In this case, its influence upon  $\nu_n$  will be diminished below that expected if the structural rearrangement forms an integral part of the electron-transfer step itself.1d

Irrespective of these details, however, the virtual exclusion of solvent dynamical effects upon  $\kappa_{el} \nu_n$  resulting from reaction nonadiabaticity provides a plausible additional means of identifying this factor and distinguishing it from inner-shell reorganization as the major reason for the observed rate retardation. While it is likely that the activation barrier for  $Ru(hfac)_3^{0/-}$  electron exchange contains a significant inner-shell contribution, it is concluded that reaction nonadiabaticity provides the major contribution to the slow kinetics observed for this couple, especially in the electrochemical environment.

Rough  $H_{12}$  estimates for Ru(hfac)<sub>3</sub><sup>0/-</sup> self-exchange and electrochemical exchange are obtained as follows. Given that Ru(hfac)<sub>3</sub><sup>0/-</sup> self-exchange exhibits log  $(k_{ex}/K_p) - (\epsilon_{op}^{-1} - \epsilon_s^{-1})$  slopes that are more negative than for Cp<sub>2</sub>Fe<sup>+/0</sup> self-exchange, even through the opposite is predicted from eq 2b, we can confidentally assert that the influence of solvent dynamics is smaller for the former reaction. It therefore follows that  $H_{12}$  for Ru- $(hfac)_3^{0/-}$  is smaller than that, ca. 0.1 kcal mol<sup>-1</sup>, deduced for  $Cp_2Fe^{+/0}$  self-exchange.<sup>2d</sup> Based on the likelihood, from reasoning given above, that  $\Delta G^*_{is}$  and  $\Delta G^*_{os}$  for Ru(hfac)<sub>3</sub><sup>0/-</sup> self-exchange are liable to be somewhat (ca. 1-2 kcal mol<sup>-1</sup>) larger and smaller, respectively, than for  $Cp_2Fe^{+/0}$ , the overall barrier for these self-exchange reactions are unlikely to differ greatly. Since for nonadiabatic processes  $\kappa_{el} \propto H_{12}^{2,7}$  we deduce that  $H_{12}$  for Ru- $(hfac)_3^{0/-}$  self-exchange is around 0.05 kcal mol<sup>-1</sup>. Given that  $\Delta G^*_{\text{os,e}}$  and  $\Delta G^*_{\text{os,h}}$  for Ru(hfac)<sub>3</sub><sup>0/-</sup> are unlikely to be greatly different (vide supra),<sup>23b</sup> the observed ca. 5–10-fold smaller  $(k_{\rm ex}/K_{\rm p})$  values for electrochemical versus self-exchange makes it likely that  $H_{12}$  is also smaller in the former environment.

## **Concluding Remarks**

Although the quantitative details of the analyses presented here are limited by several factors, the findings are believed to add significantly to the extant experimental evidence of the essential synergic nature of electronic coupling and solvent dynamical effects in electron transfer.<sup>2d</sup> Given the particular sensitivity of the latter effect to the former, examination of solvent-dependent kinetics in electrochemical as well as homogeneous redox environments can in favorable cases provide insight into electronic coupling factors that cannot easily be deciphered from the rates in a given solvent.

It remains to account for the likelihood, based on the foregoing analysis, that  $H_{12}$  is smaller for Ru(hfac)<sub>3</sub><sup>0/-</sup> electrochemical versus self-exchange. This result might be viewed as surprising, given that the opposite could be predicted on theoretical grounds.<sup>11</sup> However, quite apart from the inevitable sensitivity of donoracceptor orbital coupling to spatial and symmetry factors, a further complication is wrought by the involvement of so-called "superexchange" mechanisms utilizing intervening ligand orbitals or, equivalently, metal-ligand orbital mixing.<sup>34</sup> While further speculation is unwarranted here, by combining the present results for Ru(hfac)<sub>3</sub><sup>0/-</sup> with those for the metallocene couples, it would appear that the molecular structural sensitivity of  $H_{12}$  is distinctly different in the electrochemical and homogeneous-phase environments. Clearly, then, bona fide theoretical calculations of  $H_{12}$ for the former type of redox environment, as for those being pursued for the latter reaction type,<sup>34</sup> would be of great interest.

