Oxidation of Formaldehyde by Chlorite in Basic and Slightly Acidic Media

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The reaction of chlorite and formaldehyde was studied in basic and slightly acidic media. Though the expected product was CO_2, the oxidation of HCHO, however, gave nearly quantitative formation of ClO_2, the oxidation product of ClO_2^-. In excess HCHO the stoichiometry of the reaction was deduced as $3ClO_2^- + HCHO + 2H^+ \rightarrow HCOOH + 2ClO_2(aq) + Cl^- + 2H_2O$; but in high excess of ClO_2^- the stoichiometry was $6ClO_2^- + HCHO + 4H^+ \rightarrow CO_2(g) + 4ClO_2(aq) + 3H_2O + 2Cl^-$. The reaction is autocatalytic in HOCl. The first step of the reaction produces HOCl, which catalyzes the formation of ClO_2 and further oxidation of HCOOH to CO_2. ClO_2 was found to be relatively unreactive toward HCHO and HCOOH, and hence it accumulated rapidly.

Introduction

In the presence of a strong oxidizing agent, for example, permanganate or acidic bromate, the oxidation of most organic compounds with a single carbon atom gives carbon dioxide as one of the final products.[1] The pathway to producing carbon dioxide can pass successively through formaldehyde and formic acid. In a recent publication from our laboratory,[2] we observed that the oxidation of hydroxymethanesulfinic acid, $HOCH_2SO_2H$ (HMSA), by chlorite gives a mechanism in which formaldehyde was a stable intermediate. Standard qualitative tests such as the silver mirror test[3] clearly showed the production of formaldehyde before forming the final products. In some instances, with less than stoichiometric amounts of the oxidant, formaldehyde could be isolated quantitatively as a product, with the following stoichiometry:[2]

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

In excess ClO_2^-, the HCHO is oxidized further through formic acid and finally to $CO_2(g)$.

The reaction of chlorite and HMSA was found to be bistable and autocatalytic in HOCl.[2] Our motivation for studying the reaction of chlorite and HMSA was because it had shown reasonable promise that it could generate a lateral instability from a point of initial perturbation.[4] It also had proved to be a good example of a chemically driven diffusion-convection-reaction system capable of undergoing symmetry-breaking bifurcations and producing patterns from unstirred homogeneous aqueous solutions.[5]

A few experiments were carried out on the reaction of HCHO and ClO_2^- to determine whether the rate of this reaction was sufficiently high enough so as not be rate-determining in the oxidation of hydroxymethanesulfinic acid. These experiments found the reaction to be quite rapid and (apparently) virtually complete in less than 2 s (see Figure 1).[2]

We found two features of the ClO_2^-/HCHO reaction extremely intriguing.

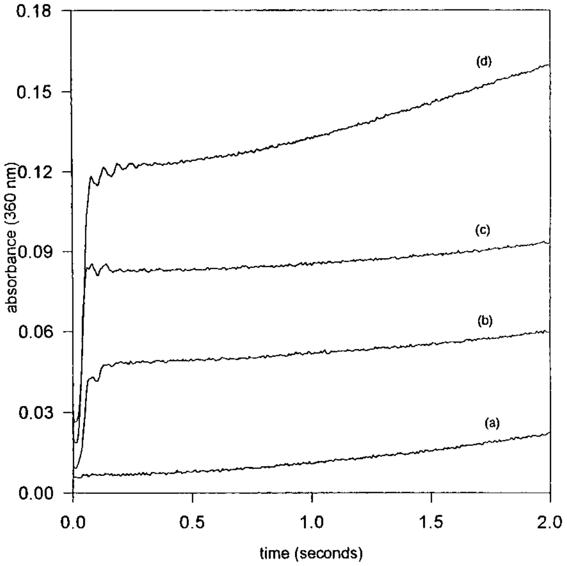

Figure 1. Oxidation of HCHO by ClO_2^- in slightly acidic pH. Rapid accumulation of ClO_2 indicates a rapid ClO_2^-/HCHO reaction. $[ClO_2^-]_0$ = (a) 0.001 M, (b) 0.002 M, (c) 0.003 M, (d) 0.004 M. $[HCHO]_0$ = 0.00133 M.

