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Oxyhalogen−Sulfur Chemistry: Oxidation of Hydroxymethanesulfinic Acid by Chlorite[1]

Mohamed A. Salem

Department of Chemistry, University of Qatar, P.O. Box 2713 Doha, Qatar

Cordelia R. Chinake and Reuben H. Simoyi*

Department of Chemistry and Center for Nonlinear Science, West Virginia University,
Morgantown, West Virginia 26506-6045

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The reaction between chlorite and hydroxymethanesulfinic acid, $HOCH_2SO_2H$, (HMSA) has been studied in the pH range 4−8. The reaction is very complex and has a variable stoichiometry that is dependent on ratio of the oxidant to the reductant. In excess HMSA, the stoichiometry is $ClO_2^- + HOCH_2SO_2H \rightarrow SO_4^{2-} + HCHO + Cl^- + 2H^+$ while in excess ClO_2^- the stoichiometry is $3ClO_2^- + 2HOCH_2SO_2H \rightarrow 2SO_4^{2-} + 2HCOOH + 4H^+ + 3Cl^-$. The reaction is very fast and is characterized by a short induction period ($\approx$1 s) which is followed by a rapid and autocatalytic ClO_2 production. The first stage in the oxidation is the cleavage of C−S bond to form SO_4^{2-} and HCHO. In the presence of excess oxidant the HCHO is oxidized to HCOOH. After prolonged standing (72 h or more), the HCOOH can be oxidized to CO_2; giving a third possible stoichiometry. The rate-determining step is a 2-electron oxidation of HMSA by ClO_2^- to give the sulfonic acid $HOCH_2SO_3H$. A 19-reaction mechanism is used to simulate the reaction. There is reasonable agreement between the experiments and simulations.

Introduction

Very little progress has been made over the years in studies of kinetics and mechanisms of reactions which involve sulfur compounds. There has been no real need for such studies until quite recently when it was discovered that sulfur compounds can participate in a variety of reactions that give rise to complex dynamical behavior.[2] Complex dynamics such as chemical oscillations,[3] pattern formation,[4] and chemical chaos[5] had previously been observed only in connection with oxyhalogen chemistry.[6−8] The chemical reactivity of some sulfur amino acids in living organisms has not yet been fully understood because of inadequate knowledge on the kinetics and mechanisms of the sulfur end of the amino acid.[9] The prevalence of sulfur compounds as environmental pollutants has also increased our need to know more about sulfur chemistry in general.[10]

The knowledge gathered so far on the chemistry of sulfur compounds highlights its complexity. Mechanistic studies on sulfur chemistry are hampered by existence of free radical mechanisms,[11] autoxidations,[12] and general propensity of sulfur compounds to aggregate.[13]

The complex reaction behavior of sulfur compounds has given rise to exotic kinetics such as oligooscillations,[14] chemical oscillations,[15] chemical wave propagation,[16] and the novel pH-driven oscillations.[17] A better understanding of this complex behavior will be possible after kinetics and mechanism of relevant reactions have been characterized.

The chlorite ion exhibits exotic nonlinear dynamics in nearly all its reactions.[18] Chlorite is the most prolific oxyhalogen species in production of clock reactions and chemical oscillators.[19] The ion has its own built-in nonlinearity in its reactions in the form of HOCl autocatalysis.[20]

Thiourea is one of the sulfur compounds which exhibits various nonlinear features when reacted with several oxidizing agents.[21] With mild oxidizing agents such as iodine, it shows autoinhibitory and oligooscillatory behavior[14] while with bromate[22] and chlorite[23] it shows clock reaction characteristics. The sulfur center passes through many oxidation state intermediates on its way to being oxidized to sulfate (oxidation state change −2 to +6).[24] There have been numerous speculations as to the type of intermediates formed. The presently accepted sequence is a series of two-electron oxidation processes which produce progressively the sulfenyl, sulfinic, and sulfonic acids.[25] By using one of the postulated intermediates as the starting material, the oxidation mechanism of thiourea can be better evaluated.

In this paper we report on the kinetics and mechanism of oxidation of hydroxymethanesulfinic acid (HMSA) by chlorite in acidic media. HMSA is a stable sulfinic acid (in basic environments) in which the sulfur center is at an oxidation state of +2. Oxidation of a sulfur center in excess oxidant can take it to the +6 oxidation state (SO_4^{2-}), a process accompanied by a cleavage of the C−S bond in HMSA. Using a compound with a +2 sulfur oxidation state eliminates many other possible intermediates (compared to starting with sulfur at oxidation state −2) and reduces the possibility of polymerizations.

The motivation for this study is to attempt to systematically evaluate kinetics and mechanism of sulfur compound reactions which are of interest in nonlinear chemistry. Reactions of chlorite with thiourea[26] and formamidinesulfinic acid (FSA) yield traveling chemical[27] wavefronts of ClO_2, as well as oscillatory behavior in a CSTR. A complete explanation for such behavior is also not possible until the kinetics and mechanism of the reactions involved are known. This study of the kinetics and mechanism of the chlorite−HMSA reaction is thus part of our continuing efforts at elucidating the kinetics and mechanisms of reactions involving sulfur compounds.[1]

A secondary motivation for our study is the importance of HMSA in industrial applications and atmospheric chemistry. Under the trade names of Rongalite and Aldanil, HMSA is a major constituent of dyes[28] and bleaches. In the troposphere, HMSA is known to reversibly decompose to formaldehyde and SO_2(aq) (or HSO_3^-) in fog and cloud water, thus contributing quite significantly to the S(IV) balance in the atmosphere.[29] A

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mechanistic study of HMSA's oxidation can help in improving dye properties as well as sulfur abatement procedures.