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# Kinetics and Mechanism of the Reaction between Chlorite Ion and Hypochlorous Acid<sup>1</sup>

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The reaction between  $ClO_2^{\bullet-}$  and HOCl has been studied by spectrophotometrically monitoring the production of  $ClO_2$  at pH 5-6. In excess ClO<sub>2</sub><sup>-</sup>, the reaction is first order in ClO<sub>2</sub><sup>-</sup>, HOCl, and H<sup>+</sup>, and the stoichiometry is given by HOCl +  $2ClO_2^- + H^+ \rightarrow 2ClO_2 + Cl^- + H_2O$ . In excess HOCl and at higher pH's,  $ClO_3^-$  is produced, and the order of the reaction is between 1 and 2 for HOCl and between 0 and 1 for H<sup>+</sup>. By combining computer simulation and least-squares analysis, we obtain a mechanism in which the reaction  $2\text{HOCl} + \text{ClO}_2^- \rightarrow \text{ClO}_3^- + \text{Cl}_2 + \text{H}_2\text{O}$  ( $k = (2.1 \pm 0.1) \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ ) plays a key role in explaining the behavior at high  $[HOC1]/[CIO_2]$ .

## Introduction

Chlorite-driven chemical oscillators were the first oscillating chemical reactions to be systematically designed,<sup>2</sup> and they now contribute perhaps the largest family of chemical oscillators.<sup>3</sup> Mechanisms for several chlorite oscillators have been proposed and have been found to be in good agreement with the observed dynamical behavior of these systems.<sup>4</sup> Among the chlorite-driven oscillators, the chlorite-thiosulfate reaction exhibits the most exotic

<sup>(1)</sup> No. 60 is the series Systematic Design of Chemical Oscillators. No. 59: Orbán, M.; Epstein, I. R. J. Am. Chem. Soc. 1989, 111, 8543.
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<sup>(4)</sup> Citri, O.; Epstein, I. R. J. Phys. Chem. 1987, 91, 6034; 1988, 92, 1865.

dynamical behavior, including periodic oscillation,<sup>5</sup> chemical chaos,<sup>6</sup> wave propagation,<sup>7</sup> and extreme sensitivity to fluctuations and mixing effects.<sup>8</sup>

Although there have been mechanistic studies of the chloritethiosulfate reaction at high pH and temperature,9 the mechanism of the reaction under the conditions at which the above phenomena occur is still a mystery. The ultimate goal of understanding these phenomena demands a knowledge of the detailed mechanism of the redox reactions of the chlorite ion. One important intermediate in all redox reactions of  $ClO_2^-$  is hypochlorous acid, HOCl. If chlorite ion and hypochlorous acid are present in the same solution, then yellow chlorine dioxide is formed, and its formation can be followed by spectrophotometric methods. The rate of ClO<sub>2</sub> formation is determined by the rate of the formation of hypochlorous acid and by the ratio between the rates of its reaction with chlorite ion and with the other species present in the system. The reaction between chlorite ion and hypochlorous acid may therefore be regarded as an indicator reaction, providing a convenient tool for kinetic study of the redox reactions of the chlorite ion. Appropriate utilization of this indicator reaction requires a thorough knowledge of its kinetics and mechanism. In this paper, we report the results of experiments to determine the mechanism of the ClO<sub>2</sub><sup>-</sup>-HOCl reaction.

The reactions of chlorite ion with hypochlorous acid and (at lower pH) with dissolved chlorine have important practical applications in water and waste water treatment.<sup>10</sup> The stoichiometry, kinetics, and mechanism of the  $ClO_2$ -HOCl reaction have therefore been a focus of interest for decades.<sup>11-15</sup> Several patents describe methods of optimizing chlorine dioxide production in the reaction.<sup>16-18</sup> Studies by Taube and Dodgen,<sup>11</sup> Gordon and Emmenegger,<sup>12</sup> and Aieta and Roberts<sup>13</sup> have led to a consensus on the most important factors governing the reaction.<sup>13</sup> Tang and Gordon<sup>14</sup> in a recent stoichiometric study explicitly call for further kinetic investigations to unravel the microscopic details of the kinetics and mechanism of this system.

In addition to our interest in the mechanisms of chlorite oscillators and the practical importance of the  $ClO_2$ -HOCl reaction, a third factor makes this a particularly attractive system to study. Recent developments in numerical analysis make it possible not only to simulate relatively complex mechanisms but also to undertake the rigorous fitting of experimental data, including statistical analysis and characterization of the kinetic parameters, by combining statistical methods with the simulation procedure.

