Oxyhalogen-Sulfur Chemistry: Oligooscillations in the Formamidinesulfinic Acid-Chlorite Reaction[1]

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The reaction between chlorite and formamidinesulfinic acid has been studied in perchloric acid between pH 1 and 3. The stoichiometry of the reaction in excess chlorite is $HO_2SC(NH)NH_2 + ClO_2^- + H_2O \rightarrow SO_4^{2-} + OC(NH_2)_2 + Cl^- + 2H^+$ (A), while the stoichiometry in excess formamidinesulfinic acid is a mixture of (A) and (B): $2HO_2SC(NH)NH_2 + ClO_2^- \rightarrow 2HO_3SC(NH)NH_2 + Cl^-$ (B). In excess chlorite at the end of the oxidation of formamidinesulfinic acid ClO_2 is formed from the reaction $2\,ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O$. The formation of ClO_2 shows some oligooscillatory behavior in which, even in excess formamidinesulfinic acid, there is transient formation of ClO_2. The reaction is autocatalytic in HOCl via the asymmetric Cl_2O_2 intermediate. The dynamics of the reaction are explained via a mechanism which is derived from the one used for the chlorite-thiourea reaction.

Introduction

Oxyhalogen chemistry has been closely linked with exotic reaction dynamics. The most well-known exotic dynamics involve oscillatory behavior, and the two original chemical oscillators known before 1980 involved oxyhalogen compounds.[2,3] Nonlinearity in oxyhalogen chemistry has been explained by invoking autocatalysis and coexisting mechanisms that occur at two different time scales.[4] The field of nonlinear dynamics, however, has been greatly expanded by the addition of sulfur chemistry. Sulfur chemistry has proved to be more complex than oxyhalogen chemistry, and, to date, a general characterization of the dynamics observed with sulfur chemistry has proved elusive. The range of exotic nonlinear dynamics produced by the reactions of sulfur compounds is unmatched in chemistry.[5] While specific reaction features can be rationalized, a generalized algorithm is still far in the future. Nonlinear dynamics in sulfur chemistry starts from the strong tendency to form S-S bonds.[6] Dimerizations and polymerizations introduce nonmonotonic behavior in the kinetics and thermodynamic functions.[7] Different aggregates of a sulfur compound do not react at the same rates. While in oxyhalogen chemistry we have been able to identify autocatalysis as omnipresent and responsible for most nonlinearities, the same cannot be said for sulfur chemistry. Each chemical system appears to have its own unique description.

Recently, we embarked on a systematic study of the oxidation mechanisms of some selected sulfur compounds.[8] In this effort we concentrated on thiocyanate ion, thiourea, and its related compounds. These sulfur compounds appear to be the easiest to handle with very limited polymerizations which only proceed as far as the dimeric species (thiocyanogen[9] and dithiobisformamidine,[7] respectively). Free radical production also appears to be suppressed in these compounds.[10,11] Our studies have shown that, although sulfur can exist in various oxidation states, only three are particularly stable: −2, 0, and +6.[12] Thus, the oxidation of a sulfide would be vulnerable to the formation of S_8, while the oxidation of a labile $S^{(0)}$ state (e.g., SCN^-) is facile all the way to SO_4^{2-} in the presence of an excess of the oxidant.[9,11] In particular, it appears that the sulfur atom oxidation proceeds via successive oxygen addition to yield successively the sulfenyl, sulfinic, and sulfonic acids.[12] The formation of SO_4^{2-} occurs after the cleavage of the C-S bond in the sulfonic acid.[12] Sulfenyl acids are unstable and cannot be isolated.[11] The sulfinic and sulfonic acids, however, are more stable and can exist in crystalline form.[13] By studying the oxidation mechanisms of the sulfinic and sulfonic acids by chlorite, it is possible to support the proposed mechanism for the thiourea oxidation reactions in which the acids were suggested as possible intermediates.[12,14]

In this paper we report on a comprehensive study of the kinetics and mechanism of the oxidation of formamidinesulfinic acid (FSA) by chlorite. This reaction is closely related to the chlorite-thiourea reaction in which FSA was postulated as a possible intermediate.[12] A computer simulation study is also performed to support the proposed mechanism.

Experimental Section

Materials. The following chemicals were used: analytical grade sodium perchlorate (Fisher), formamidinesulfinic acid, $HO_2SC(NH)NH_2$ (Aldrich), perchloric acid (Fisher, 72%), potassium iodide (Fisher), and sodium thiosulfate (Fisher). Technical grade sodium chlorite (Aldrich, 81%) was recrystallized once from a methanol/water mixture. A single recrystallization brought the chlorite assay to 96%. Chlorite was standardized iodometrically by adding excess acidified iodide and titrating the liberated iodine against standard sodium thiosulfate.[15] The major impurity left was chloride, and, in controlled experiments, chloride did not influence the rate of reaction on the time span under study (about 2 s). Chlorine dioxide was prepared by oxidizing potassium chlorate in a sulfuric acid/oxalic acid mixture and then stored in perchlorate acid[16] at 4 °C. It was standardized spectrophotometrically ($\epsilon_{360} = 1265\ M^{-1}\ cm^{-1}$).[17]