Experimental Section

Materials. The following reagent-grade chemicals were used without purification: hydroxymethanesulfinic acid monosodium salt dihydrate, (Aldrich), perchloric acid, 72% (Fisher), and sodium perchlorate (Fisher). All solutions were prepared using singly-distilled water. Technical grade sodium chlorite (Aldrich) was 78−81% pure. The sodium chlorite was recrystallized once from a water−methanol mixture to bring assay value to 96%. The recrystallized chlorite was standardized iodometrically by adding acidified potassium iodide and titrating liberated iodine against sodium thiosulfate with freshly prepared starch as indicator.[30] Chlorine dioxide was prepared by a standard method of oxidizing potassium chlorate in acidic medium.[31] Chlorine dioxide was stored in acidic medium in volumetric flasks wrapped in aluminum foil at 4 °C. The chlorine dioxide was then standardized by its molar absorptivity coefficient of 1265 M^{-1} cm^{-1} at 360 nm[32] on a Perkin-Elmer Lambda 2S UV/vis spectrophotometer.

Methods. All experiments were carried out at 25 °C and at an ionic strength of 0.50M ($NaClO_4$). The ClO_2^-/HMSA reaction was monitored spectrophotometrically at $\lambda = 360$ nm. Kinetics measurements were performed on a Hi-Tech Scientific SF-61AF stopped-flow spectrophotometer. The data from the spectrophotometer were amplified and digitized via an Omega Engineering DAS-50/1 16-bit A/D board interfaced to a Tandon 386SX computer for storage and data analysis. Stoichiometric determinations were perfomed by analyzing for ClO_2^-, HCHO, HCOOH, SO_4^{2-} , Cl^-, and HMSA. Sulfate was analyzed gravimetrically as $BaSO_4$[33,34] while HMSA[35] and ClO_2^- were analyzed titrimetrically.[30] Spot tests were used for HCHO,[35] HCOOH,[36] and Cl^-. For quantitative determination of SO_4^{2-}, reaction solutions were allowed to stand for at least 24 h before addition of $BaCl_2$. The precipitate was also allowed to settle for 24 h before filtering, drying, and weighing.

Reactions were perfomed in excess chlorite so as to utilize the formation of chlorine dioxide as an indicator reaction. HMSA is known to be a powerful reducing agent especially in the presence of alkali and is also known to decompose to carbon monoxide, carbon dioxide, and oxides of sulfur in presence of dilute acids.[37]

Results

The stoichiometry of the reaction is complex and variable. At least three plausible stoichiometries could be deduced from varying initial conditions. In approximately equimolar and excess HMSA conditions the stoichiometry was determined as

$$ClO_2^- + HOCH_2SO_2H \rightarrow SO_4^{2-} + HCHO + Cl^- + 2H^+ \quad (R1)$$

Qualitative analysis tests confirmed the aldehyde product (Tollen's reagent).[35] The complete consumption of ClO_2^- was confirmed by the inability of the product solution to oxidize acidified iodide.[30]

In excess ClO_2^- ($3 > R = [ClO_2^-]/[HMSA] > 1$), the stoichiometry became

$$3ClO_2^- + 2HOCH_2SO_2H \rightarrow 2SO_4^{2-} + 2HCOOH + 4H^+ + 3Cl^- \quad (R2)$$

The excess ClO_2^- is used for the further oxidation of formaldehyde:[38]

$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^- \quad (R3)$$

For ratios between 1 and 1.5 the product solution contained a mixture of formaldehyde and formic acid. Sulfate formation in stoichiometry R2 was quantitative based upon the initial HMSA concentrations. In high excess ClO_2^-, $R > 3$ and after prolonged standing (24 h or longer), formic acid is further oxidized to CO_2:[39]

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad (R4)$$

Reaction R4 is so slow that a clean stoichiometric determination of the ClO_2^- − HMSA reaction could not be deduced even after 48 h. The decomposition of ClO_2^- [40] occurs on same time scale as reaction R4, and thus after prolonged standing, the ClO_2^- oxidant concentration decreased as ClO_2 accumulated.

Qualitative tests during and at end of the reaction were negative for sulfite.[41] Thus the postulated reversible decomposition of HMSA into sulfite and HCHO[42] does not seem to occur at a rate compatible with the time scale of the ClO_2^- − HMSA reaction.

Reaction Kinetics. The ClO_2^- − HMSA reaction presents reaction dynamics which are much more complex than those normally obtained from oxyhalogen−sulfur chemistry.[1] In the UV/visible region the reaction mixture has no absorbing species except for ClO_2 at 360 nm. This was confirmed by a three-dimensional reaction kinetics profile which confirms lack of spectral activity except for the peak at 360 nm which grows with time.

The reaction itself was very fast, often going to completion in 2 s or less. The reactions with $R > 1$ were all characterized by a short induction period (0.2 to 1 s) in which no activity was observed in the absorbance at 360 nm. The induction period gave way to a rapid formation of ClO_2 (Figure 1a). Formation of ClO_2 is in three parts. In the first stage there is a gentle increase in rate of formation of ClO_2. In the second stage the rate starts to decrease but then rapidly picks up again in an autocatalytic manner, heading to an abrupt halt. In the third stage the ClO_2 continues to increase at a very slow rate that is not on the same time scale as the first two stages. The induction period is inversely proportional to initial chlorite concentration $[ClO_2^-]_0$ (Figure 1b). The maximum chlorine dioxide absorbance, after the second stage, ($\lambda = 360$ nm) shows a direct relationship with $[ClO_2^-]_0$ with saturation (Figure 1c).

The reaction had a complex dependence on $[HMSA]_0$ (Figure 2a). At higher $[HMSA]_0$, with fixed $[ClO_2^-]_0$, formation of ClO_2 only shows a single autocatalytic step. Maximum ClO_2 absorbance also shows a positive dependence on $[HMSA]_0$, and at constant $[ClO_2-]_0$, the induction period decreases with $[HMSA]_0$ (Figure 2b). This was an unexpected result as most clock reactions are expected to show retardation in rate as the concentration of the reductant is increased at constant oxidant concentrations.