### **Experimental Section**

*Materials*. The carbonate content of commerically available (Aldrich) NaClO<sub>2</sub> was precipitated with BaCl<sub>2</sub> solution. The excess Ba<sup>2+</sup> ions were eliminated by adding a calculated amount of Na<sub>2</sub>SO<sub>4</sub> solution. The resulting NaClO<sub>2</sub> was recrystallized twice from an 80% ethanol-water mixture in the temperature

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TABLE I: Fixed Concentrations and Concentration Ranges in the Nine Series of Experiments (mM dm<sup>-3</sup>)

	[HOCI]	[ClO <sub>2</sub> <sup>-</sup> ]	[CH <sub>3</sub> COOH]	no. of runs	
1	0.1331	4.683	17-100	8	
2	0.05-0.2	4.683	50.0	6	
3	0.0799	2.8-14	50.0	7	
4	0.1-1.9	1.9-0.1	177.4	15	
5	0.1-1.9	1.9-0.1	50.0	15	
6	0.1-1.9	1.9-0.1	17.74	15	
7	2.856	0.3020	17-170	7	
8	2.856	0.1-1.0	50.0	7	
9	1.0-3.5	0.2013	50.0	7	



Figure 1. Initial rate studies. Symbols: ( $\blacksquare$ - $\blacksquare$ ) x = pH - 5.0,  $y = -log v_0 - 5.0$ ,  $[HOCI]_0 = 1.331 \times 10^{-4}$  M,  $[CIO_2^-]_0 = 4.683 \times 10^{-3}$  M; ( $\bigcirc$ - $\bigcirc$ )  $x = -log [HOCI]_0 - 3.0$ ,  $y = -log v_0 - 5.0$ , pH = 5.55,  $[CIO_2^-]_0 = 4.683 \times 10^{-3}$  M; ( $\triangle - \triangle$ )  $x = -log [CIO_2^-]_0 - 1.0$ ,  $y = -log v_0 - 5.0$ , pH = 5.55,  $[HOCI]_0 = 7.99 \times 10^{-5}$  M; ( $\square - \square$ ) x = pH - 4.0,  $y = -log v_0 - 4.5$ ,  $[HOCI]_0 = 2.865 \times 10^{-3}$  M,  $[CIO_2^-]_0 = 3.019 \times 10^{-4}$  M; ( $\bigcirc$ - $\bigcirc$ )  $x = -log [HOCI]_0 - 2.5$ ,  $y = -log v_0 - 5.0$ , pH = 5.55,  $[CIO_2^-]_0 = 2.013 \times 10^{-4}$  M; ( $\triangle - \triangle$ )  $x = -log [CIO_2^-]_0 - 3.0$ ,  $y = -log v_0 - 4.5$ , pH = 5.55,  $[HOCI]_0 = 2.856 \times 10^{-3}$  M.

range 25 to -20 °C. No Cl<sup>-</sup> and no alkaline impurities could be detected in the purified NaClO<sub>2</sub>, and iodometric titrations showed that its purity was better than 99.5%. The HOCl stock solution was freshly prepared by dissolving chlorine gas in a slurry of yellow HgO in water and distilling the solution from the HgO.<sup>19</sup> All other chemicals were the highest purity commericially available and were used without further purification. The stock solutions were freshly prepared for each series of experiments.

Methods. All kinetic runs were carried out in 0.5 M sodium acetate, with the pH of the solutions regulated between 5 and 6 by adding acetic acid. Solutions for the kinetic runs were prepared in a 10-mm quartz cuvette equipped with Teflon stopper and stirrer. The last component (either NaClO<sub>2</sub> or HOCl solution in 0.1 M NaAc) was introduced directly into the cuvette from a fast delivery pipet, just before the cuvette and the cuvette compartment of the spectrophotometer were closed. The volume of the solution was always 3.0 cm<sup>3</sup>, and the air above the solution occupied less than 10% of the volume of the solution. Since the distribution coefficient of ClO<sub>2</sub> between an aqueous solution and the gas phase is 23,<sup>20</sup> less than 0.5% of the evolving ClO<sub>2</sub> could