Methods. All experiments were carried out at 25 °C and an ionic strength of 0.5 M ($NaClO_4$). Due to the reaction dynamics which were sensitive to initial conditions, three series of experiments were performed in which the ratio of initial chlorite concentrations to FSA, $R = [ClO_2^-]_0/[HO_2SC(NH)NH_2]_0$, was varied. In the first series R was less than one; in the second it was greater than one; and in the third R was equal to one. The

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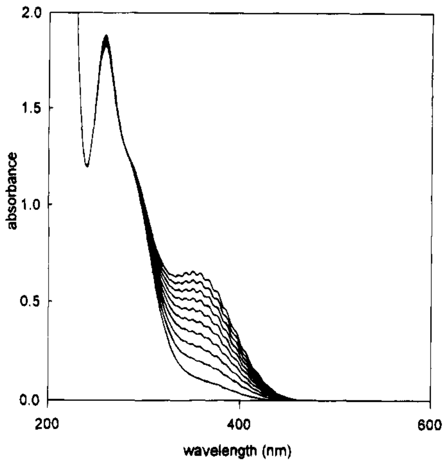

Figure 1. Spectral scans taken every 30 s showing absorbance activity at 360 nm (ClO_2) and no activity at 270 nm (FSA). $[ClO_2^-]_0 = 0.005$ M; $[FSA]_0 = 0.001$ M; $[H^+]_0 = 0.005$ M.

reactions were followed spectrophotometrically by using the absorbance of ClO_2 at 360 nm. The reactions of ClO_2^- and formamidinesulfinic acid were generally too fast to follow by conventional means, often going to completion in 1 s or less. The kinetics measurements were performed on a Hi-Tech Scientific SF-61AF stopped-flow spectrophotometer with an M300 monochromator and an MG3010 SpectraScan accessory. The data from the spectrophotometer were amplified and digitized via an Omega Engineering DAS-50/1 16-bit A/D board and interfaced to a Tandon 386SX computer for storage. Some of the $ClO_2^- - HO_2SC(NH)NH_2$ reactions were slow enough to follow by conventional means. They were followed by monitoring the depletion of the ClO_2 peak (at 360 nm) on a Perkin-Elmer Lambda 2S UV/vis spectrophotometer interfaced to a DEC 486-33DX computer.

The stoichiometric determinations were performed at the same conditions of $R > 1$, $R = 1$, and $R < 1$. With $R > 1$ the reactants were mixed and stored overnight in volumetric flasks and analyzed for excess oxidizing power (iodometric),[15] sulfate (gravimetric), and FSA (spot tests).[18] At $R = 1$ the product solutions were tested for the presence of the remaining reactants: chlorite (iodometric)[15] and FSA (titrimetric).[19] With $R < 1$ the product solutions were analyzed for FSA (titrimetric),[19] sulfonic acids (spot tests),[18] and sulfate (gravimetric).

Results

An unambiguous way of following the reaction would involve monitoring the depletion of the FSA which has an absorption peak at 270 nm. No activity in the absorbance values could be observed at this wavelength. It appears that other reactive species absorb at this wavelength as well: the sulfonic acid intermediate (precursor to the formation of SO_4^{2-}) has a maximum absorbance at 268 nm. One of the postulated intermediates, Cl_2O_2, also absorbs at 270 nm.[20] By scanning the spectrum between 200 and 600 nm at regular intervals, activity was observed at 360 nm (Figure 1). This corresponds to the absorbance of chlorine dioxide; hence, the reaction was followed by the formation of ClO_2.

Stoichiometry. The stoichiometry of the reaction in excess ClO_2^- was determined as follows:

$$ClO_2^- + HO_2SC(NH)NH_2 + H_2O \rightarrow SO_4^{2-} + OC(NH_2)_2 + Cl^- + 2H^+ \quad (A)$$

All the sulfur in FSA was quantitatively changed to sulfate.

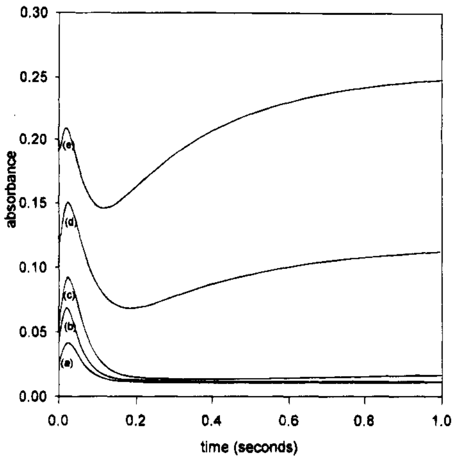

Figure 2. Absorbance traces at 360 nm at varying initial chlorite concentrations. For the first three traces (a–c), $[FSA]_0 \geq [ClO_2^-]_0$, and all the ClO_2 is consumed at the end of the reaction. In traces d and e, $[ClO_2^-]_0 > [FSA]_0$. The excess ClO_2^- in these conditions forms ClO_2. $[FSA]_0 = 0.003$ M; $[H^+]_0 = 0.025$ M. $[ClO_2^-]$: a = 0.001 M; b = 0.002 M; c = 0.003 M, d = 0.004 M; e = 0.005 M.