A. The fascinating features observed in Figure 1 were the irregular (or oscillatory-like) response to absorbance at 360 nm near the end of the reaction. Several experiments were performed which all produced what appeared to be oscillatory behavior at that same point. The number of oscillations and their amplitudes could not be reproduced exactly, but they were present. The question that needed an answer was whether the behavior observed in the ClO_2−HCHO reaction could be termed as oligooscillatory[6] and what possible mechanism could be involved.

B. Despite the fact that the aldehyde is known to reduce ClO_2^- to Cl^-, this reaction has been utilized as the easiest and most quantitative method of preparing chlorine dioxide.[7] What

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is the mechanism by which a Cl(III) species can be reduced and yet a Cl(IV) product is obtained in very high yields?

We would like to report, in this article, on our follow-up studies on the kinetics and mechanisms of the oxidation of formaldehyde by chlorite.

Experimental Section

Materials. Sodium chlorite (Aldrich) was first recrystallized from a water−ethanol mixture at 45 °C. It was later assayed by addition of acidified iodide and then titrating the released iodine against standard thiosulfate.[8] ACS-certified 37% w/w formaldehyde (Fisher) with 10% methanol as a preservative was used. Ionic strength was maintained at 1.0 M ($NaClO_4$). Chlorine dioxide was prepared by the standard method of oxidizing potassium chlorate in strongly acidic media[9] ($HClO_4$). It was standardized by using its absorptivity coefficient of 1265 M^{-1} cm^{-1} at 360 nm.[10]

Methods. All experiments were carried out at 25 ± 0.2 °C. The ClO_2^-/HCHO reaction was followed on a Hi-Tech Scientific SF-61AF stopped-flow spectrophotometer. Stoichiometric determinations were performed by analyzing reaction solutions for HCHO, ClO_2^-, CO_2, and Cl^-. Spot tests were used for HCHO[11] and HCOOH.[12] Quantitative determinations were made only for ClO_2 in conditions of excess ClO_2^-. Although the ClO_2^-/HCHO reaction produces $ClO_2(aq)$ in an extraneous oxyhalogen reaction, the total oxidizing power does not change after depletion of the reductant, HCHO.

Reactions were followed mainly by monitoring the formation of $ClO_2(aq)$, labeled as ClO_2 in this article, at its absorption maximum of 360 nm.

Results

The stoichiometry of the reaction was determined as

$$6ClO_2^- + HCHO + 4H^+ \rightarrow CO_2 + 4ClO_2 + 3H_2O + 2Cl^- \qquad (R2)$$

in high excess of ClO_2^-, ($[ClO_2^-]_0/[HCHO]_0 \geq 6$). Stoichiometry R2 was not obtained cleanly, as a slow continuing reaction of chlorite disproportionation occurs in all solutions of chlorite with chloride:[13]

$$5ClO_2^- + 4H^+ \rightarrow 4ClO_2 + Cl^- + 2H_2O \qquad (R3)$$

In lower ratios of chlorite to formaldehyde, the stoichiometry is

$$3ClO_2^- + HCHO + 2H^+ \rightarrow HCOOH + 2ClO_2 + Cl^- + 2H_2O \qquad (R4)$$

The difference between the two stoichiometries (R2 and R4) is the further oxidation of HCOOH to CO_2 in R2. These stoichiometries were determined by mixing chlorite and formaldehyde in steadily increasing ratios of oxidant to reductant. Figure 2 shows a series of scans of solutions of various ratios. The desired stoichiometry was the maximum ratio used before the detection of ClO_2 as a product ($\lambda = 360$ nm). The solutions were allowed to sit for up to two weeks before final stoichiometric determinations were performed. Stoichiometry R4 was first attained, and upon incubating the solutions further, stoichiometry R2 was obtained.

Reaction Kinetics. The reaction was very fast with respect to the production of ClO_2. The reaction mixture turned yellow almost instantly upon the addition of chlorite to formaldehyde.

