time that is determined by initial conditions, the quiescent period gives way to an active period where the redox potential suddenly shoots up from 0.6 to 1.05 V (see Figure 1 in ref 11), and the solution slowly begins to turn yellow due to the formation of aqueous bromine. If the reaction is run in the presence of small quantities of barium chloride (about 10^{-3} M to avoid precipitation of barium bromate), barium sulfate is quickly and suddenly formed at the point where bromine production commences and the redox potential suddenly shoots up. All three events occur simultaneously. The reaction dynamics are so reproducible that three separate experiments could be set up and these events would be synchronized, despite the fact that the redox potential experiments were performed in a vigorously stirred reaction cell, while absorbance measurements were performed in an unstirred spectrophotometer cuvette. The significant parameters we recorded are (i) induction period (time taken for the quiescent period to end), (ii) rate of formation of bromine at the end of the induction period, and (iii) final absorbance of bromine.

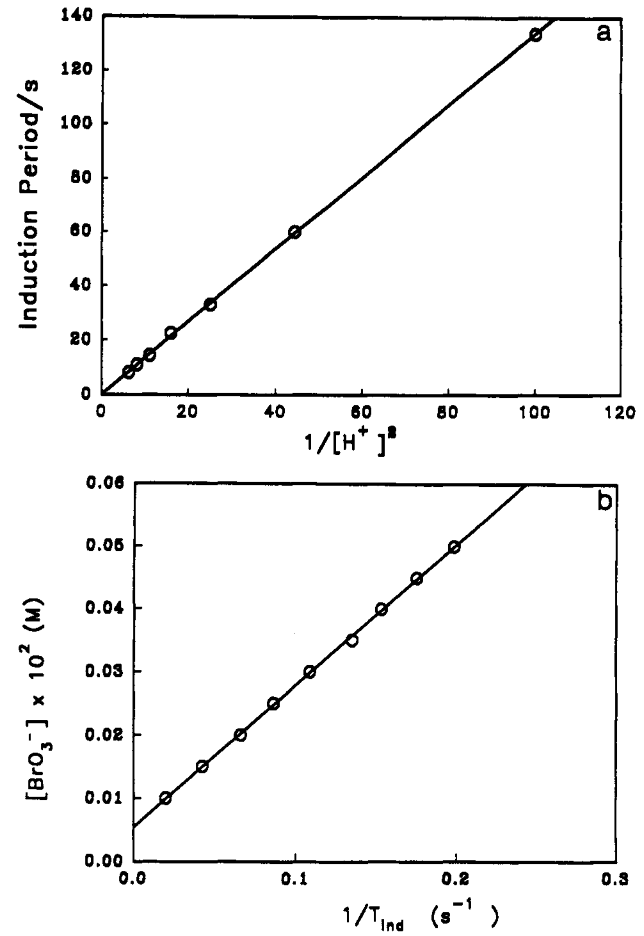

Figure 1. (a) Plot of induction period vs $1/[H^+]_0^2$. The zero intercept suggests that the mechanism contains no contributions from non-acid-catalyzed pathways. $[BrO_3^-]_0 = 5 \times 10^{-2}$ M; $[SC(NH_2)_2]_0 = 4 \times 10^{-3}$ M. (b) Plot of initial bromate concentrations vs the inverse of the induction period. The induction period will be infinitely long (intercept value) if $[BrO_3^-]_0 < 5.5 \times 10^{-3}$ M. $[H^+]_0 = 0.3$ M; $[SC(NH_2)_{20} = 4 \times 10^{-3}$ M.

Effect of Acid. The reaction speeds up when acid concentration increases, although acid is a product not a reactant. Between pH 0.5 and 2, a plot of the induction period against $1/[H^+]^2$ gave a straight line which passes through the origin (Figure 1a). Acid is a very important catalyst in the reaction. Above pH 5 the reaction does not proceed at all.