The excess ClO_2^- could not be directly measured, because at the end of the reaction, when all the FSA had been consumed, oxyhalogen chemistry took over the production of chlorine dioxide through the reaction of the remaining chlorite and the HOCl intermediate:

$$2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \quad (B)$$

The oxidizing power, however, did not change, and this was determined iodometrically by adding excess acidified potassium iodide and determining the liberated iodine.[15] These experiments demonstrated the 1:1 stoichiometric ratio of ClO_2^- to FSA. Another method utilized the fact that the ClO_2 formed is from an extraneous oxyhalogen reaction which requires excess ClO_2^-. By running reactions at varying $[ClO_2^-]_0$ and constant $[FSA]_0$, the stoichiometric amount of ClO_2^- is found to be the highest concentration at which no ClO_2 is formed. A series of such experiments were performed as shown in Figure 2. With an initial concentration of FSA of 0.003 M, the highest concentration needed in this case was 0.003 M, also confirming the 1:1 ratio. With excess FSA the reaction stoichiometry was not as clean as in reaction A and stoichiometry C below also became relevant:

$$ClO_2^- + 2HO_2SC(NH)NH_2 \rightarrow Cl^- + 2HO_3SC(NH)NH_2 \quad (C)$$

Qualitative tests were positive for both sulfate[9] and sulfonic acid.[18] The relative amounts of sulfate and sulfonic acid were also variable and could not be used to determine the relative importance of (A) and (C).

Reaction Kinetics. The reaction was surprisingly very fast with nonlinearity in the formation of ClO_2. Depending upon the acid concentrations, the reaction rapidly formed ClO_2, which attained some peak concentration before it was consumed. In excess ClO_2^- concentrations, $[ClO_2^-]_0/[FSA]_0 > 1$, the consumption of the ClO_2 is only temporary as the ClO_2 is reformed at the end of the reaction (Figure 2 traces d and e). This is considered oligooscillatory behavior in which reaction intermediates and/or products display more than one maximum in a closed system. A number of factors influence the maximum concentration of ClO_2 formed, among them, the initial chlorite concentrations. In general, the maximum ClO_2 formed was directly proportional to the initial chlorite concentration (Figure 3).

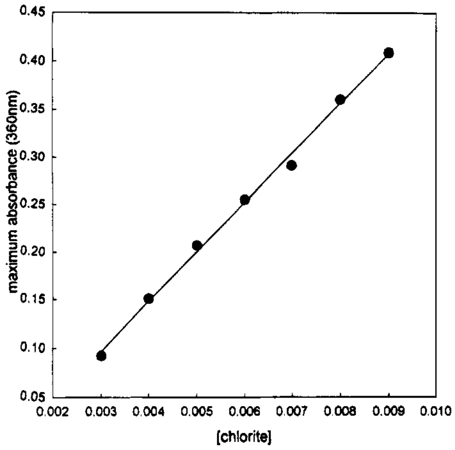

Figure 3. Effect of chlorite on the transient formation of ClO_2. The linear relationship between the two shows that the formation of ClO_2 is catalyzed by ClO_2^-. $[FSA]_0 = 0.003$ M; $[H^+]_0 = 0.025$ M.

All the ClO_2 formed in excess FSA was consumed by the end of the reaction (Figure 4a). Although stoichiometrically ClO_2 is not a product of the reaction, the coupling of some reactions in the reaction mixture produces transient ClO_2 on the way to chemical equilibrium. The maximum ClO_2 produced was observed as a function of $[FSA]_0$, and higher initial concentrations of FSA gave lower amounts of transient ClO_2 (Figure 4b). FSA is thus involved in the reaction which consumes ClO_2. Initial acid concentrations also affect the transient formation of ClO_2. More ClO_2 is formed at lower acid concentrations (Figure 4c). Either acid inhibits the reactions that form ClO_2, or acid catalyzes the reactions which consume ClO_2.

The effect of acid on the reaction was also studied. Reactions run at equimolar ClO_2^- and FSA concentrations (Figure 5a) are similar to reactions run at excess FSA (Figure 4a), although with $R < 1$ the reactions are faster, and the amount of transient ClO_2 formed is much higher at equimolar reactant concentrations. Acid also retards the formation of ClO_2, and there is a general decrease in maximum ClO_2 formed with increase in acid (Figure 5b).

Oligooscillations are observed at excess ClO_2^- ($R > 1$). Oligooscillatory behavior is more pronounced at higher acid concentrations where the ClO_2 consumption is much more extensive before it is reformed (Figure 6). The first ClO_2 peak appears to be a result of many reactions in the mixture, but the second peak appears to be dominated by oxyhalogen chemistry alone, without contributions from the sulfur compound, which will have been consumed at that point. Figure 4c (squares) also shows the inhibitory effect of acid on the production of ClO_2 at $R > 1$.