<sup>(19)</sup> Mellor, J. W. Comprehensive Treatise on Inorganic and Theoretical Chemistry; Longmans, Green & Co.: London, 1946; Vol. 2 p 245.
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**Figure 2.** Job's plots of maximum concentration of  $[ClO_2]$  evolved in the reaction as a function of initial concentration of HOCI. The sum of initial concentrations,  $[HOCI]_0 + [ClO_2^{-1}]_0$  is fixed at  $2 \times 10^{-3}$  M. Symbols:  $(\Box - \Box) pH = 5.00; (O - O) pH = 5.55; (\Delta - \Delta) pH = 6.00.$ 

escape from the solution. All experiments were performed in the thermostated compartment of a Perkin-Elmer 552A spectro-photometer at 25 °C.

Nine series of experiments were carried out under the conditions summarized in Table I. The first three series were performed in chlorite excess and the last three in HOCl excess. In series 4, 5, and 6 the sum of the reactant concentrations was kept constant and their ratio varied as in the Job's plot method in the chemistry of complex equilibria. The absorbance of the  $ClO_2$ evolved was followed at 360 nm until no further increase was detected. At least one experiment in each series was repeated in a larger volume, and over a period of 2 h the samples were analyzed iodometrically for total oxidizing power.<sup>14</sup> Within this period no detectable decrease in the total oxidation power was found. Thus the evolution of O<sub>2</sub> reported by Tang and Gordon<sup>14</sup> need not be taken into account under our experimental conditions, where the only products formed are Cl<sup>-</sup>, ClO<sub>2</sub>, and ClO<sub>3</sub><sup>-</sup>.

### Results

The experiments listed in Table I covered a wide range of conditions, with half-times varying from 10 to 500 s. For each experiment we first evaluated the initial rate of  $ClO_2$  production and  $[ClO_2]_{\infty}$ . The results of the initial rate studies (series 1-3 and 7-9) are summarized in Figure 1. The figure demonstrates that in chlorite excess (series 1-3) the rate of  $ClO_2$  production is first order with respect to [HOCI],  $[ClO_2^{-}]$ , and  $[H^+]$ . To calculate  $[H^+]$  we take into account that  $pK_a = 4.55$  for acetic acid at ionic strength 0.5 and 25 °C.<sup>21</sup>

In the first three series of experiments the concentration of  $ClO_2$  evolved always reached at least 90% of the value calculated from eq 1. Above this 90% level, the fraction of the theoretical  $ClO_2$ 

$$HOCI + 2CIO_2^- + H^+ = 2CIO_2 + H_2O + CI^-$$
 (1)

found increases slightly with decreasing pH and with increasing initial chlorite concentration. From the 21 runs in chlorite excess we obtain a preliminary result for the rate law:

$$\frac{1}{2} \frac{d[ClO_2]}{dt} = {(1.10 \pm 0.03) \times 10^6 \text{ M}^{-2} \text{ s}^{-1}}[HClO][ClO_2^{-1}][H^+] (2)$$

Experimental series 4-6 were carried out to see if the same relation remains valid as we gradually shift from excess  $ClO_2^-$  to excess HOCI. The  $[ClO_2]_{\infty}$  values obtained are shown as Job's plots in Figure 2. The figure clearly shows a 2:1 stoichiometry. We note, however, a continuous shift toward chlorate formation as the  $[HOCI]/[ClO_2^-]$  ratio increases. This shift becomes more



**Figure 3.** Job's plots to determine kinetic order. Normalized initial rates (see text) as a function of initial HOCl concentration. [HOCl]<sub>0</sub> +  $[ClO_2^{-}]_0 = 2 \times 10^{-3}$  M. Full line: calculated assuming first-order reaction for both components. Dashed line: calculated assuming first-order reaction with respect to  $[ClO_2^{-}]_0$  and second order with respect to  $[HOCl]_0$ . ( $\Box$ - $\Box$ ) Experimental data at pH = 5.00. (O-O) experimental data at pH = 6.00.

pronoucned as the pH increases from 5 to 6.