The reaction also had a complex dependence on pH (Figure 3a). The instability of HMSA at low pH[37] did not permit the running of reactions below pH 4. In general, the reaction is faster in lower pH conditions, although no relationship was evident. At constant $[ClO_2^-]_0$ and $[HMSA]_0$, the maximum ClO_2 concentrations did not seem to vary with pH, except for the expected decrease at higher pH due to ClO_2 hydrolysis.[43] The traces in Figure 3a were obtained by running the reaction in different buffers. Predictable behavior is obtained in conditions of pH $\rangle$ 4.0. The reaction dynamics change completely

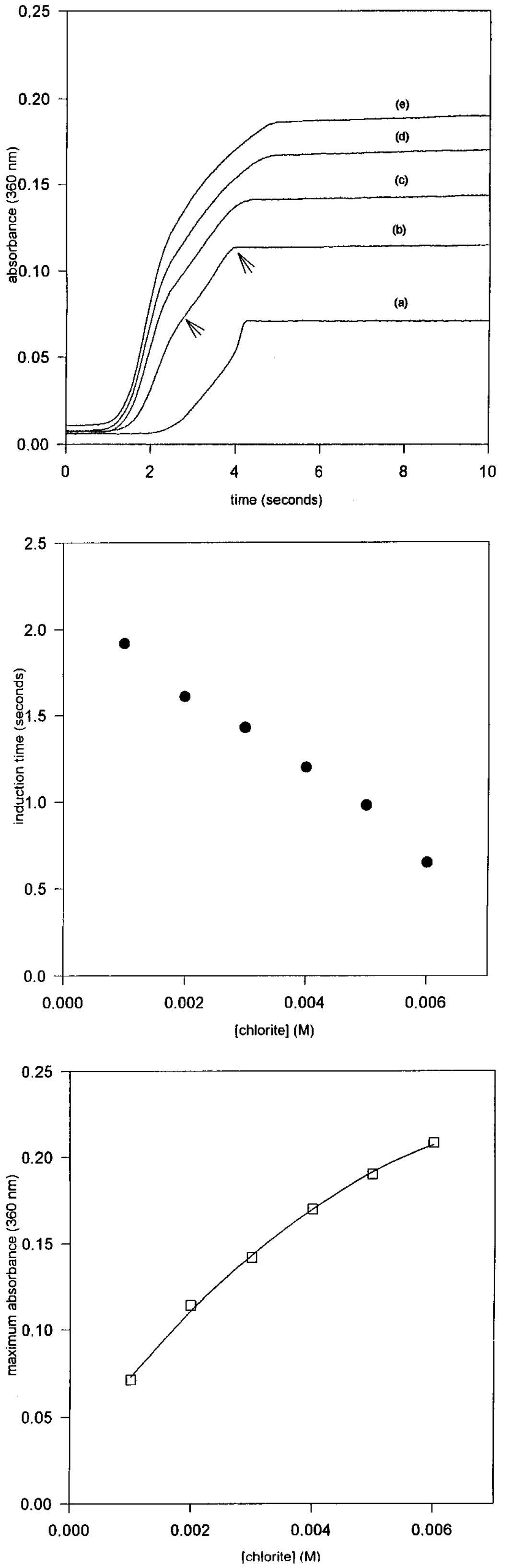

Figure 1. (a, top) Absorbance traces at 360 nm at varying initial chlorite concentrations and in slightly alkaline conditions (pH = 7.3). $[HMSA]_0 = 0.0005$ M; $[ClO_2^-]_0 =$ (a) 0.001, (b) 0.002, (c) 0.003, (d) 0.004, and (e) 0.005 M. The arrows on trace (b) indicate the end of the first period and the end of the second period. (b, middle) Relationship between $[ClO_2^-]_0$ and the induction period for data in Figure 1a. (c, bottom) Effect of $[ClO_2^-]_0$ on the maximum $[ClO_2]$ obtained after the end of the second period. Maximum absorbance goes to zero when $[ClO_2^-]_0 = [HMSA]_0 = 0.0005$ M. ClO_2 obtained only when ClO_2^- is in stoichiometric excess.

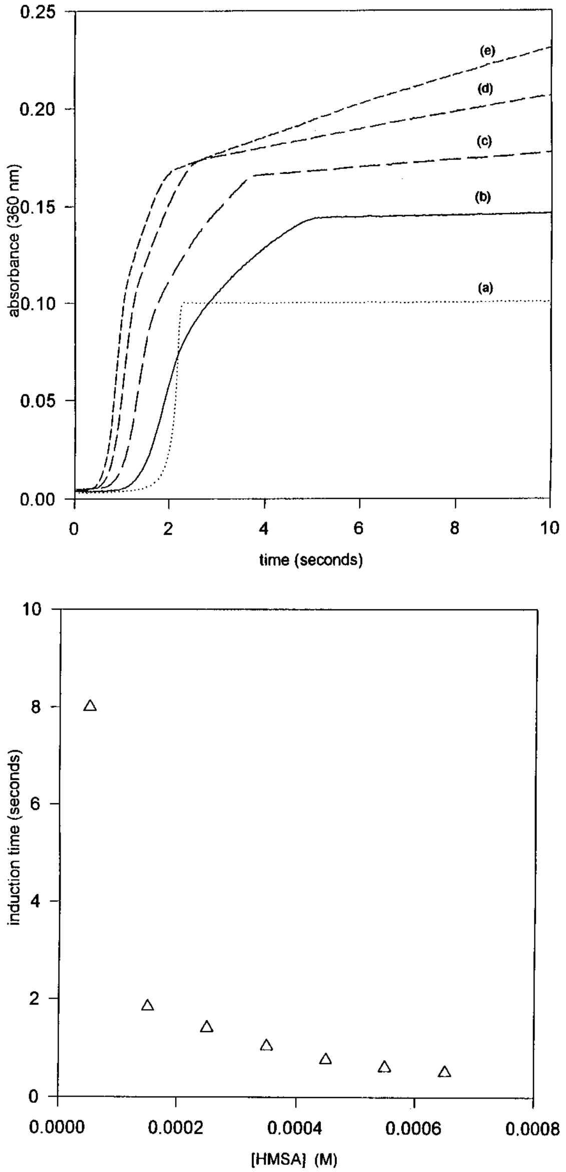

Figure 2. (a, top) Absorbance traces at 360 nm showing the effect of $[HMSA]_0$ in slightly alkaline conditions. $[ClO_2^-]_0 = 0.0015$ M; $[HMSA]_0 =$ (a) 0.000 15, (b) 0.000 25, (c) 0.000 35, (d) 0.000 55, and (e) 0.000 65 M. (b, bottom) Effect of $[HMSA]_0$ on the induction period for data in Figure 2a. ClO_2 is not formed in stoichiometric excess of HMSA.