Direct reaction between ClO_2 and FSA was also monitored (Figure 7a). The reaction appeared to be too slow (about 1000 s for completion) for it to couple with the ClO_2^-−FSA reaction, which has a lifetime of only about a second. Addition of a little ClO_2^-, however, greatly speeds up the reaction (Figure 7b). It appears that ClO_2^- is the precursor initially formed before oxidation of FSA proceeds at a rapid rate. The consumption of ClO_2 is catalyzed by acid (Figure 7a).

Mechanism

The mechanism has to be deduced from the observed oligooscillatory production of ClO_2, since the rate of oxidation of the FSA itself cannot be directly measured. The oligooscillations suggest that at least three reactions couple to produce the observed dynamics. In order for the three processes to couple, they should react at similar rates. At least one of the processes must be nonlinear, either autoinhibitory or autocatalytic. It is essential that there be some nonlinearity in this mechanism. The three major processes are immediately evident: (a) oxidation of FSA, (b) formation of ClO_2, and (c) consumption of ClO_2. Each of these processes can be assessed in isolation in terms of reaction kinetics and single-step mechanisms.

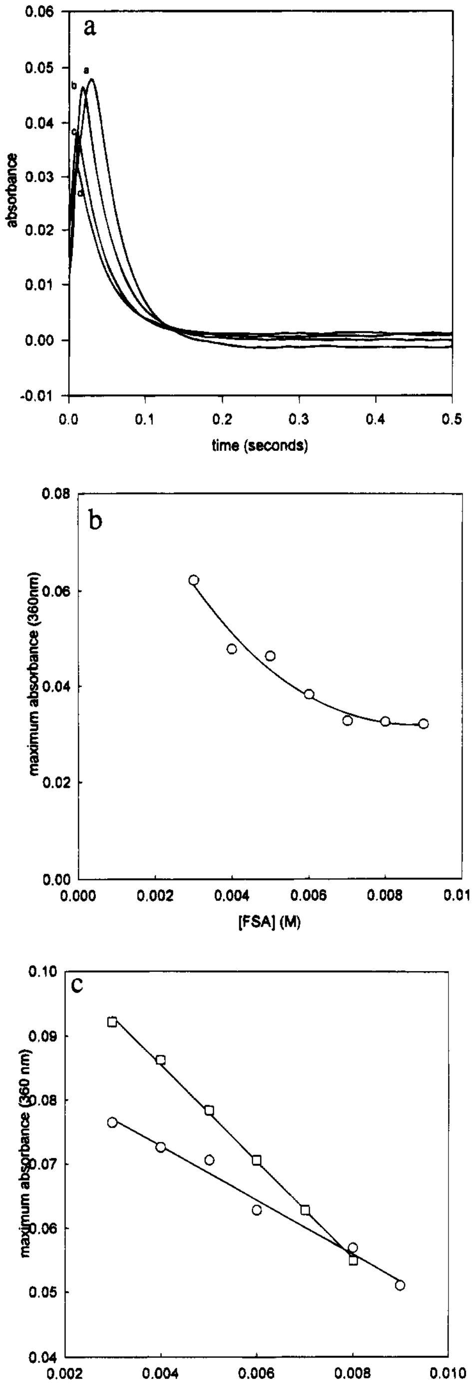

Figure 4. (**a**) Absorbance traces in excess FSA concentrations. Higher ClO_2 concentrations are obtained at lower $[FSA]_0$. $[ClO_2^-]_0 = 0.003$ M; $[H^+]_0 = 0.025$ M. [FSA]: a = 0.004 M; b = 0.005 M; c = 0.007 M; d = 0.008 M. (**b**) Plot of $[ClO_2]_{max}$ versus $[FSA]_0$ for the data in part a. This type of hyperbolic behavior was maintained only when FSA was in excess over chlorite. (**c**) Effect of acid on $[ClO_2]_{max}$. □ denote dependence on excess chlorite concentrations ($[ClO_2^-]_0 = 0.005$ M; $[FSA]_0 = 0.003$ M), and ○ represent excess FSA conditions ($[ClO_2^-]_0 = 0.001$ M; $[FSA]_0 = 0.003$ M). In both cases the $[ClO_2]_{max}$ decreases with acid.