Bromate Dependence. The induction period was found to be inversely proporational to the bromate concentration. Unlike the acid dependence plot in Figure 1a, this plot does not pass through the origin. By plotting initial bromate concentrations against the inverse of the induction period, we obtained a linear plot with a positive intercept (Figure 1b). The value of the intercept is very significant and can be used to check our deduced stoichiometry for the reaction. For example, in Figure 1b, 4 × 10^{-3} M thiourea was used throughout, and the stoichiometric amount of bromate required is 5.3 × 10^{-3} M (4:3 ratio). With stoichiometric and lesser amounts of bromate, bromine is never produced and the induction period would be infinitely long. From Figure 1b, at the intercept, where the induction period would approach infinity, the bromate concentration is 5.3 × 10^{-3} M, consistent with the deduced stoichiometry. Many other series of experiments were performed with varying initial thiourea concentrations and, in all cases, the intercept gave the expected stoichiometric amount of bromate.

Bromide Dependence. For $[H^+]_0$, $[BrO_3^-]_0 \gg [Br^-]_0$ (Figure 2a) the effect of bromide on the reaction was catalytic. A plot of induction period vs $1/[Br^-]$ shows some form of saturation (Figure 2b). At low bromide concentration, bromide ceases to be an effective catalyst, and the catalytic effect levels off. The

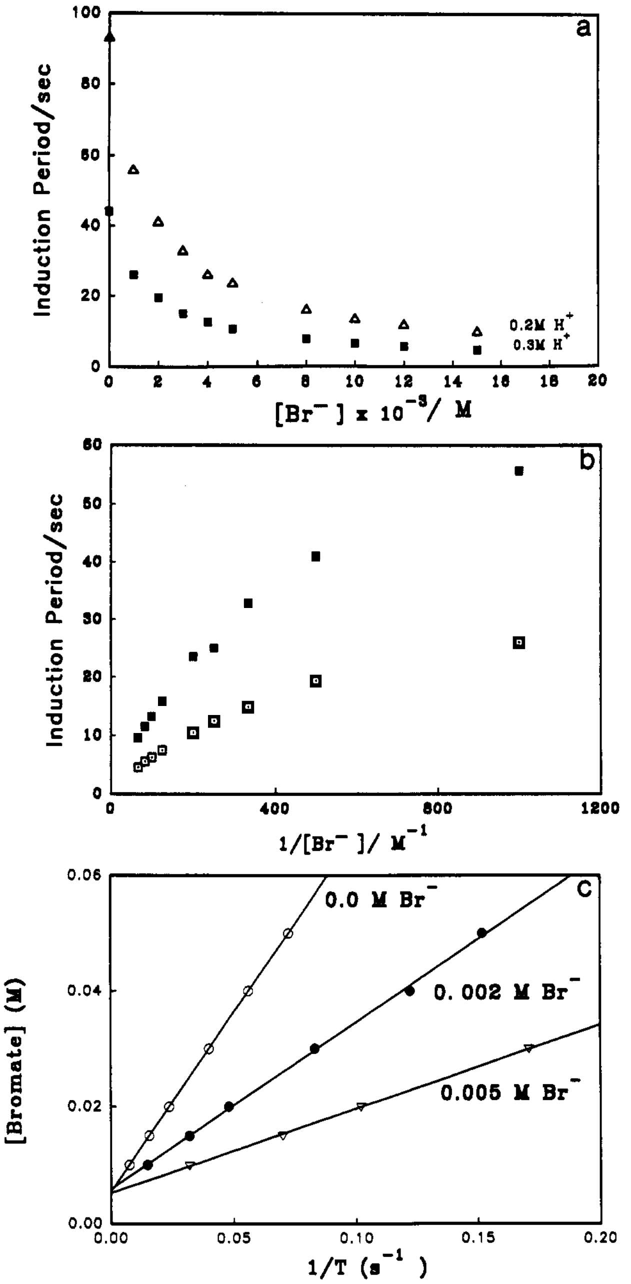

Figure 2. (a) Effect of bromide on the induction period of the reaction. The experiments performed at $[H^+] = 0.2$ M (▲) are consistently slower than those run at $[H^+] = 0.3$ (■). $[SC(NH_2)_2]_0 = 4 \times 10^{-3}$ M; $[BrO_3^-]_0 = 2 \times 10^{-2}$ M. (b) Plot of induction period vs inverse of bromide concentrations showing the strong catalytic effect of bromide at high bromide concentrations. Initial conditions are the same as in Figure 2a. (c) Plot of initial bromide concentrations vs inverse of induction period showing once again the catalytic effect of bromide. $[H^+]_0 = 0.3$ M; $[SC(NH_2)_2]_0 = 4 \times 10^{-3}$ M.