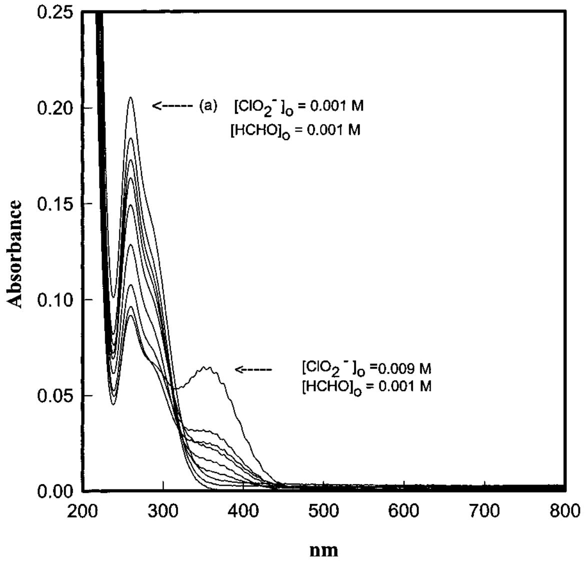

Figure 2. Spectral scans between $\lambda = 200$ and 800 nm used in the determination of the reaction's stoichiometry. The reaction solutions were incubated for 2 weeks before these spectra were taken. The correct stoichiometry is indicated as the maximum $[ClO_2^-]_0$ to $[HCHO]_0$ ratio that does not give $ClO_2(aq)$. $[ClO_2^-]_0 = 0.001$ M; $[HCHO]_0 =$ (a) 0.001 M, and each successive run is at an increment of 0.001 M in [HCHO].

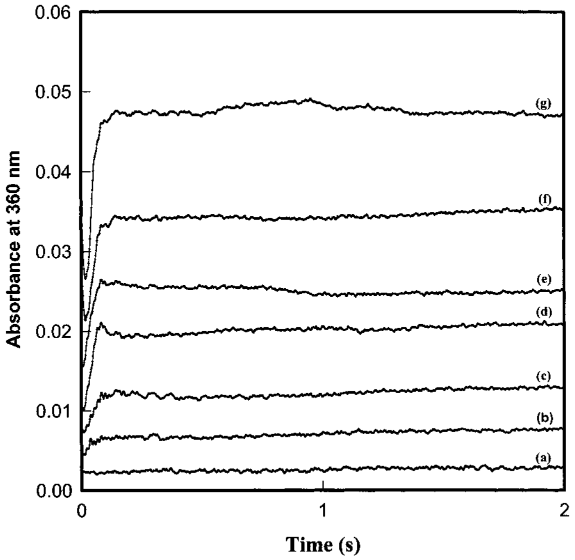

Figure 3. Absorbance traces showing the effect of ClO_2^- in slightly basic conditions (pH = 8). The basic conditions discourage rapid formation of ClO_2. $[HCHO]_0 = 0.0002$ M $[ClO_2^-]_0 =$ (a) 0.0002 M, and all others separated in $[ClO_2^-]$ by 0.0002 M up to part g with $[ClO_2^-]_0 = 0.0014$ M.

There is no noticeable induction period in the formation of chlorine dioxide. Figure 3 shows the absorbance−time traces obtained for different initial chlorite concentrations. It shows that the rate of formation of ClO_2 is proportional to the initial ClO_2^- concentrations. Qualitative tests for aldehydes showed that, despite the rapid formation of ClO_2, most of the HCHO would still not have reacted within the 2 s of data shown in Figure 3. The pH of the solution affected the rate and, to an extent, the quantity of the ClO_2 formed (see Figure 4). High-pH environments discouraged the rapid and quantitative formation of ClO_2. ClO_2 is considered to be much more stable in acidic environments and will disproportionate to ClO_3^- in strongly basic conditions:[14]

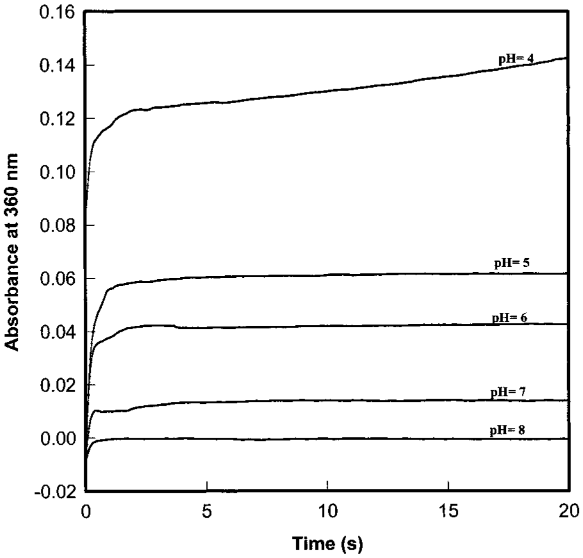

Figure 4. Effect of pH on the production of ClO_2 up to pH 4. ClO_2 is more stable in acidic conditions, while it disproportionates to ClO_3^- and Cl^- in basic environments. $[HCHO]_0 = 0.001$ M; $[ClO_2^-]_0 = 0.003$ M.