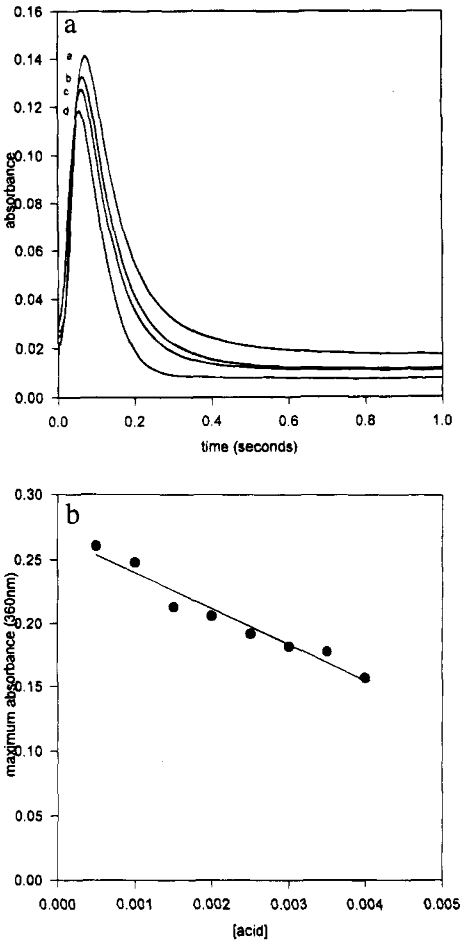

Figure 5. (**a**) Effect of varying acid on the absorbance traces at stoichiometric concentrations of chlorite and FSA; i.e., $[ClO_2^-]_0 = [FSA]_0 = 0.003$ M. $[H^+]$: a = 0.002 M, b = 0.003 M, c = 0.004 M, d = 0.005 M. (**b**) Effect of acid on $[ClO_2]_{max}$ at equimolar concentrations: $[ClO_2^-]_0 = [FSA]_0 = 0.003$ M.

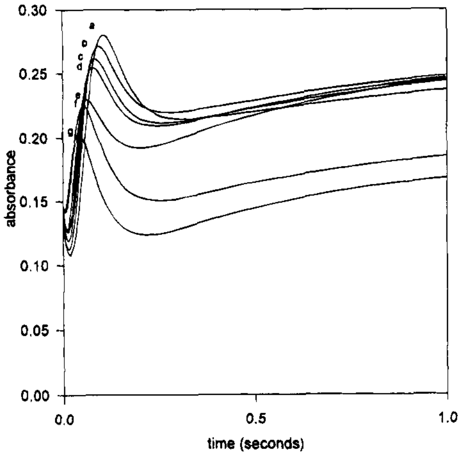

Figure 6. Oligooscillatory behavior in the chlorine dioxide absorbance at varying initial acid concentrations. Such traces were only obtained in excess chlorite conditions. $[ClO_2^-]_0 = 0.005$ M; $[FSA]_0 = 0.003$ M. $[H^+]$: a = 0.002 M; b = 0.003 M; c = 0.004 M; d = 0.005 M; e = 0.007 M; f = 0.008 M; g = 0.009 M.

(**a**) **Oxidation of FSA.** This is the reaction which initiates the rest of the observed processes. It is thus reasonable to assume that this reaction produces reactive intermediates which initiate further reactions. If a nonradical pathway is assumed, then a series of two-electron transfers can be envisaged. The first step is the formation of the sulfonic acid and HOCl:

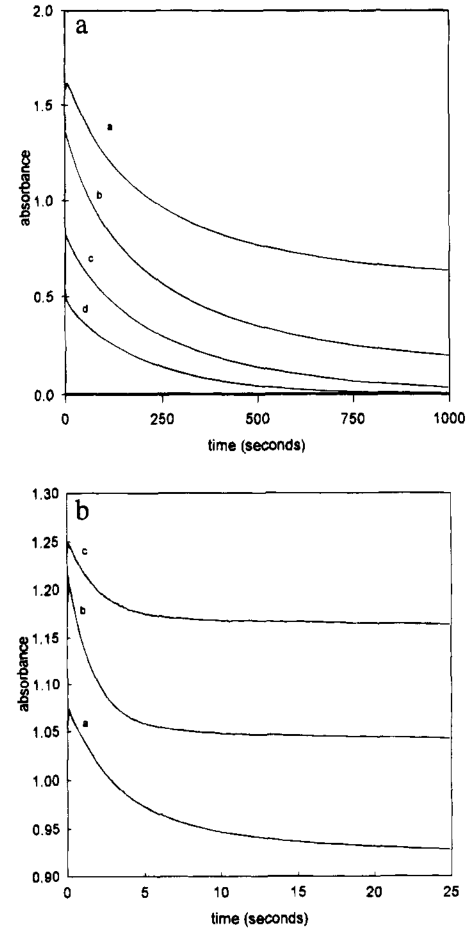

Figure 7. (**a**) Direct reaction between ClO_2 and FSA. The reaction is catalyzed by acid. $[ClO_2]_0 = 7.7 \times 10^{-4}$ M; $[FSA] = 4.4 \times 10^{-4}$ M. $[H^+]$: a = 0.001 M; b = 0.002 M; c = 0.003 M; d = 0.004 M. (**b**) Direct reaction of ClO_2 and FSA showing the catalytic effect of ClO_2^-. $[ClO_2]_0 = 7.7 \times 10^{-4}$ M; $[FSA]_0 = 4.4 \times 10^{-4}$ M. $[ClO_2^-]$: a = 1×10^{-4} M; b = 3×10^{-4} M; c = 4×10^{-4} M.

$$ClO_2^- + HO_2SC(NH)NH_2 + H^+ \rightarrow HO_3SC(NH)NH_2 + HOCl \quad (D)$$

HOCl is a very reactive intermediate and is a more powerful oxidizing agent than ClO_2^-. The sulfonic acid intermediate can be oxidized to sulfate in the presence of further oxidizing agent but is stable if there is no further oxidant.[21]

$$HOCl + HO_3SC(NH)NH_2 + H_2O \rightarrow SO_4^{2-} + OC(NH_2)NH_2 + Cl^- + 3H^+ \quad (E)$$

Further oxidation of the sulfonic acid can be brought about by either ClO_2^- or HOCl. Reaction E involves cleavage of the C-S bond, and one can assume that this will be an irreversible process.