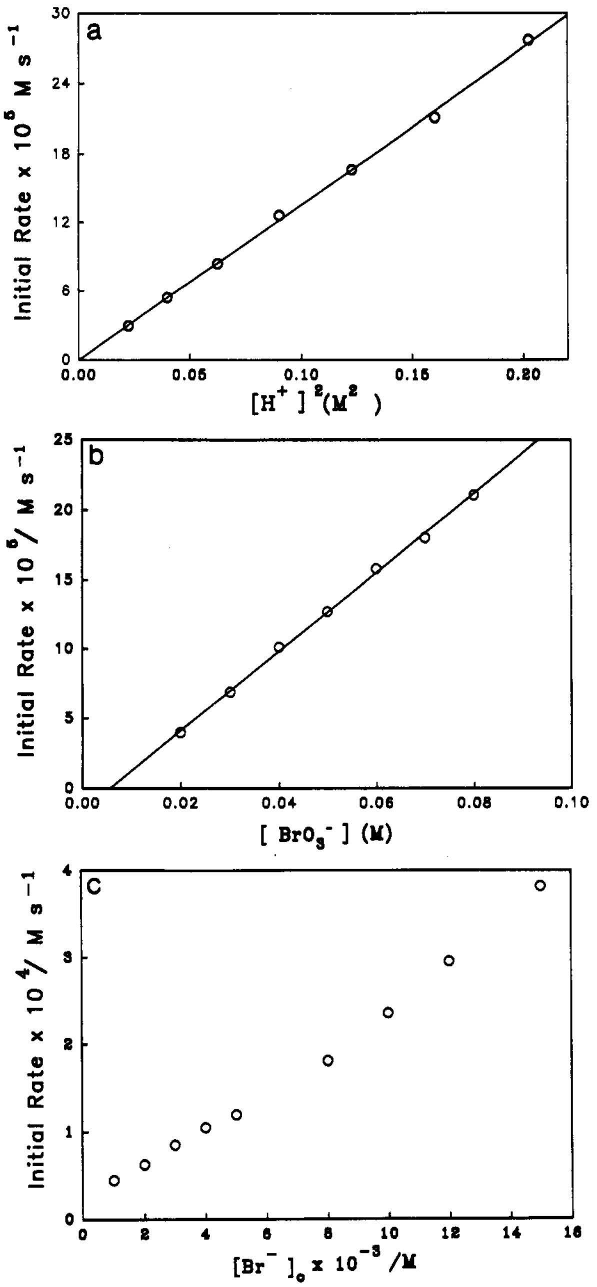

Figure 3. (a) Plot of initial rate of bromine formation (after the induction period) against the square of the initial acid concentration. $[BrO_3^-]_0 = 2 \times 10^{-2}$ M, $[SC(NH_2)_2]_0 = 4 \times 10^{-3}$ M. (b) Plot of initial rate of formation of bromine vs $1/[BrO_3^-]_0$. $[H^+]_0 = 0.3$ M, $[SC(NH_2)_2]_0 = 4 \times 10^{-3}$ M. (c) Plot of initial rate of formation of bromine vs $[Br^-]_0$. Linearity is lost at high bromide concentrations. $[H^+]_0 = 0.3$ M; $[BrO_3^-]_0 = 2 \times 10^{-2}$ M; $[SC(NH_2)_2]_0 = 4 \times 10^{-3}$ M.

relationships between induction period and $[H^+]_0$, $[BrO_3^-]_0$ are unaltered by addition of bromide. Plots of $[BrO_3^-]_0$ against the inverse of the induction period with and without bromide are both straight lines (Figure 2c); they have the same intercept, which represents the stoichiometric amount of bromate needed.