when pH goes below 4. The reaction is also self-destructing. A reaction run in an unbuffered solution at pH 5 will have a pH of approximately 3 at the end of the reaction as the reaction produces H^+ as an important product (see stoichiometries R1, R2, and R3). The limit of the reaction's reproducibility can be seen in Figure 3b. By varying acid concentrations gradually, the reaction profile can be maintained for some range of $[H^+]_0$. At a critical $[H^+]_0$ (typically $\approx$ pH 4), the reaction profile changes dramatically as the system becomes essentially irreproducible. In Figure 3b, reproducibility is obtained for traces a−d, and irreprodicibility becomes evident in traces e and f as the acid is increased. Direct reaction between HMSA and ClO_2 was also monitored. The reaction is very fast (Figure 4) in both excess HMSA and excess ClO_2.

The rate of the reaction between ClO_2^- and HCHO was also estimated. Upon mixing the two reagents (neutral to slightly acidic pH) there was an immediate formation of ClO_2 after a very short induction period (Figure 5). The rapid formation of ClO_2 indicates either that the oxidation of HCHO by ClO_2^- is

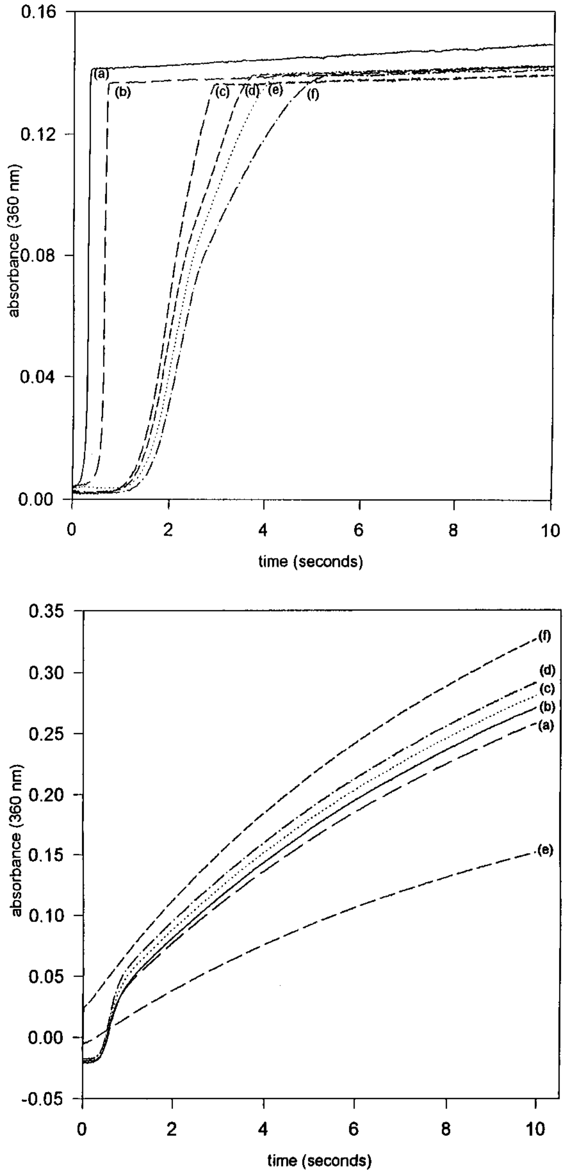

Figure 3. (a, top) Effect of pH on the reaction. HMSA rapidly decomposes at pH lower than its pK_a. $[ClO_2^-]_0 = 0.003$ M; $[HMSA]_0 = 0.0005$ M. pH = (a) 4.0, (b) 4.3, (c) 7.0, (d) 7.3, (e) 7.6, and (f) 7.8. (b, bottom) Effect of acid over a small range of $[H^+]_0$. As $[H^+]_0$ increases, the reaction becomes irreproducible at some critical $[H^+]_0$ which is determined by the initial reactant concentrations. $[ClO_2^-]_0 = 0.003$ M; $[HMSA]_0 = 0.002$ M. $[H^+]_0 =$ (a) 6.0×10^{-5}, (b) 7.0×10^{-5}, (c) 8.0×10^{-5}, (d) 9.0×10^{-5}, (e) 1.0×10^{-4}, and (f) 1.5×10^{-4} M.

very fast, or that the ClO_2 formed reacts very slowly with HCHO. It appears the answer is a combination of both since the reaction of ClO_2 with HCHO was observed to be very slow. The ClO_2/HCHO reaction has a half-life of more than 1 h which is ineffective on our reactions' time scale. Thus the rapid buildup of ClO_2 in the ClO_2^-/HCHO reaction is due to the very slow ClO_2 consumption rate by HCHO and HCOOH.

Mechanism

The experimental data suggest that the complete oxidation of HMSA is the prerequisite for ClO_2 formation. The observation that the reaction between ClO_2 and HMSA is complete within a fraction of a second (Figure 4), while that between ClO_2^- and HMSA requires about 0.5 s to get to the end of the induction period appears to confirm this.

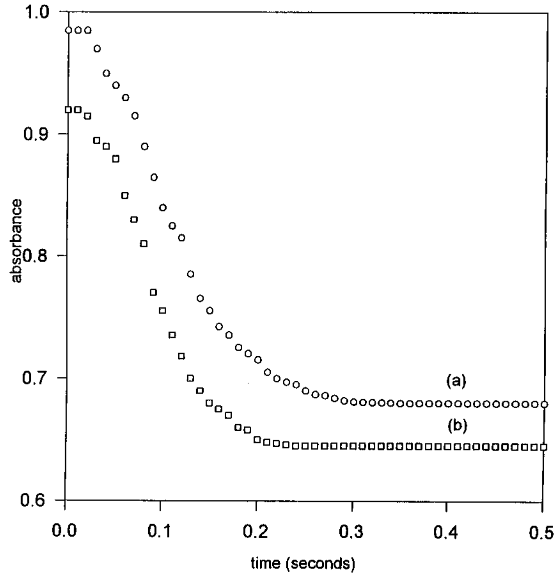

Figure 4. Rapid reaction between ClO_2 and HMSA. The reaction is faster than the ClO_2^-/HMSA reaction and is catalyzed by ClO_2^-. $[ClO_2]_0 = 0.000\,77$ M; $[HMSA]_0 = 0.0004$ M. Trace (a) no ClO_2^-; (b) $[ClO_2^-]_0 = 0.000\,02$ M.