HOCl also reacts rapidly with ClO_2^- to give the asymmetric intermediate Cl_2O_2:[22]

$$ClO_2^- + HOCl + H^+ \rightarrow Cl_2O_2 + H_2O \quad (F)$$

The intermediate can then oxidize FSA or the sulfonic acid:

$$Cl_2O_2 + 2H^+ + 2e^- \rightarrow 2HOCl \quad (G)$$

If reaction F is faster than (E), then the oxidation of FSA is autocatalytic in HOCl. HOCl is autocatalytically produced in the combined F + G reaction. The result is an ever-increasing rate of oxidation of FSA. The reaction's runaway kinetics can only be halted by the depletion of chemical reactants.

(b) Formation of Chlorine Dioxide. This is a purely oxyhalogen process that does not involve the sulfur compound. It is initiated by reaction D. Chlorine dioxide can be formed by the decomposition of chlorite:[23]

$$5ClO_2^- + 4H^+ \rightarrow 4ClO_2 + Cl^- + 2H_2O \qquad (H)$$

but process H is very slow and would be insignificant at the time scales of less than 1 s where most of the activity occurs. Formation of ClO_2 is much faster via the oxidation of ClO_2^- by the HOCl intermediate:[24]

$$2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \qquad (I)$$

Reaction I represents an overall process in which HOCl is the autocatalytic species via steps (F) and (G).

It appears that both the oxidation of FSA and the formation of ClO_2 compete for the same reagent, HOCl. Although HOCl is initially formed by the first step in the oxidation of FSA (reaction D) the autocatalytic nature of HOCl production means that subsequent reaction activity is sustained by autocatalytic production of HOCl. Thus the two processes (a) and (b) can occur simultaneously with process (b) bypassing (a) depending on initial conditions. This explains the almost instantaneous production of ClO_2 without the expected induction period which is prevalent in oxyhalogen chemistry.

(c) Consumption of ClO_2. ClO_2 can disproportionate to ClO_3^- and Cl^- in basic solutions, but this reaction is so slow that it will be uncompetitive on the time scale of the ClO_2^-–FSA reaction:[25]

$$6ClO_2 + 3H_2O \rightarrow 5ClO_3^- + Cl^- + 6H^+ \qquad (J)$$

It appears that all consumption of ClO_2 is due to its reduction by the sulfinic and sulfonic acids.

ClO_2 is an odd-electron species which can oxidize via a one-electron transfer.[13] The ClO_2^-–FSA reaction data show a smooth monotonic decay in ClO_2 concentrations (Figure 7a) implying the absence of nonlinear kinetics. The transfer of an electron from FSA to ClO_2 forms an FSA radical species which is not long-lived and can lose another electron to form the sulfonic acid:

$$ClO_2 + HO_2SC(NH)NH_2 \rightleftharpoons ClO_2^- + [HO_2SC(NH)NH_2]^{\bullet+} \qquad (K\text{-}1)$$

followed by

$$ClO_2 + [HO_2SC(NH)NH_2]^{\bullet+} + H_2O \rightarrow ClO_2^- + HO_3SC(NH)NH_2 + 2H^+ \qquad (K\text{-}2)$$

Giving the overall reaction

$$2ClO_2 + HO_2SC(NH)NH_2 + H_2O \rightarrow 2ClO_2^- + HO_3SC(NH)NH_2 + 2H^+ \qquad (K\text{-}3)$$

Although the oxidation of FSA by ClO_2 is slow, addition of ClO_2^- greatly increases the rate of reaction (Figure 7b). Consumption of ClO_2 is catalyzed by acid. Acid forms chlorous acid, $HClO_2$, with ClO_2^-. This pulls reaction K-1 to the right, thereby increasing the rate of reaction.

A number of experiments were performed in which the FSA was varied at constant ClO_2. This was done to estimate the stoichiometry of the reaction. The stoichiometric ratio of ClO_2 to FSA was determined from the composition at which the absorbance of ClO_2 just vanished. This ratio was found to be 4:5. After considering the mass balance, the stoichiometry was deduced as

$$4ClO_2 + 5HO_2SC(NH)NH_2 + 7H_2O \rightarrow 5SO_4^{2-} + 5OC(NH_2)_2 + 4Cl^- + 14H^+ \qquad (L)$$

Still, the stoichiometry was not clean, as it appeared from our quantitative determinations that some of the sulfonic acid was not fully oxidized to SO_4^{2-}.