Postinduction Period. Bromine is first detected at the end of the induction period. The shapes of the bromine absorbance–time curves are not sigmoidal, which rules out autocatalysis. Therefore, one can evaluate "initial" rates at this point and relate them to the corresponding "initial" conditions. Since bromate and acid are in overwhelming excess over thiourea and bromide, we have assumed that concentrations of bromate and acid differ insignificantly from their values at the start of the induction period. It is found experimentally that the rate of formation of bromine is directly proportional to the square of the acid concentration (Figure 3a) and proportional to the bromate concentration (Figure 3b). Bromide affects not only the induction period but also the rate of formation of bromine at the end of the induction period. The plot of rate of formation of bromine vs concentration of initially added bromide is linear at low bromide concentrations (Figure 3c). At higher bromide concentrations complications arise from the rapidly established Br_2/Br_3^- equilibrium:[23]

$$Br_2 + Br^- \rightleftarrows Br_3^- \qquad \text{(E1)}$$

Thus the apparent sharp increase in rate of formation of bromine may actually be an increase in absorptivity due to the formation of Br_3^-, which has a higher molar absorptivity than bromine at 390 nm. It is difficult to quantify this effect, since the reaction continuously produces bromide ions.

Comparative, qualitative experiments were performed with the oxidants bromate, bromite, and hypobromous acid (derived from titration of aqueous bromine with silver nitrate and then filtering off the silver bromide). To detect termination of thiourea consumption through precipiation of barium sulfate, a small amount of barium chloride was added to each of three beakers containing thiourea solution. Oxidation of thiourea by HOBr was almost instantaneous; barium sulfate was formed as soon as HOBr was added. Oxidation by sodium bromite was also fast; barium sulfate precipitated within 5 s. Oxidation by bromate was the slowest; barium sulfate did not appear until several minutes elapsed.

Mechanism

Any proposed mechanism for the bromate–thiourea reaction is complicated by the large number of possible reactions to consider: oxybromine interactions, oxysulfur interactions, and oxybromine–oxysulfur reactions. Fortunately, the data present several features that allow the most important steps to be selected. To begin, we note that by the time bromine is produced, all the thiourea has been oxidized to sulfonic acid and sulfate. From the postinduction period data, the rate of bromine formation is

$$\text{rate} = {}^1/_4 d[Br_2]/dt = k[Br^-][BrO_3^-][H^+]^2 \quad (1)$$

Since no bromide ion is present until bromate begins to react, we postulate that the reaction sequence begins with oxidation of thiourea by bromate:

$$BrO_3^- + SC(NH_2)_2 + H^+ \rightarrow HOSC(NH)NH_2 + HBrO_2 \quad (R4)$$

or

$$BrO_3^- + [HSC(NH_2)_2]^+ \rightarrow HOSC(NH)NH_2 + HBrO_2 \quad (R5)$$

where $[HSC(NH_2)_2]^+$ is the protonated thiourea species.[24]

Once bromide is produced, the data concerning the catalytic effect of bromide suggest that the initial part of the reaction is dominated by the bromate–bromide reaction:[25]

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

In the qualitative experiments we have already demonstrated how much more reactive bromous and hypobromous acids are compared with bromate ions. Although normal reagent grade sodium bromate probably contains sufficient sodium bromide impurity to yield 5×10^{-6} M [Br⁻] in a 0.02 M solution of sodium bromate,[26] this amount is too little to initiate the reaction. The bromide used for reaction R6 comes from the R4–(R5)–R6–R7–R8 sequence. The $HBrO_2$ produced in R4 and R5 is very reactive and quickly generates bromide which produces more bromous acid in R6:

$$HBrO_2 + SC(NH_2)_2 \rightarrow HOSC(NH)NH_2 + HOBr \quad (R7)$$

$$HOBr + SC(NH_2)_2 \rightarrow HOSC(NH)NH_2 + Br^- + H^+ \quad (R8)$$

It is not important whether the bromide is generated by further oxidation (by bromous acid) of sulfenyl acid or by oxidation of fresh thiourea since sulfate production is not gradual; it is observed only at the end of the induction period. It appears, then, that there is extensive sulfur–sulfur interaction ultimately leading to $HO_3SC(NH)NH_2$ before formation of sulfate.

One mole of bromide in reaction R6 produces two more moles of bromide from the reduction of $HBrO_2$ and HOBr, and thus it is expected that the reaction will be autocatalytic in bromide.