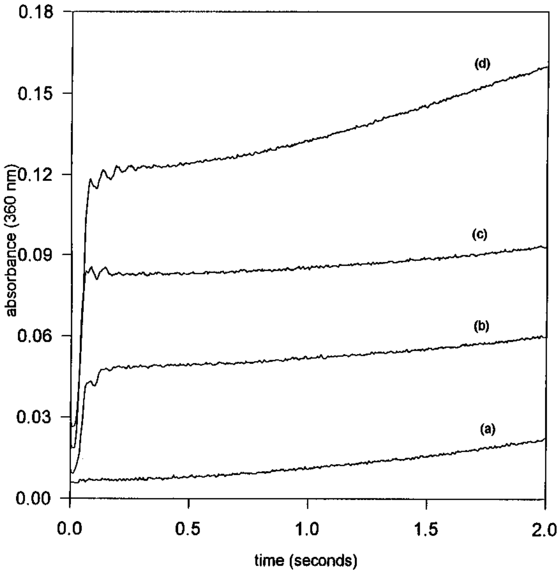

Figure 5. Oxidation of HCHO by ClO_2^- in slightly acidic pH. Rapid accumulation of ClO_2 indicates a rapid ClO_2^-/HCHO reaction. $[ClO_2^-]_0 =$ (a) 0.001, (b) 0.002, (c) 0.003, and (d) 0.004 M. $[HCHO]_0 = 0.00133$ M.

The first step in this oxidation is the 2-electron oxidation of HMSA by the Cl(III) species:

$$HOCH_2SO_2H + ClO_2^- + H^+ \rightarrow HOCH_2SO_3H + HOCl \quad (R5)$$

Two possible routes exist for sulfonic acid: one involves further oxidation to SO_4^{2-}:

$$HOCH_2SO_3H + H_2O \rightarrow SO_4^{2-} + HCHO + H^+ + 2e^- \quad (R6)$$

and another is an initial hydrolyis of the sulfonic acid followed by an oxidation:

$$HOCH_2SO_3H + H_2O \rightarrow HSO_4^- + CH_3OH + H^+ \quad (R7)$$

$$CH_3OH \rightarrow HCHO + 2H^+ + 2e^- \quad (R8)$$

Paths R6 and (R7 + R8) are kinetically indistinguishable if R5 is the rate-determining step.

In excess oxidant, the organic residue, HCHO, can be further oxidized to formic acid:

$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^- \tag{R9}$$

Any of the oxychlorine species can act as the oxidant. Since reaction R9 is of same order in rate as the ClO_2^-−HMSA reaction, the coupling of these two reactions will produce very complex overall kinetics.

A further reaction is oxidation of HCOOH:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \tag{R10}$$

Reaction R10, being very slow, will not affect the overall reaction dynamics on the time scale of the HMSA oxidation reaction.

ClO_2^- has to be oxidized to form ClO_2, yet in the reaction being studied, ClO_2^- is reduced by the sulfur compound to Cl^-. ClO_2 is formed only when the ClO_2^- is in stoichiometric excess over reductant. In the presence of excess oxidant the ClO_2^- can disproportionate after prolonged sitting in acidic solution:[44]

$$5ClO_2^- + 4H^+ \rightarrow 4ClO_2 + Cl^- + 2H_2O \tag{R11}$$

Reaction R11, however, is too slow to be effective in 1−5 s. The formation of ClO_2 is very rapid and appears autocatalytic. The HOCl intermediate plays a crucial role in accelerating rate of production of ClO_2. The generally accepted ClO_2^-−HOCl reaction has the stoichiometry:[45]

$$2ClO_2^- + HOCl + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O \tag{R12}$$

The stoichiometry of the ClO_2 formation is ultimately reaction R11 but catalyzed by HOCl. Autocatalysis in reaction R11 can be explained by the asymmetric intermediate Cl_2O_2, which yields 2 HOCl molecules when subjected to a 2-electron reduction:

$$ClO_2^- + HOCl + H^+ \rightarrow Cl_2O_2 + H_2O \tag{R13}$$

$$Cl_2O_2 + 2H^+ + 2e^- \rightarrow 2HOCl \tag{R14}$$

TABLE 1: Mechanism of the Oxidation of Hydroxymethanesulfinic Acid by Chlorite

reaction no.	reaction
M1	$ClO_2^- + H^+ \rightleftarrows HClO_2$
M2	$2ClO_2 + Cl^- + H_2O \rightarrow HClO_2 + ClO_2^- + HOCl$
M3	$ClO_2^- + HOCl + H^+ \rightleftarrows Cl_2O_2 + H_2O$
M4	$Cl_2O_2 + 2ClO_2^- + 2H^+ \rightleftarrows 2ClO_2 + 2HOCl$
M5	$ClO_2^- + HOCH_2SO_2H + H^+ \rightarrow HOCl + HOCH_2SO_3H$
M6	$ClO_2^- + HOCH_2SO_3H \rightarrow HOCl + SO_4^{2-} + H_2C{=}O + H^+$
M7	$ClO_2^- + H_2C{=}O + H^+ \rightarrow HOCl + HCOOH$
M8	$HOCl + HOCH_2SO_2H \rightarrow Cl^- + HOCH_2SO_3H + H^+$
M9	$HOCl + HOCH_2SO_3H \rightarrow Cl^- + SO_4^{2-} + H_2C{=}O + 3H^+$
M10	$HOCl + H_2C{=}O \rightarrow Cl^- + HCOOH + H^+$
M11	$HOCl + HCOOH \rightarrow CO_2 + Cl^- + H_2O + H^+$
M12	$2ClO_2 + HOCH_2SO_2H + H_2O \rightarrow 2ClO_2^- + HOCH_2SO_3H + 2H^+$
M13	$2ClO_2 + HOCH_2SO_3H + H_2O \rightarrow 2ClO_2^- + H_2C{=}O + SO_4^{2-}$
M14	$2ClO_2 + H_2C{=}O + H_2O \rightarrow HCOOH + 2ClO_2^- + 2H^+$
M15	$Cl_2O_2 + HOCH_2SO_2H + H_2O \rightarrow 2HOCl + HOCH_2SO_3H$
M16	$Cl_2O_2 + HOCH_2SO_3H + H_2O \rightarrow 2HOCl + SO_4^{2-} + H_2C{=}O + 2H^+$
M17	$Cl_2O_2 + H_2C{=}O + H_2O \rightarrow 2HOCl + HCOOH$
M18	$HOCl + Cl^- + H^+ \rightarrow Cl_2 + H_2O$
M19	$Cl_2 + 2ClO_2^- \rightarrow 2ClO_2 + 2Cl^-$