Computer Simulation

The reaction scheme was divided into two groups of reactions: oxyhalogen reactions and oxyhalogen–sulfur reactions. Most of the oxyhalogen–sulfur reactions, which involve the simultaneous oxidation of the sulfur center and the reduction of the chlorine center, can be regarded as being essentially irreversible. The rate constants for the oxyhalogen reactions are known from literature. Those for the oxyhalogen–sulfur reactions were found by fitting the mechanism to the experiment. The full 12-reaction mechanism used in the simulations is shown in Table 1. The integrator used the semi-implicit Runge Kutta method devised by Kaps and Rentrop.[26] The kinetic parameters for reactions M1–M4 were based on the literature values,[9,12] leaving the forward rate constants for reactions M5–M12 to be fitted. Reactions M8 and M9 are composites of two consecutive one-electron transfers. Autocatalytic HOCl production can be observed in reaction M3 in conjunction with reactions M4, M11, and M12. Reaction M2 stops the uncontrolled production of ClO_2 and is important in other ClO_2^- oxidations as well. Reaction M2 is a composite of three steps in which the first step is a nucleophilic attack by Cl^- on ClO_2

$$ClO_2 + Cl^- \rightleftharpoons Cl_2O_2^-$$

followed by

$$Cl_2O_2^- + ClO_2 \rightleftharpoons Cl_2O_2 + ClO_2^-$$

and finally

$$Cl_2O_2 + H_2O \rightarrow ClO_2^- + HOCl + H^+$$

$HClO_2$ is considered an inert nucleophile toward sulfur compounds. If it does react, the rate of reaction should be slow compared to unprotonated ClO_2^-. Reaction M4 is a composite of the following reactions:

$$ClO_2^- + Cl^- + 2H^+ \rightarrow 2HOCl \qquad (M)$$

$$ClO_2^- + Cl_2O_2 \rightarrow 2ClO_2 + Cl^- \qquad (N)$$

Reaction M, however, is quite slow and thus would not be a major factor on our time scale. Hence, composite reactions M and N were not used, which suggests that reaction M4 may go through successive one-electron transfers from the Cl_2O_2 intermediate to the ClO_2^- ion.

The simulations were successful in excess FSA concentrations (Figure 8a). The simulations appear to be inaccurate at the end of the reaction, but this is not so. Simulations are based on the concentration of a single chemical species, ClO_2, while experimental data are based on absorbance readings, which could arise from other species in solution, not just the species of interest.

TABLE 1: Mechanism of the Chlorite–FSA Reaction

reactn no.	reaction	rate constant
(M1)	$ClO_2^- + H^+ \rightleftharpoons HClO_2$	$1. \times 10^9\ M^{-1}\ s^{-1}$ $3.1 \times 10^3\ s^{-1}$
(M2)	$2ClO_2 + Cl^- + H_2O \rightarrow HClO_2 + ClO_2^- + HOCl$	$8 \times 10^7\ M^{-2}\ s^{-1}$
(M3)	$ClO_2^- + HOCl + H^+ \rightleftharpoons Cl_2O_2 + H_2O$	$5 \times 10^7\ M^{-2}\ s^{-1}$ $1. \times 10^1\ s^{-1}$
(M4)	$Cl_2O_2 + 2ClO_2^- + 2H^+ \rightleftharpoons 2ClO_2 + 2HOCl$	$4. \times 10^7\ M^{-4}\ s^{-1}$ $1. \times 10^3\ M^{-3}\ s^{-1}$
(M5)	$ClO_2^- + HO_2SC(NH)NH_2 + H^+ \rightarrow HOCl + HO_3SC(NH)NH_2$	$8.5 \times 10^3\ M^{-2}\ s^{-1}$
(M6)	$ClO_2^- + HO_3SC(NH)NH_2 + H_2O \rightarrow HOCl + SO_4^{2-} + OC(NH)_2NH_2 + H^+$	$6.5 \times 10^3\ M^{-1}\ s^{-1}$
(M7)	$HOCl + HO_2SC(NH)NH_2 \rightarrow HO_3SC(NH)NH_2 + H^+ + Cl^-$	$9.5 \times 10^3\ M^{-1}\ s^{-1}$
(M8)	$HOCl + HO_3SC(NH)NH_2 + H_2O \rightarrow SO_4^{2-} + Cl^- + OC(NH_2)_2$	$6.5 \times 10^3\ M^{-1}\ s^{-1}$
(M9)	$2ClO_2 + HO_2SC(NH)NH_2 + H_2O \rightarrow 2ClO_2^- + HO_3SC(NH)NH_2 + 2H^+$	$6. \times 10^2\ M^{-2}\ s^{-1}$
(M10)	$2ClO_2 + HO_3SC(NH)NH_2 + 2H_2O \rightarrow 2ClO_2^- + SO_4^{2-} + OC(NH_2)_2 + 4H^+$	$1. \times 10^1\ M^{-2}\ s^{-1}$
(M11)	$Cl_2O_2 + HO_2SC(NH)NH_2 + H_2O \rightarrow HO_3SC(NH)NH_2 + 2HOCl$	$4. \times 10^5\ M^{-1}\ s^{-1}$
(M12)	$Cl_2O_2 + HO_3SC(NH)NH_2 + 2H_2O \rightarrow SO_4^{2-} + OC(NH_2)_2 + 2H^+ + 2HOCl$	$8. \times 10^4\ M^{-1}\ s^{-1}$