The initial rates can also be analyzed by a straightforward extension of Job's method to kinetic studies. Suppose there are components, X and Y, with the sum of their initial concentrations held constant at a value C. If the reaction is of order a and b in X and Y, respectively, the initial rate as a function of the initial [X] is given by

$$v = [X]^{a}(C - [X])^{b}$$
 (3)

At 
$$v = v_{max}$$
,  $dv/d[X] = 0$ , i.e.,

$$a/b = [X]_{max}/(C - [X]_{max})$$
 (4)

Dividing v by the measured  $v_{max}$  yields the normalized initial rate. Normalized rate curves predicted in this fashion are illustrated in Figure 3. The full line corresponds to a reaction first order in each component; the dashed line is calculated for a reaction first order with respect to  $[ClO_2^-]$  and second order with respect to [HOCl].

Comparing the experimental points with the theoretical curves, we observe indications of a second-order dependence on [HOCI] at pH 6. This observation prompted us to carry out additional initial rate studies in HOCI excess. The results are illustrated in Figure 1, where we see that no simple rate law is applicable to the system under these conditions. The formal order of the reaction is between 1 and 2 for [HOCI]; it is between 0 and 1 for [H<sup>+</sup>] and gradually increases from 1 for  $[CIO_2^{-}]$  as its concentration decreases.

The same trends in  $[ClO_2]_{max}$  were observed in excess HOCl as in excess chlorite; i.e., decreasing the pH and increasing the chlorite concentration increase the amount of  $ClO_2$  formed. At constant chlorite concentration and pH, however, the yield of  $ClO_2$ decreases significantly with [HOCl]. This relation is illustrated in Figure 4.

### Calculations

A computer program was developed to obtain the "best" rate constants and associated statistical parameters from the experimental data and various mechanisms put forward to explain them. The program is based on the Gauss-Newton method,<sup>22</sup> with the required derivatives obtained numerically by using an increment equal to 1% of the estimated value of the parameter to be calculated. Integration of the rate equations was performed with the GEAR program.<sup>23</sup> Because the ClO<sub>2</sub> concentration measured

<sup>(21)</sup> Sillen, L. G.; Martell, A. E. Stability Constants of Metal Ion Complexes; The Chemical Society: London, 1964.

<sup>(22)</sup> Hildebrand, F. B. Introduction to Numerical Analysis; McGraw-Hill: New York, 1972.



**Figure 4.** Effect of increasing initial HOCl concentration on the rate and yield of ClO<sub>2</sub> production. pH = 5.55;  $[ClO_2^{-1}]_0 = 2.0127 \ 10^{-4} \text{ M}. (\Box - \Box)$  (dashed line)  $[HOCl]_0 = 9.521 \times 10^{-4} \text{ M}. (O-O)$  (dotted line)  $[HOCl]_0 = 1.428 \times 10^{-3} \text{ M}.$  ( $\blacksquare - \blacksquare$ ) (dot-dash line)  $[HOCl]_0 = 2.38 \times 10^{-3} \text{ M}.$  ( $\blacksquare - \blacksquare$ ) (full line)  $[HOCl]_0 = 3.332 \times 10^{-3} \text{ M}.$ 

under different conditions varied by more than 1 order of magnitude, each experimental point was weighted by the reciprocal of the  $[ClO_2]_{max}$  for that experiment. The function to be minimized is

$$s = \sum_{i=1}^{87} \sum_{j=1}^{p_i} [([\text{ClO}_2]_{i,j}^e - [\text{ClO}_2]_{i,j}^e) / [\text{ClO}_2]_{i,\max}^e]^2$$
(5)

The superscripts e and c denote the experimentally measured and calculated concentrations, respectively, while  $[ClO_2]_{i,max}^{e}$  is the maximum value of  $[ClO_2]$  measured experimentally in the *i*th experiment which contains  $p_i$  points read off the chart recordings. These data are given in the supplementary material. The last point in each experiment has always reached at least 95% of  $[ClO_2]_{\infty}^{e}$ . For an overall fit of the experimental data, the concentration deviations in each of the 87 experiments are divided by  $[ClO_2]_{max}^{e}$  and then averaged. The average of this deviation over all the experiments is used to compare the results of the calculations based on the various models we consider.