The sulfenyl acid formed can either be further oxidized or react with thiourea to give the dimeric species dibisformamidine

$$HOSC(NH)NH_2 + SC(NH_2)_2 \rightarrow NH_2(NH)CS\text{–}SC(NH)NH_2 + H_2O \quad (R9)$$

Dimer formation has been found to be extensive in some sulfur systems[12] and at least measurable in others.[9] The dimer can now be further oxidized by either HOBr, $HBrO_2$, or BrO_3^- to yield two sulfenyl acid molecules; with HOBr, for example, the reaction is

$$NH_2(NH)CS\text{–}SC(NH)NH_2 + HOBr + H_2O \rightarrow 2HOSC(NH)NH_2 + Br^- + H^+ \quad (R10)$$

The sequence R9 + R10 is autocatalytic in sulfenyl acid.

As bromide accumulates, reaction R6 begins to compete with the bromine hydrolysis reaction[27] for bromide ions:

$$HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O \quad (R11)$$

As long as thiourea is present in the reaction medium, bromine cannot accumulate, because the reaction between bromine and thiourea is essentially diffusion-controlled:[10]

$$Br_2 + SC(NH_2)_2 + H_2O \rightarrow HOSC(NH)NH_2 + 2Br^- + 2H^+ \quad (R12)$$

Bromous acid also reacts with bromide to give hypobromous acid:[28]

$$HBrO_2 + Br^- + H^+ \rightleftharpoons 2HOBr \quad (R13)$$

which can further oxidize sulfenyl acid.

Although the bromine–thiourea reaction is fast, further reaction between bromine and sulfenyl acid ($HOSC(NH)NH_2$) is relatively slow, with a bimolecular rate constant of 27.8 $M^{-1}\ s^{-1}$.[10] The reaction between HOBr and $HOSC(NH)NH_2$ is, however, still quite fast; the overall rate of reaction therefore becomes determined by the rate of formation of HOBr which is, mechanistically, eq 1.[25]

A plausible sequence of reactions leading to sulfate is as follows:

$$HOBr + HOSC(NH)NH_2 \rightarrow HO_2SC(NH)NH_2 + Br^- + H^+ \quad (R14)$$

$$HOBr + HO_2SC(NH)NH_2 \rightarrow HO_3SC(NH)NH_2 + Br^- + H^+ \quad (R15)$$

or

$$HBrO_2 + HOSC(NH)NH_2 \rightarrow HO_3SC(NH)NH_2 + Br^- + H^+ \quad (R16)$$

Bromine will still not accumulate because its rate of reaction with $HO_2SC(NH)NH_2$ and $HO_3SC(NH)NH_2$ is higher than its rate of production.

Further oxidation of $HO_3SC(NH)NH_2$ yields the end product, SO_4^{2-}. The oxidant can be BrO_3^-, $HBrO_2$, HOBr, or Br_2. With HOBr, for example, the reaction is

$$HO_3SC(NH)NH_2 + HOBr + H_2O \rightarrow SO_4^{2-} + OC(NH_2)_2 + 3H^+ + Br^- \quad (R17)$$

However, $HO_3SC(NH)NH_2$ has a higher affinity for lower

TABLE 1: Proposed Mechanism for the Bromate–Thiourea Reaction

no.	reaction	rate const[a] ($M^{-1}\ s^{-1}$)
M1	$BrO_3^- + 2H^+ + Br^- \rightleftharpoons HBrO_2 + HOBr$	2.1 (M^{-2}), 1E4
M2	$HBrO_2 + H^+ + Br^- \rightleftharpoons 2HOBr$	2E6 (M^{-1}), 11
M3	$HOBr + H^+ Br^- \rightleftharpoons Br_2 + H_2O$	8.9E8 (M^{-1}), 110 (M)
M4	$Br_2 + SC(NH_2)_2 + H_2O \rightarrow NH_2(NH)CSOH + 2Br^- + 2H^+$	1E9
M5	$Br_2 + NH_2(NH)CSOH + H_2O \rightarrow NH_2(NH)CSO_2H + 2Br^- + 2H^+$	27.8
M6	$Br_2 + NH_2(NH)CSO_2H + H_2O \rightarrow NH_2(NH)CSO_3H + 2Br^- + 2H^+$	5E2
M7	$Br_2 + NH_2(NH)CSO_3H + 2H_2O \rightarrow SO_4^{2-} + CO(NH_2)_2 + 2Br^- + 4H^+$	1E2
M8	$HOBr + SC(NH_2)_2 \rightarrow NH_2(NH)CSOH + Br^- + H^+$	4E5
M9	$HOBr + NH_2(NH)CSOH \rightarrow NH_2(NH)CSO_2H + Br^- + H^+$	45
M10	$HOBr + NH_2(NH)CSO_2H \rightarrow NH_2(NH)CSO_3H + Br^- + H^+$	1E5
M11	$HOBr + NH_2(NH)CSO_3H + H_2O \rightarrow SO_4^{2-} + CO(NH_2)_2 + Br^- + 3H^+$	5E1
M12	$BrO_3^- + SC(NH_2)_2 + H^+ \rightleftharpoons NH_2(NH)CSOH + HBrO_2$	7.5 (M^{-1}), 5E–8
M13	$2NH_2(NH)CSOH \rightleftharpoons HO_2(NH)CSOH + SC(NH_2)_2$	1E6
M14	$NH_2(NH)CSO_3H + NH_2(NH)CSOH \rightleftharpoons 2NH_2(NH)CSO_2H$	5E5, 4E7