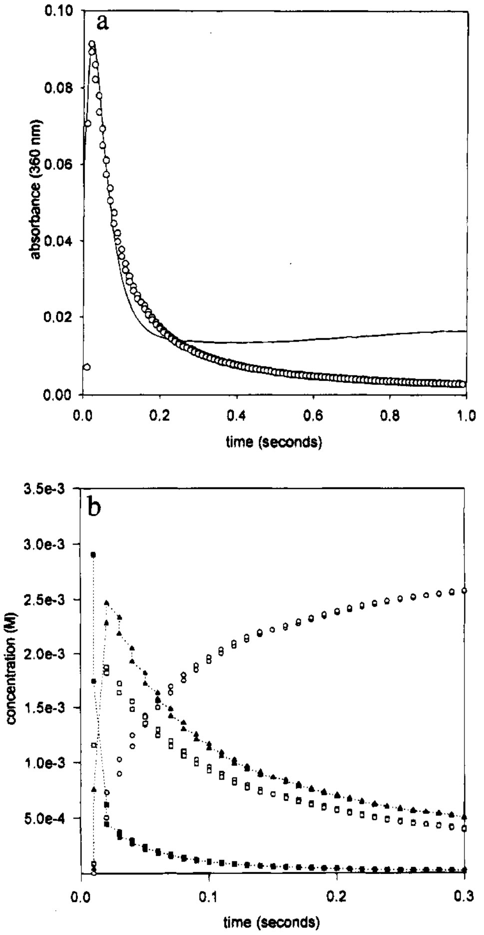

Figure 8. (**a**) Simulations at stoichiometric conditions: $[FSA]_0 = [ClO_2^-]_0 = 0.003$ M, $[H^+]_0 = 0.025$ M. The solid line represents experimental data, while ○ represents simulations. (**b**) Computer simulation of other species under the conditions in part a. ■ = FSA; □ = HOCl; ▲ = $HO_3SC(NH)NH_2$; ○ = SO_4^{2-}. The mechanism produces SO_4^{2-} quantitatively on the time scale of the reaction.

In excess ClO_2^- the simulations did not successfully reproduce the second ClO_2 peak. This is due to the fact that the activity coefficient of aqueous ClO_2 is not known for the current experimental conditions.

The simulations also allow the estimation of other species in solution which we would otherwise not be able to measure. Figure 8b shows the results of the simulations of the reactive intermediates HOCl and $HO_3SC(NH)NH_2$ as well as product SO_4^{2-} and reactant FSA. As expected, the intermediates increase in concentration during the initial part of the reaction but are consumed by the end of the reaction.

Discussion

The overall observed reaction dynamics are a result of three major processes: oxidation of FSA (stoichiometry A), production of ClO_2 (stoichiometry H), and the consumption of ClO_2 (stoichiometry L). Nonlinear behavior in the form of autocatalysis can be deduced in reactions A and H. The simple mechanism presented appears to successfully model the observed reaction dynamics.

Response to FSA Concentrations. From Figure 4a–b, one notes that at constant ClO_2^-, as initial FSA concentration is increased, the maximum ClO_2 concentration decreases. This is consistent with the assertion that ClO_2 is consumed by oxidizing the sulfur compounds (reactions M9, M10 in the mechanism).

Response to Acid Concentrations. Acid influences nearly all the reactions in the mechanism. Figures 4c and 5b show that high acid concentrations inhibit the formation of ClO_2. This is unexpected from our knowledge of oxyhalogen chemistry. Increasing acid concentrations will convert most Cl(III) species into the relatively unreactive $HClO_2$ form (reaction M1). This will inhibit the oxidation of FSA (reactions M5 and M6) as well as the subsequent formation of ClO_2 (reactions M3 and M4). High acid, however, will catalyze the consumption of ClO_2 (Figure 7). Due to the imposed irreversibility, acid will have no effect on reactions M9 and M10 and will enhance reaction M2 by forming more $HClO_2$.

Response to Chlorite Concentrations. Chlorite concentrations can alter the absorbance versus time traces from those in Figure 4a to those in Figure 6. Transient ClO_2 formation is greatly enhanced by high initial chlorite concentrations (Figure 3). The mechanism shows that ClO_2^- has no effect on the consumption of ClO_2 but does enhance the oxidation of FSA (reactions M5 and M6) as well as the formation of ClO_2 (reactions M3 and M4). After all the FSA is consumed (excess ClO_2^- conditions), the remaining oxyhalogen species ClO_2^-, HOCl, and Cl^- react to form the ClO_2 which is observed at the end of the reaction (Figure 6).

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References and Notes

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