$$6ClO_2 + 3H_2O \rightarrow 5ClO_3^- + Cl^- + 6H^+ \qquad (R5)$$

From the data obtained in Figure 4, the effect of adding pure acid ($HClO_4$) to high-acid environments (pH $<$ 3), which is shown in Figure 5, was surprising. Further addition of acid retarded the formation of ClO_2, although all the reaction traces shown in Figure 5 gave the same final ClO_2 absorbance. The same type of "oligooscillations" in ClO_2 absorbance shown in Figure 1 persist through all the other traces. The rate of formation and the quantity of ClO_2 formed (see Figure 6) is directly proportional to the initial HCHO concentrations. This, however, is only true if an excess of ClO_2^- is assumed. The moment the ratio falls to less than 6, then ClO_2 formation will be decreased by additional HCHO. In some instances, the formation of ClO_2 becomes transient.

Role of ClO_2. Since ClO_2 is rapidly formed and is present in the reaction mixture before all the reductants (HCHO, HCOOH) are consumed, a set of reactions were performed in which ClO_2 was featured as the oxidant. Surprisingly, ClO_2 did not display any noticeable reactivity with either HCHO or HCOOH. Mixtures of ClO_2 with these reductants maintained most of their titer even after a day of incubation. The reactions were thus so slow that they did not interfere with our monitoring of the ClO_2^-/HCHO reaction, which showed rapid ClO_2 formation within 1−2 s.

Role of Preservative, Methanol. Methanol was added into the reaction mixture because it is present as a preservative in the formaldehyde reagent preparation. Thus its reaction with ClO_2^- and ClO_2 could be important if the reaction rates were comparable to the ClO_2^-/HCHO reaction. In both cases, none of the reactions were rapid enough to interfere with the ClO_2^-/HCHO reaction, and any interactions between methanol and chlorite were not considered when the kinetics model for the reaction system was devised.

Mechanism

Explanation of Possible Oligooscillatory Behavior. The ClO_2^-/HCHO reaction has a very large driving force toward completion such that it is unlikely to generate any oligooscillatory behavior. Any of the expected steps, HCHO → HCOOH → CO_2 will have large entropy terms such that reversibility is virtually impossible. In particular, as the oligooscillations occurred in the formation of ClO_2, it would be impossible (at the reaction's time scale) to generate any activity in the ClO_2 concentrations apart from its production. Standard reactions of ClO_2 with all the reductants in solution showed that ClO_2 was relatively unreactive toward these reductants. Thus there was no reaction in solution that could consume ClO_2 at a rate comparable to its rapid formation. The lack of control over how many oligooscillations as well as their amplitudes was evidence that they were mechanically generated. Stoichiometry R2 shows that the reaction produces CO_2 as a product. The production of CO_2 gas bubbles leads to deviations from the Beer−Lambert law because of the changes in refractive index as the light passes from the solution to gas. Previous studies in which CO_2 was a product had not shown such behavior.[2] In the ClO_2^-/HCHO reaction, however, the production of both CO_2

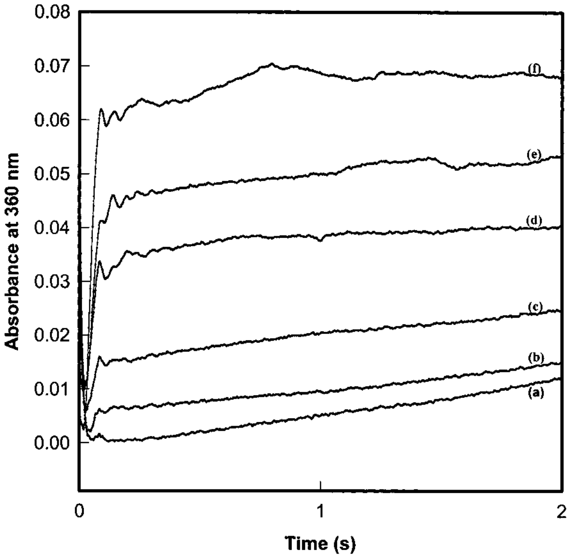

Figure 5. Effect of further decrease in pH below pH 3. Predominant Cl(III) species is now $HClO_2$, which reacts slower with HCHO than ClO_2^-, a better nucleophile. $[HCHO]_0 = 0.001$ M, $[ClO_2^-]_0 = 0.006$ M. $[H^+]_0 =$ (a) reference run, pH = 5, (b) 0.005 M, (c) 0.004 M, (d) 0.003 M, (e) 0.002 M, (f) 0.001 M.