[a] The number following the comma is the reverse rate constant.

oxidation state sulfur compounds than for the oxidizing agent:

$$HO_3SC(NH)NH_2 + HOSC(NH)NH_2 \rightleftharpoons 2HO_2SC(NH)NH_2 \quad (R18)$$

$$HO_3SC(NH)NH_2 + SC(NH_2)_2 \rightarrow HO_2SC(NH)NH_2 + HOSC(NH)NH_2 \quad (R19)$$

Reactions R18 and R19 are fast enough to delay formation of sulfate until all the lower oxidation states of sulfur have been oxidized.

Computer Simulations

A simplified mechanism (Table 1) suitable for computer simulation has been adapted from the more complete mechanism discussed above. There are five possible oxidizing species in solution (BrO_3^-, BrO_2, $HBrO_2$, HOBr, and Br_2), but in the simplified mechanism we utilize only HOBr and Br_2, with BrO_3^- serving just to initiate reaction (M12) and to react with bromide ion (M1). At the highly acidic conditions used for this reaction and in the presence of Br^- ions, all bromine species will be unstable with respect to Br_2. Therefore, Br_2 is the most important oxidizing species, but since no Br_2 accumulates during the induction period, we assume it is consumed as soon as it is formed, which is reasonable because the rate of reaction between bromine and thiourea is diffusion-controlled.[10] A permutation of the possible oxidants with the possible reductants ($SC(NH_2)_2$, $HOSC(NH)NH_2$, $HO_2SC(NH)NH_2$, and $HO_3SC(NH)NH_2$) yields 20 possible reactions. Coupling these reactions to oxybromine and sulfur–sulfur reactions would give a network of over 30 reactions. Reduction of the mechanism to a smaller set of reactions involves neglecting less viable reactions on the basis of either (a) relatively low reaction rate constants or (b) relatively low concentrations of reactive species. For example, BrO_3^- oxidations are generally very slow and hence their omission. Oxidations involving BrO_2 radical are strongly autocatalytic in $HBrO_2$ and would show very rapid formation of Br_2 at the end of the induction period. From the observed reaction dynamics, it is evident that a free radical pathway is not involved in this reaction system, and bromine dioxide has not been included in the mechanism.

As the reaction proceeds, all $HBrO_2$ oxidations become less viable as $[HBrO_2]$ decreases. The dynamics of the reaction will not change if $HBrO_2$ yields its position in the oxidation hierarchy to HOBr, and we assume that oxidation is carried out by HOBr alone, since the production of HOBr from $HBrO_2$ should be very fast in acidic media. Since reaction M3 is fast and competitive, Br_2 should be included as a major oxidizing species. However, as long as there still is some sulfur species with an oxidation state less than six, Br_2 cannot accumulate. Having Br_2 as the main oxidizing species is the only way Br^- autocatalysis can be justified through reactions M1 and M3.

Reactions M4–M12 are bromine–sulfur reactions in which oxidation of the sulfur compound and reduction of the bromine species occur. Reactions M13 and M14 are sulfur–sulfur interactions of importance, because they prevent oxidation of $HO_3SC(NH)NH_2$ to SO_4^{2-} before Br_2 appears.