Three different correlation coefficients<sup>22</sup> are also calculated from the elements of the matrix

$$\mathbf{B} = \mathbf{J}^{\mathrm{T}} \cdot \mathbf{J} \tag{6}$$

where J is the Jacobian used in the Gauss-Newton method and  $J^{T}$  is its transpose. The partial correlation coefficients  $r_{ij}$  give a measure of the interdependence between two calculated rate constants, assuming that the other constants have fixed values.

$$r_{ij} = -B_{ij} / (B_{ii} B_{jj})^{1/2}$$
(7)

The total correlation coefficients  $S_{ij}$  also provide a measure of the interdependence between two constants, the other constants now being regarded as fitted parameters.

$$S_{ij} = C_{ij} / (C_{ii}C_{jj})^{1/2}$$
(8)

The  $C_{ij}$  are the elements of the inverse matrix  $\mathbf{C} = \mathbf{B}^{-1}$ .

The multiple correlation coefficients  $R_i$  measure the independence of the *i*th rate constant from the others.

$$R_i = \{1 - 1 / (B_{ii}C_{ii})\}^{1/2}$$
(9)

Mechanistic Considerations. It has long been established that the rate law given in eq 2 results from a mechanism in which reaction 10 is the rate-determining step. As the pK of HClO<sub>2</sub>

$$HOCl + HClO_2 = Cl_2O_2 + H_2O$$
 (10)

is about 2.0, the protonation of chlorite ion may be regarded as

TABLE II: Mechanistic Steps Considered To Explain the Experimental Results

$ClO_2^- + HOCl + H^+ \rightarrow Cl_2O_2 + H_2O$
$2Cl_2O_2 \rightarrow 2ClO_2 + Cl_2$
$Cl_2O_2 + ClO_2 \rightarrow 2ClO_2 + Cl^2$
$2HOCI + ClO_2^- \rightarrow ClO_3^- + Cl_2 + H_2O$
$ClO_2^- + Cl_2 \rightarrow Cl_2O_2 + Cl^-$
$Cl_2O_2 + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+$
$Cl_2 + H_2O \Rightarrow HOCl + Cl^- + H^+$

a preequilibrium. Thus the protonation and the above elementary step together explain the third-order kinetics of eq 2. The earlier experimental finding that mostly chlorate is formed in dilute solution, while  $ClO_2$  is the predominant product in more concentrated solution, was explained by the further reactions of the reactive intermediate<sup>12</sup>

$$2CI_2O_2 = 2CIO_2 + CI_2$$
(11)

$$H_2O + Cl_2O_2 = ClO_3^- + Cl^- + 2H^+$$
 (12)

The  $Cl_2$  formed in step 11 may either hydrolyze to give back HOCl, or it may react with  $ClO_2^-$  to produce  $ClO_2$  and  $Cl^-$ . Which further reaction of  $Cl_2$  takes place has no influence on the kinetics and stoichiometry so long as reaction 10 is the rate-determining step.

Another explanation for the concentration dependence of the  $ClO_2$  production is that the hydrolysis of  $Cl_2O_2$  competes with the elementary step 13 instead of with reaction 11. An argument

$$Cl_2O_2 + ClO_2^- = 2ClO_2 + Cl^-$$
 (13)

in favor of this process is that the encounter of a reactive intermediate with one of the reactants is much more probable than the encounter of two molecules of the intermediate.

Our experiments prove that reaction 10 cannot be regarded as the sole rate-determining step in excess HOCl. To explain the observations that the reaction order is greater than 1 in HOCl and less than 1 in  $H^+$ , we suggest that the following process plays an important role:

$$2HOC1 + CIO_2^{-} = CIO_3^{-} + CI_2 + H_2O$$
(14)

This reaction is not an elementary step but may be regarded as occurring via a preequilibrium between  $ClO_2^-$  and HOCl forming a hydrogen-bonded intermediate.

Another possibility is that HOCl might play the role of  $H^+$  in reaction 10, resulting in the following reaction:

$$2HOCI + CIO_2^{-} = CI_2O_2 + H_2O + OCI^{-}$$
(15)

However, reaction 15 cannot explain the decrease in  $[ClO_2]$  that results from increasing [HOCI], which is illustrated in Figure 4. To account for this feature, we must include the increase in the production of chlorate at the expense of  $ClO_2$ , as in eq 14. Similarly, the formation of chlorate ion by a simple nucleophilic displacement

$$HOC1 + C1O_2^- = C1^- + C1O_3^- + H^+$$

would imply that at a given pH the ratio of  $ClO_2$  to  $ClO_3^-$  would be constant, which would contradict our experimental findings (see Figure 2).