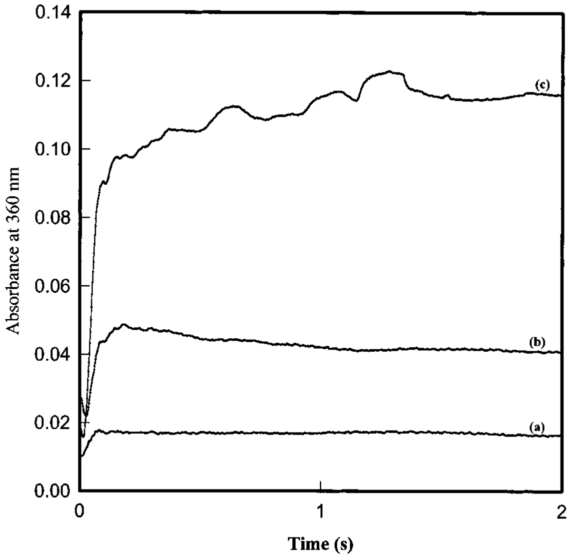

Figure 6. Rate of formation of ClO_2 is proportional to the initial HCHO concentration due to reaction R6. $[ClO_2^-]_0 = 0.006$ M; $[HCHO]_0 =$ (a) 0.004 M, (b) 0.006 M, (c) 0.0014 M.

TABLE 1: Mechanism for the Chlorite−Formaldehyde Reaction

	reaction	rate constant[a]
M1	$ClO_2^- + H^+ \rightleftharpoons HClO_2$	$1.0 \times 10^{10}\ M^{-1}\ s^{-1}$, $3.16 \times 10^{7}\ s^{-1}$
M2	$ClO_2^- + HCHO + H^+ \rightarrow HCOOH + HOCl$	$5.4 \times 10^{4}\ M^{-2}\ s^{-1}$
M3	$ClO_2^- + HCOOH + H^+ \rightarrow CO_2 + HOCl + H_2O$	$4.0 \times 10^{2}\ M^{-2}\ s^{-1}$
M4	$HOCl + HCHO \rightarrow HCOOH + Cl^- + H^+$	$6.0 \times 10^{4}\ M^{-1}\ s^{-1}$
M5	$HOCl + HCOOH \rightarrow CO_2 + Cl^- + H_2O$	$1.0 \times 10^{-1}\ M^{-1}\ s^{-1}$
M6	$HOCl + ClO_2^- + H^+ \rightleftharpoons Cl_2O_2 + H_2O$	$5.0 \times 10^{7}\ M^{-2}\ s^{-1}$, $6.6 \times 10^{2}\ s^{-1}$
M7	$Cl_2O_2 + 2ClO_2^- + 2H^+ \rightleftharpoons 2ClO_2 + 2HOCl$	$5.4 \times 10^{6}\ M^{-4}\ s^{-1}$, $1.0 \times 10^{-2}\ M^{-3}\ s^{-1}$
M8	$Cl_2O_2 + HCHO + H_2O \rightarrow HCOOH + 2HOCl$	$6.0 \times 10^{5}\ M^{-1}\ s^{-1}$
M9	$Cl_2O_2 + HCOOH \rightarrow CO_2 + 2HOCl$	$4.5 \times 10^{2}\ M^{-1}\ s^{-1}$
M10	$HOCl + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O$	$8.9 \times 10^{9}\ M^{-2}\ s^{-1}$, $1.1 \times 10^{2}\ s^{-1}$
M11	$Cl_2 + 2ClO_2^- \rightarrow 2ClO_2(aq) + 2Cl^-$	$9.8 \times 10^{6}\ M^{-2}\ s^{-1}$
M12	$2ClO_2 + H_2O \rightleftharpoons ClO_3^- + ClO_2^- + 2H^+$	$1.0 \times 10^{1}\ M^{-1}\ s^{-1}$, $1.0 \times 10^{3}\ M^{-3}\ s^{-1}$
M13	$2ClO_2 + Cl^- + H_2O \rightarrow 2ClO_2^- + HOCl + H^+$	$5.0 \times 10^{1}\ M^{-2}\ s^{-1}$