Sequence R13 + R14 shows normal quadratic autocatalysis in HOCl.[38] After reaction R5, which acts as an initiator, most of the oxidation of substrate will be done by HOCl. The autocatalytic HOCl production thus can explain the observed nonlinear kinetics. While HOCl can react with ClO_2^- as in R13, it can also simultaneously react with the other substrates, especially organic residues. Possible reductants in solution include $HOCH_2SO_2H$, $HOCH_2SO_3H$, CH_3OH, HCHO, HCOOH, and Cl^-. With the exception of HCOOH and Cl^- all the reductants are expected to react rapidly and irreversibly with HOCl to produce Cl^-. The reaction of HOCl with Cl^- should rapidly produce Cl_2 which can undergo reactions analogous to R12, R13−type reactions:

$$HOCl + Cl^- + H^+ \rightarrow Cl_2(aq) + H_2O \tag{R15}$$

$$2ClO_2^- + Cl_2 \rightarrow 2ClO_2 + 2Cl^- \tag{R16}$$

$$ClO_2^- + Cl_2 \rightarrow Cl_2O_2 + Cl^- \tag{R17}$$

The sequence R15−R17 may be kinetically inconsequential if R16 and R17 are of the same (or higher) order of magnitude in rate as R12 and R13.

Induction Period. During this period no ClO_2 is formed. Either there is not enough HOCl to make reaction R12 effective, or that all ClO_2 formed is quickly reduced by the reducing species in solution. ClO_2 is thermodynamically unstable with respect to ClO_2^- in the presence of a reducing agent (either a one- or a two-electron reductant):

$$ClO_2 + e^- \rightarrow ClO_2^- \tag{R18}$$

In general reaction R18 is slow especially with a 2-electron reductant and normally starts slowly as ClO_2^- accumulates, and one observes a sigmoidal decay curve.[46] Further reduction of ClO_2^- yields Cl^- which acts to produce more ClO_2^-:

$$2ClO_2 + Cl^- + H_2O \rightarrow 2ClO_2^- + HOCl + H^+ \tag{R19}$$

The reaction mixture has enough Cl^- to make R19 important and render the rate of ClO_2 consumption rapid. Thus in this system the ClO_2^-−HMSA reaction is fast enough such that the appearance of ClO_2 indicates total consumption of HMSA. Kinetic data, however, indicates that the ClO_2^-−HCHO and ClO_2−HCOOH reactions are not as rapid, and thus concurrent accumulation of ClO_2, HCHO, and HCOOH is possible within the reaction mixture.

Computer Simulations

A simplified mechanism suitable for computer simulation was distilled from the comprehensive mechanism described above. Table 1 shows our proposed 19-reaction scheme. The scheme only has two types of reactions: normal oxychlorine reactions and oxychlorine−sulfur reactions. Standard sulfur−sulfur

TABLE 2: Rate Constants and Rate Laws Used in the Numerical Simulations

reaction no.	*V* (forward rate)	*V* (reverse rate)
M1	$1 \times 10^9[ClO_2^-][H^+]$	$3.16 \times 10^7[HClO_2]$
M2	$5 \times 10^2[ClO_2][ClO_2][Cl^-]$	
M3	$5 \times 10^6[ClO_2^-][HOCl][H^+]$	$6.6 \times 10^2[Cl_2O_2]$
M4	$9.8 \times 10^5[Cl_2O_2][ClO_2^-][ClO_2^-][H^+][H^+]$	$1 \times 10^{-2}[ClO_2][ClO_2][HOCl][HOCl]$
M5	$2.1 \times 10^4[ClO_2^-][HOCH_2SO_2H][H^+]$	
M6	$1.0 \times 10^3[ClO_2^-][HOCH_2SO_3H]$	
M7	$4 \times 10^3[ClO_2^-][H_2C{=}O][H^+]$	
M8	$1.5 \times 10^5[HOCl][HOCH_2SO_2H]$	
M9	$2.5 \times 10^3[HOCl][HOCH_2SO_3H]$	
M10	$6 \times 10^4[HOCl][H_2C{=}O]$	
M11	$1 \times 10^{-1}[HOCl][HCOOH]$	
M12	$6 \times 10^4[ClO_2][ClO_2][HOCH_2SO_2H]$	
M13	$1 \times 10^{-1}[ClO_2][ClO_2][HOCH_2SO_3H]$	
M14	$3 \times 10^{-2}[ClO_2][ClO_2][H_2C{=}O]$	
M15	$2.4 \times 10^4[Cl_2O_2][HOCH_2SO_2H]$	
M16	$8 \times 10^3[Cl_2O_2][HOCH_2SO_3H]$	
M17	$6 \times 10^5[Cl_2O_2][H_2C{=}O]$	
M18	$1.8 \times 10^4[HOCl][Cl^-][H^+]$	$1.1 \times 10^1[Cl_2]$
M19	$1.8 \times 10^6[Cl_2][ClO_2^-][ClO_2^-]$	

interactions were ignored since there was no experimental evidence for any polymerizations of the substrate. The existence of only one intermediate, $HOCH_2SO_3H$, before formation of product, SO_4^{2-}, justifies this assumption.