Reactions M4, M5, M6, and M7 can be combined to give the composite reaction:

$$4Br_2(aq) + SC(NH_2)_2 + 5H_2O \rightarrow SO_4^{2-} + OC(NH_2)_2 + 8Br^- + 10H^+ \quad (R20)$$

This is the normal stoichiometry of the aqueous bromine-thiourea reaction. Reactions M8, M9, M10, and M11 can also be combined to give the related HOBr composite reaction:

$$4HOBr + SC(NH_2)_2 + 2H_2O \rightarrow SO_4^{2-} + OC(NH_2)_2 + 4Br^- + 6H^+ \quad (R21)$$

The stoichiometry of the reaction in excess thiourea can be obtained from a sum of the following steps:

$$4M1 + 4M2 + 4M3 + M4 + M5 + M6 + M7 + 2M8 + 2M9 + 2M10 + 2M11 = R3 \quad (2)$$

and in excess bromate the stoichiometry can be obtained from

$$8M1 + 8M2 + 8M3 + M4 + M5 + M6 + M7 + 4M8 + 4M9 + 4M10 + 4M11 = R1 \quad (3)$$

The 14-reaction mechanism (Table 1) was used to simulate the observed bromine time plots using a semiimplicit Runge–Kutta numerical integration.[29] The only known kinetics parameters were those for reactions M1, M2, M3, and M5; the remainder were estimated. All the bromine–sulfur reactions were made irreversible, thereby reducing the number of estimated rate constants. The simulations were rather insensitive to the values of the kinetics parameters for reactions M8–M11. If M8–M11 were all shut down, the reaction dynamics would be similar, but the stoichiometry would not be valid. With reactions M8–M11 the reduced mechanism (Table 1) gives the correct stoichiometry.

The induction period was most dependent on the rate constant for M12. The value of the rate constant we used for this reaction was 7.5 $M^{-2}\ s^{-1}$, which was arrived at by fitting the experimental data. For a successful simulation, reaction M14 had to be rapid in both directions. This ensured that SO_4^{2-} was formed only at the end of the induction period and not before. Reactions M7 and M11 were thus much slower than M14.

The simulations give a good fit to the experimental data (Figure 4a,b). Most importantly, they reproduce the acid and bromide dependence results. They also show that SO_4^{2-} is formed simultaneously with bromine. The time dependences of the concentrations of Br_2, $SC(NH_2)_2$, $HO_3SC(NH)(NH_2)$, SO_4^{2-},