[a] Rate constants separated by a comma represent the forward and reverse rate constants, respectively. Rate constant units can be deduced from the reaction's molecularity, except for M8, M10, M12, and M13 where water is not considered.

and ClO_2 is so rapid that there is no time for the dissolution of the gas molecules formed, and hence the gas bubbles out. Higher initial concentrations produced more bubbles of CO_2 (cf. the rather smoother ClO_2 formation in Figure 4 (3:1 ratio) with the more turbulent formation shown in Figure 5 (6:1 ratio)). Control experiments run in an open test tube also showed formation of gas bubbles at high initial concentrations of reactants. Kinetics traces obtained from a spectrophotometer equipped with a stirrer gave absorbance traces with much less pronounced fluctuations.

Kinetics Mechanism. The inertness of ClO_2 to the reductants in solution easily explains the rapid formation of ClO_2 observed. Any ClO_2 formed is not consumed further. Thus one would observe no induction period but a steady and rapid increase in ClO_2 concentrations as soon as the reagents are mixed.

The initial step in this mechanism is a nucleophilic attack on the carbon atom of formaldehyde by ClO_2^-:

$$ClO_2^- + HCHO + H^+ \rightarrow HCOOH + HOCl \qquad (R6)$$

The proton shown in reaction R6 is used to expel HOCl from the activated complex made by the nucleophilic attack of ClO_2^- on HCHO. This is to differentiate it from a proton that might come into the reaction scheme as $HClO_2$:

$$H^+ + ClO_2^- \rightleftharpoons HClO_2 \qquad (R7)$$

The HOCl formed in reaction R6 will rapidly react with excess ClO_2^- to produce ClO_2:[15]

$$HOCl + 2ClO_2^- + H^+ \rightleftharpoons 2ClO_2(aq) + Cl^- + H_2O \qquad (R8)$$

Any of the ClO_2 formed in reaction R8, on the time scale of this reaction, becomes a sink for the oxyhalogen species.

HOCl, also, can oxidize HCOOH:

$$HOCl + HCOOH \rightarrow CO_2(g) + Cl^- + H^+ + H_2O \qquad (R9)$$

This is the carbon dioxide that bubbles off in the reaction mixture. ClO_2^- can also oxidize HCOOH, but at a much slower rate. Reaction R6 is the rate-determining step with respect to the consumption of HCHO. It is also an initiation step for the formation of ClO_2. HOCl is the reactive species that controls all the oxyhalogen reactions in solution. It appears to be the autocatalytic species responsible for the very rapid increase in the rate of production of ClO_2. Deriving a single-step mechanism for the process represented in reaction R6 gives the following scheme:[16]

$$ClO_2^- + HOCl + H^+ \rightleftharpoons Cl_2O_2 + H_2O \qquad (R10)$$

$$Cl_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2HOCl \qquad (R11)$$

Addition of R10 and R11 gives quadratic autocatalysis in HOCl in the presence of excess ClO_2^-.

Effect of Acid. If reaction R6 is rate-determining, then the rate of reaction is:

$$-d[HCHO]/dt = k_{R6}[ClO_2^-][HCHO][H^+] \qquad (1)$$

There is an observed increase in rate of reaction with respect to [HCHO] and $[ClO_2^-]$, but acid appears to retard formation of ClO_2 (Figure 5). The estimated pK_a of chlorous acid[17] is 2.5, and thus the equilibrium of reaction R7 lies to the right in pH conditions of less than 2.5. Reaction R6 is faster than the corresponding reaction of $HClO_2$ with HCHO:

$$HClO_2 + HCHO \rightarrow HCOOH + HOCl \qquad (R12)$$

Chlorous acid is a much poorer nucleophile than the chlorite ion. One would expect retardation of the reaction with respect to acid especially when the pH falls below 2.5, as can be observed in Figure 5. If one assumes that $HClO_2$ is relatively inert, then the rate of reaction will be given by

$$-d[HCHO]/dt = k_{R6}[Cl(III)]_T[HCHO][H^+]/(1 + K_a[H^+]) \qquad (2)$$

where the total chlorine(III) species, $[Cl(III)]_T$, is $[HClO_2] + [ClO_2^-]$ and K_a is the acid dissociation constant for chlorous acid. The lower rate of formation of ClO_2 at higher pH can be explained by the instability of ClO_2 in base.[13] The reverse of reaction R8 becomes important in basic environments, thus stunting the formation of ClO_2. The rate of formation of HOCl is acid-catalyzed, but experimentally, we can only observe the rate of formation of ClO_2, which is retarded by base.