The 19-reaction scheme is quite exhaustive, and it was arrived at after considering all the possible reactions in solution and discarding those that would have been ineffective based on rate considerations and abundance of reactive species. There are four oxidizing species in solution, ClO_2, ClO_2^-, HOCl, and Cl_2, and four reducing species, $HOCH_2SO_2H$, $HOCH_2SO_3H$, HCHO, and HCOOH (excluding CH_3OH, whose existence is speculative). A permutation of these species should give 16 possible reactions. Control experiments of HCOOH with ClO_2 and ClO_2^- showed no activity on the time scale of the ClO_2^-−HMSA reaction and were not considered.

Cl_2 is a powerful oxidizing agent, but it has mostly been omitted in the mechanism. This is because of the expected quantity of Cl_2 (very low) and the reversibility of reaction M18. Reaction M19 should be able to halt the accumulation of Cl_2. Addition of three more reactions involving the oxidation by chlorine of $HOCH_2SO_2H$, $HOCH_2SO_3H$, and HCHO did not alter the observed reaction dynamics in the simulations although it made the reaction system much stiffer.[47] Cl_2, if formed, is unstable with respect to Cl^- and ClO_2 in presence of excess ClO_2^- (see sequence R15−17).

Although reactions involving oxidation by ClO_2^- are very slow compared to the HOCl oxidation reactions, ClO_2^- reactions have, however, been used in this mechanism because ClO_2^- is the most abundant oxyhalogen species and would contribute significantly to the rate of reaction on the basis of pure mass-action kinetics (M3, M5−M7).

The most important features of the mechanism in Table 1 are the following:

(a) *Consumption of HMSA:* This is initiated in reaction M5 by a 2-electron oxidation of HMSA to give sulfonic acid and HOCl. HOCl is a much more powerful oxidizing agent and will quickly react with more reductant to give Cl^- (reaction M8). The rate-determining step for the ClO_2^-−HMSA reaction is thus reaction M5. It is known that sulfonic acids are very stable and are not easy to further oxidize. Reactions M6, M9, M13 and M16 involve irreversible cleavage of the C−S bond to form SO_4^{2-}.

(b) *Oxidation of the organic residues:* Reactions M6, M9, M13, and M16, apart from forming SO_4^{2-}, also form the organic residue, formaldehyde, HCHO. Control experiments have shown that HCHO reacts rapidly with HOCl, Cl_2, and ClO_2^-, but only very slowly with ClO_2. Reactions M7, M10, M14, and M17 involve the oxidation of HCHO. On the time scale of ClO_2^-−HMSA reaction, it is doubtful reaction R7 would contribute significantly to the mechanism, which is why the oxidation of CH_3OH was not considered. While oxidation of HCHO is facile, the oxidation of HCOOH is not. Oxidation of HCOOH requires a high acid environment and a catalyst.[39] The oxidation of HCOOH will be the slowest step in this mechanism.

(c) *Formation of ClO_2:* In the presence of HOCl, formation of ClO_2 from ClO_2^- is very rapid. This reaction (M3 + M4) is on the same time scale as reactions M12−M14. Accumulation of ClO_2 will depend on the balance between M3 + M4 and reactions that consume ClO_2.

(d) *Autocatalysis:* The sharp increase in $[ClO_2]$ at end of the induction period has been rationalized in this mechanism by the quadratic HOCl autocatalysis evident in M3 + M4. Intermediate Cl_2O_2 is then involved in the oxidation of all the reducing agents in solution: reactions M4 and M15−M17.

The mechanism in Table 1 was simulated using semiimplicit Runge−Kutta methods implemented for stiff systems of ordinary differential equations by Kaps and Rentrop.[48] Table 2 shows the rate laws and rate constants used in the simulations. Only the oxychlorine reactions were made reversible (M1, M3, M4, and M18). The kinetics constants used for these 4 reactions as well as reactions M2 and M19 were available from literature. Reactions M5−M17 involve an oxidation by an oxychlorine species of a sulfur compound or an organic residue. These were assumed to be irreversible, thus reducing the number of kinetics variables needed.

Estimation of unknown rate constants: The rate constant for reaction M5, k_{M5}, was estimated from this study using induction period data (e.g., Figure 1a). A very good estimate of the rate constant could be made by assuming that the total consumption of HMSA is a prerequisite for the end of the induction period. The initial estimate for k_{M6} was derived from an earlier study involving the reaction of chlorite and thiourea.[26] k_{M7} was estimated from this study (see data shown in Figure 5). The value of k_{M8} was not very significant in the simulations as long as it was higher than k_{M5}. The value accepted for k_{M9}, 2.5×10^3 M^{-1} s^{-1}, was determined by the best fit for the simulations. The initial estimate for k_{M11} was taken from similar work done by Shilov et al.[49] k_{M12} was also estimated from the data in Figure 1.

The simulations were most sensitive to kinetics parameters for reactions M3, M5, M9, M12, and M13. The simulations correctly predicted the induction period and the quantity of ClO_2