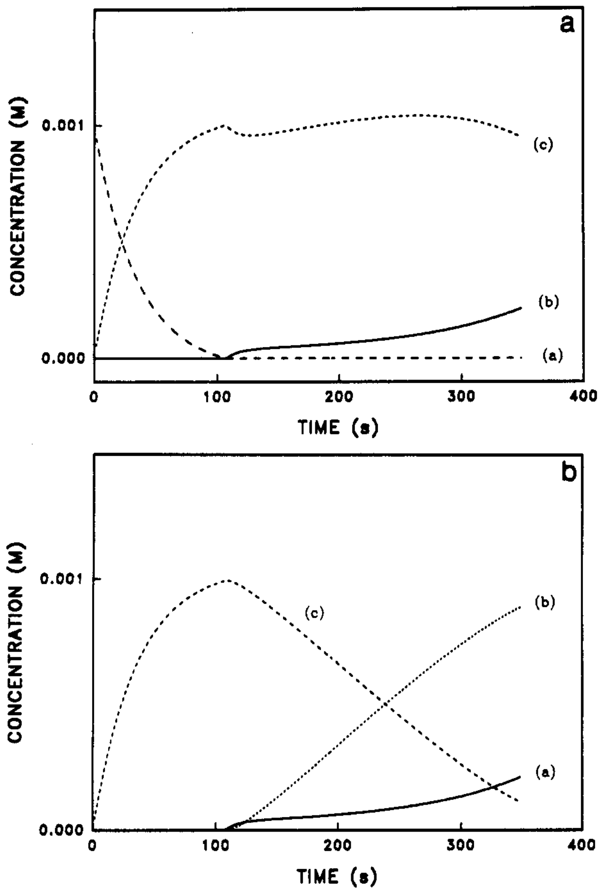

Figure 4. (a) Simulation traces for the bromate-thiourea reaction. $[H^+]_0 = 0.06$ M; $[BrO_3^-]_0 = 0.05$ M; $[SC(NH_2)_2]_0 = 0.001$ M. a, $[SC(NH_2)_2]$; b $[Br_2]$; c $[Br^-]$. The simulations show that bromine does not start to accumulate until all the thiourea has been consumed. (b) Initial concentrations same as (a). a, $[Br_2]$; b, $[SO_4^{2-}]$; c, $[HO_3SC(NH)NH_2]$. The simulations show that sulfate production commences when bromine production starts, as observed experimentally. The sulfonic acid rises to a maximum at the end of the induction period. It can coexist with Br_2 for a limited time, but is eventually oxidized by bromine and HOBr to sulfate.

and Br^- have been simultaneously plotted. The mechanism successfully simulates the reaction and shows the following key features: (i) Br_2 starts to accumulate only after thiourea is consumed (Figure 4a); (ii) SO_4^{2-} formation commences simultaneously with Br_2 production (Figure 4b); (iii) $HO_3SC(NH)(NH_2)$ accumulates to a maximum value before falling after Br_2 production starts (Figure 4b); (iv) Br^- also rises to a maximum concentration and its consumption is related to Br_2 production (Figure 4a).

Discussion

The bromate–thiourea reaction is quite well behaved and is not subject to the irreproducible behavior that characterizes many reactions of sulfur compounds. The formation of bromine (at the end of the induction period) does not involve the bromate–thiourea reaction. It is merely an indicator reaction that denotes the end of thiourea oxidation. Because of the fast bromine–thiourea reaction, bromine cannot coexist with thiourea, and thus its production should indicate the total consumption of thiourea. The rate of formation of bromine is affected by initial conditions in much the same manner as in the pure bromate–bromide reaction without thiourea. It also has the same rate law.

A significant species omitted in our condensed mechanism is the dimeric thiourea species in reaction R9.[30] Its formation is kinetically inconsequential, however, since the oxybromine species are such strong oxidizing agents that the dimer, if formed, would be quickly oxidized to the sulfenyl acid (R10).

A comparable study with iodate as the oxidant gave oligooscillatory behavior[9] in which the concentration of iodide exhibits several maxima. With less than stoichiometric amounts of iodate present, there is also transient formation of iodine. Iodine reacts in a slow autoinhibitory manner with thiourea. Thus, as the Dushman reaction produces iodine,[31] the iodine does not react fast enough with thiourea to avoid its accumulation. Clearly, this behavior is not exhibited in the bromate reaction, because of the much more rapid bromine–thiourea reaction.

Previous studies have reported that bromide catalyzes the reaction between bromine and thiourea.[12] The catalysis observed in our reaction must arise solely from the enhancement of the BrO_3^-–Br^- reaction which produces the reactive species $HBrO_2$ and HOBr. The bromine–thiourea reaction is fast enough in the bromate–thiourea system that its catalysis cannot be kinetically consequential.

Three major processes are important in this reaction system: (a) oxidation of thiourea by bromate to give sulfate and bromide (R3); (b) reaction of bromate with bromide in acidic medium:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O \quad (R22)$$

and (c) oxidation of thiourea by bromine to give sulfate and bromide (R20). The global reaction dynamics obtained are a result of the interplay between these three major processes. In the bromate–thiourea reaction, process (c) is always faster than processes (a) and (b); hence the induction period.

The sulfonic acid $HO_3SC(NH)(NH_2)$ is not easily oxidized to sulfate. Successive oxidations thiourea → sulfenyl acid → sulfinic acid → sulfonic acid, are much faster than further oxidation of sulfonic acid which, therefore, accumulates during the course of the reaction (Figure 4b). Once sulfate is formed, the reaction is irreversible. The sulfonic acid oxidation is shut down until the end of the induction period because of a combination of the slow rate of oxidation and the low concentrations of the oxidants during the induction period. Concentrations of HOBr and Br_2, which are most important for sulfonic acid oxidation, are negligible during the initial part of the reaction. If and when Br_2 is formed, it is instantly consumed by reaction M4.

We believe the mechanism given here is the most concise mechanism that can explain all the observed reaction dynamics. The highly acidic conditions utilized in the experiments allowed us to assume that the major oxidizing species is Br_2, which is the key to simplification.

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References and Notes

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