Rate of Formation of ClO_2. The formation of HOCl in reaction R6 controls the subsequent formation of ClO_2. In high excess of ClO_2^-, the rate of formation and quantity of ClO_2 formed is directly proportional to the initial HCHO concentration (see stoichiometry R2). This is supported by eqs 1 and 2. Without any reductants to consume ClO_2, such correlations can easily be made in high-acid environments.

Kinetics Model and Computer Simulations. The full kinetics model used to simulate the oxidation of formaldehyde by chlorite is shown in Table 1. The inertness of ClO_2 greatly simplifies the reaction scheme, which can be distilled to only 13 reactions. Only five reactions were made reversible: the acid dissociation reaction of $HClO_2$, the formation of the Cl_2O_2 intermediate (reactions M6 and M7), the hydrolysis reaction of Cl_2, (reaction M10), and the reaction which controls the formation of ClO_2 in high-pH environments (reaction M12).

Only three oxidizing agents were assumed to exist in the reaction mixture: ClO_2^-, HOCl, and Cl_2O_2. There were also only two reductants: HCHO and HCOOH. The remaining seven possible reactions are M1, M6, M7 (formation of ClO_2), and M11−M13. These listed 13 reactions were exhaustive, as there are no other reactions that are possible in the reaction mixture.

Seven of the reactions listed, M1, M6, M7, M10, M11, M12, and M13, are pure oxyhalogen reactions whose kinetics parameters can be obtained from literature. Kinetics data for M1 were taken from Chinake et al.,[18] and care was taken to maintain the pK_a of chlorous acid. Reaction M6 had been studied by Peintler et al.[15] as the composite M6 + M7 reaction. M7 was taken from the work of Jones et al.[19] Reaction M10 was studied by relaxation techniques by Eigen and Kustin,[20] and the kinetics parameters used were taken from this study. Kinetics parameters for reactions M10 were derived from the work of Peintler et al.,[15] and those of reaction M11 are from Epstein et al.[21] Reactions M12 and M13 are not simple single-step elementary reactions.[13] They control the final ClO_2 concentrations with respect to pH. They are the only reactions in which ClO_2 is consumed. At high pH, most of the ClO_2 disproportionates to ClO_3^-, ClO_2^-, and Cl^- (see reaction M12), hence the observed lower ClO_2 absorbances at high pH (see Figure 4).[22−24] Rapid autocatalytic formation of ClO_2 is halted by reaction M13.[15] The Cl^- obtained from the reduction of HOCl by the substrate species (reactions M4 and M5) halts the uncontrolled buildup of ClO_2 (reaction M13).

The derived 13 ordinary differential equations were numerically integrated by using a semiimplicit Runge−Kutta procedure.[25] The simulations were insensitive to the rate constants used for reaction M1 as long as the acid dissociation constant ($pK_a = 2.5$)[17] was maintained and the rate constants maintained such that M1 was not rate-determining. Higher kinetics parameters for M1 increased the stiffness of the integration but did not change the simulations result. The forward rate constant for reaction M2 was estimated from this study. Using reaction R8 (a composite of M6 and M7 in the table), we observe that in the initial stages of ClO_2 production the rate of formation of ClO_2 is proportional to the rate of production of HOCl (assuming R8 is fast).

The rate constants for reactions M3, M4, and M5 initially were estimated and then refined to give the best fit to the data. The simulations were most sensitive to the value of the rate constant for reactions M2 and M6 and insensitive to the values given for M7 and M8. Increasing the rate constant for reaction M2 rapidly built up the autocatalyst, HOCl, resulting in a much more rapid buildup of ClO_2. The major production of the autocatalyst, HOCl, is through M6 but is initiated by reaction M2.