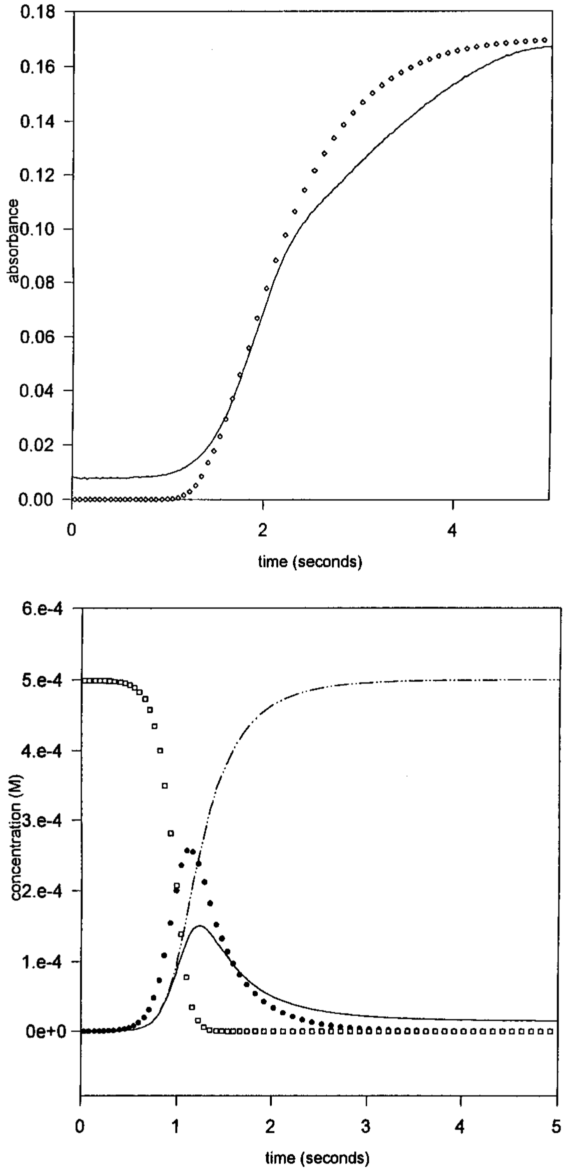

Figure 6. (a, top) Comparison between experimental (solid line) and calculated (circles) results at conditions: $[\mathrm{HMSA}]_0 = 0.0005$ M, $[\mathrm{ClO_2^-}]_0 = 0.003$ M. The reaction is not buffered. Species followed is $\mathrm{ClO_2}$. (b, bottom) Simulations results for other species in solution that cannot be followed spectrophotometrically. Solid line [HCHO], dotted line $[\mathrm{SO_4^{2-}}]$; squares [HMSA]; filled circles $[\mathrm{HOCH_2SO_2H}]$.

formed (Figure 6a). The simulations also show that the sulfonic acid, $\mathrm{HOCH_2SO_3H}$, rises to a maximum before falling at the end of the induction period (Figure 6b). This could not be observed experimentally but was conjectured to be happening. Of interest in Figure 6b is the time dependence of [HCHO] (solid line). The aldehyde is formed during the course of the reaction, reaching a peak at the point where [HMSA] goes to zero. It then decays, vanishing at the point where $\mathrm{SO_4^{2-}}$ attains its (stoichiometric) maximum concentration value. The simulations show that HCHO can coexist with $\mathrm{ClO_2}$ since the rate of HCHO oxidation by $\mathrm{ClO_2}$ is slow (from Figure 6a,b).

Discussion

The reaction dynamics, though complex, can be adequately described by the mechanism in Table 1. The complexity of the reaction is brought about by the organic residues which are formed as intermediates after the full oxidation of the sulfur center to the +6 oxidation state. Comparable systems have produced oligooscillations.[50] The $\mathrm{ClO_2^-}$−HMSA reaction is not oligooscillatory, though $\mathrm{ClO_2}$ production is very complex. The most important reaction in the mechanism is M5 (from the table) which initiates the reaction and forms HOCl. The balance between reactions M12−M14 and reaction M4 determines the global dynamics of the reaction. The importance of M4 reaction over M12−M14 ensures nonlinear kinetics as the autocatalytic pathway contributes more to the observed global reaction dymanics. The rapid HCHO−HOCl/$\mathrm{Cl_2}$ reaction coupled with the relatively slow HCHO−$\mathrm{ClO_2}$ reaction voids the possibility for oligooscillations. The end of the induction period gives way to autocatalytic $\mathrm{ClO_2}$ production, hence the sigmoidal $\mathrm{ClO_2}$ production curve.

Reaction R11 gives the stoichiometry of the $\mathrm{ClO_2^-}$ disproportionation in acidic medium. The availability of reactive intermediates, HOCl, $\mathrm{Cl_2}$ from reduction of $\mathrm{ClO_2^-}$ fuels a rapid $\mathrm{ClO_2}$ production. This explains the variable rate of $\mathrm{ClO_2}$ production. $\mathrm{ClO_2^-}$ first oxidizes the organic residue:

$$\mathrm{ClO_2^- + HCHO + H^+ \rightarrow HCOOH + HOCl} \quad \mathrm{(R20)}$$

The HOCl produced can also oxidize HCHO:

$$\mathrm{HCHO + HOCl \rightarrow HCOOH + Cl^-} \quad \mathrm{(R21)}$$

or participate in reactions R13 and R14 to autocatalytically produce $\mathrm{ClO_2}$. Thus rate of $\mathrm{ClO_2}$ production will be proportional to the rate of formation of HOCl in R19. The slower $\mathrm{ClO_2}$−HCHO reaction permits the autocatalytic buildup of $\mathrm{ClO_2}$.

After the total oxidation of HCHO, the production of $\mathrm{ClO_2}$ decreases as no further formation of HOCl takes place. The very slow $\mathrm{ClO_2}$ production at the end of the reaction is due to the slow HCOOH oxidation:

$$\mathrm{ClO_2^- + HCOOH + H^+ \rightarrow CO_2(g) + HOCl + H_2O} \quad \mathrm{(R22)}$$

which produces the reactive intermediate, HOCl, at a very slow rate. The reactive intermediate then reacts with $\mathrm{ClO_2^-}$ (R12) to produce $\mathrm{ClO_2}$. This explains the very slow $\mathrm{ClO_2}$ production at the end of the reaction. The proposed mechanism has also been able to explain Figure 2b in which the induction period decreased with $[\mathrm{HMSA}]_0$. Reaction R5 initially produces HOCl which then takes over the bulk of the oxidations. The HOCl also produces $\mathrm{ClO_2}$ (reaction R12) which can be rapidly consumed only as long as HMSA still exists in solution. $\mathrm{HOCH_2SO_3H}$, HCHO, and HCOOH all react very slowly with $\mathrm{ClO_2}$. Higher $[\mathrm{HMSA}]_0$ rapidly produces HOCl from $\mathrm{ClO_2^-}$, thus fuelling the reaction and diminishing the induction period.

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