Using these 13 reactions, the simulations were quite simple and gave a very close fit to the experimental data (see Figure 7a,b). Our simulations easily predicted the rate of formation of ClO_2 (Figure 7a). The slightly lower concentrations predicted for ClO_2 are expected, as our simulations do not account for the absorbance contributions at 360 nm from the intermediate species. Figure 7b gives the model's predictions for the concentration variations of HCHO, HCOOH, and CO_2(g). There are no experimental data available for comparison, but the model shows the expected autocatalytic consumption of HCHO as well as the autocatalytic production of CO_2(g). HCOOH, as expected, shows a transient formation. The model can be checked from the reaction's material balance in which the total concentration of the carbon-containing species is always constant: $[HCHO](t) + [HCOOH](t) + [CO_2(g)](t) = [HCHO](t{=}0)$ (initial HCHO concentration at time = 0). No further production of CO_2 is expected as HCOOH concentration vanishes since CO_2 is only produced in reactions M3, M5, and M9, all involving oxidation of HCOOH. Several initial conditions were simulated which gave the same fit as the one in Figure 7a: good fits at the beginning and at the end of the reaction with a slight deviation some time into the reaction. Figure 7a represents a typical simulations fit for conditions of excess HCHO and Figure 7b is for excess chlorite, the only conditions in which CO_2 is produced as a product.

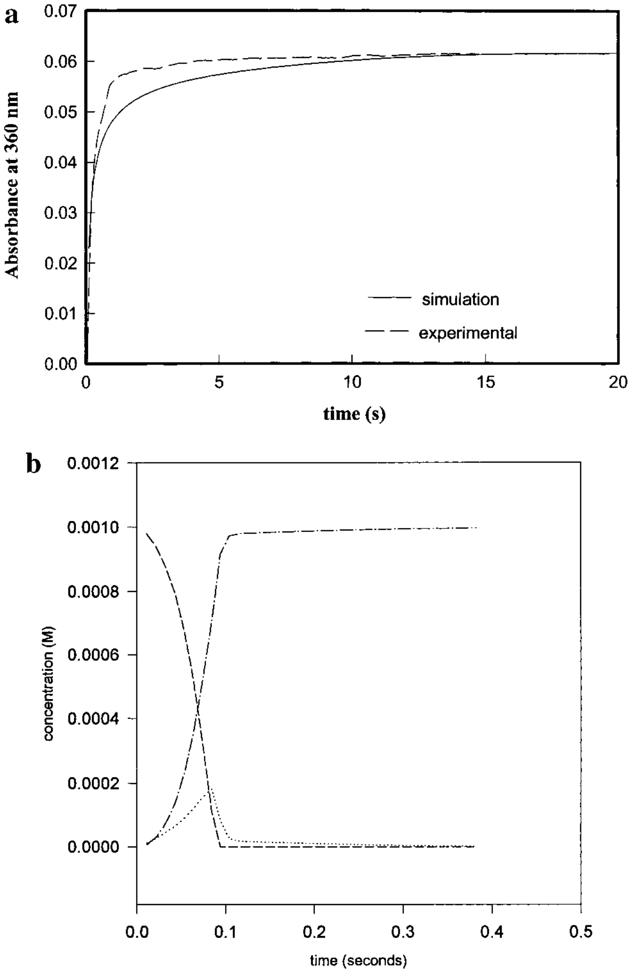

Figure 7. (a) Comparison of computer simulations with experimental data for the ClO_2^-−HCHO reaction. The simulations are generated from the mechanism shown in Table 1. Conditions simulated are $[ClO_2^-]_0 = 0.001\,33$ M; $[HCHO]_0 = 0.001$ M; pH = 3.7. (b) Other computer simulations results predicting the concentration−time variations for HCHO (dashed line), CO_2 (dots and dashed line), and HCOOH (dotted line). Conditions simulated are $[ClO_2^-]_0 = 0.006$ M; $[HCHO]_0 = 0.001$ M; pH = 3.7.

Conclusion

Our results prove that what looks like oligooscillatory behavior in the production of ClO_2 is not derived from an oligooscillatory mechanism, but from a mechanical effect. The reaction is still nonlinear, with an autocatalytic production of ClO_2 and an autocatalytic consumption of HCHO. The inertness of ClO_2 in the reaction solution can explain why the reaction of ClO_2^- and HCHO is such an effective and quantitative method for preparing ClO_2. The autocatalyst formed in the first step, HOCl, reacts much more rapidly with ClO_2^- to produce ClO_2 than it does with the reductants to form the oxidation products.

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