The mechanistic steps considered for analysis by the leastsquares treatment are summarized in Table II. The reaction numbers assigned in that table will be used throughout the discussion that follows.

The rate constants for reaction C7 are known from previous studies.<sup>24-26</sup> The values<sup>24</sup>  $k_7 = 11$  s<sup>-1</sup> and  $k_{-7} = 1.8 \times 10^4$  M<sup>-2</sup> s<sup>-1</sup> were used throughout the calculations.

As reaction C3 seemed to be more realistic than reaction C2, step C2 was omitted in the first set of calculations. With the remaining five steps included in the model, complete correlation

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was found between reactions C3 and C6, and the system of linear equations used in the Gauss-Newton procedure became ill-conditioned. If either  $k_3$  or  $k_6$  was kept at a constant value, however, the other constant could be calculated. This behavior of the equations is the manifestation of the fact that  $Cl_2O_2$  is a reactive intermediate, and only the ratio of the rates of its two pathways can be calculated.

If we apply the steady-state approximation to  $Cl_2$  and  $Cl_2O_2$ , the following simplified differential equations can be derived for the system:

$$\frac{d[CIO_2]}{dt} = \frac{2k_3'B}{1+k_3'B} \left( k_1 ABH + \frac{k_4 k_5' A^2 B^2}{1+k_5' B} \right)$$
(16)

$$\frac{d[HOC1]}{dt} = -k_1 ABH - k_4 A^2 B \frac{1 + 2k_5' B}{1 + k_5' B}$$
(17)

$$\frac{d[ClO_2^{-}]}{dt} = -k_1 ABH \frac{1 + 2k_3'B}{1 + k_3'B} - k_4 A^2 B \left( 1 + \frac{k_5'B}{1 + k_5'B} \left\{ 1 + \frac{k_3'B}{1 + k_5'B} \right\} \right) (18)$$

where  $A = [HOC1], B = [ClO_2^-], H = [H^+], k_3' = k_3/k_6, k_5' = k_5/k_7$ .

If the approximate eqs 16–18 are used instead of the full set of rate equations derived from the mechanistic steps in Table II, the average deviations are unchanged to the four significant figures. The calculations yield the following results:

$$k_{1} = (1.12 \pm 0.01) \times 10^{6} \text{ M}^{-2} \text{ s}^{-1} [0.65]$$

$$k_{3}' = (5.4 \pm 0.2) \times 10^{4} \text{ M}^{-1} [0.88]$$

$$k_{4} = (2.1 \pm 0.1) \times 10^{3} \text{ M}^{-2} \text{ s}^{-1} [0.68]$$

$$k_{5}' = (3.7 \pm 0.2) \times 10^{3} \text{ M}^{-1} [0.84]$$

The numbers in brackets are the total correlation coefficients. All of the pairwise coefficients were found to be smaller than these. The average deviation was 3.46%. Comparison of replicate experiments shows that the reproducibility of the individual curves is about 1-3%. Thus this average deviation can be regarded as satisfactory. There is no firm experimental basis for further refinement of the model.

The question arises, however, if all of the four parameters are necessary for the description of the experimental data. Steps C1 and C4 must evidently be retained in order to obtain the observed stoichiometry. Excluding processes C5 and C7 cannot be justified either, since both of these steps have been independently studied by many workers, and their rate constants are well-known.

If  $k_3'$  can be eliminated, we must have  $v_3 \gg v_6$  over the whole concentration range; i.e.,  $ClO_3^-$  is formed only through process C4 and not by the spontaneous hydrolysis of  $Cl_2O_2$ . In this case the following simplified mechanism would be valid:

HOCI + 
$$2CIO_2^-$$
 + H<sup>+</sup>  $\rightarrow$   $2CIO_2$  + H<sub>2</sub>O + Cl<sup>-</sup>  
 $v_1 = k_1[HOCI][CIO_2^-][H^+]$ 

 $2\text{HOCl} + \text{ClO}_2^- \rightarrow \text{ClO}_3^- + \text{Cl}_2 + \text{H}_2\text{O} \qquad v_4 = k_4[\text{HOCl}]^2[\text{ClO}_2^-]$  $2\text{ClO}_2^- + \text{Cl}_2 \rightarrow 2\text{ClO}_2 + 2\text{Cl}^- \qquad v_5 = k_5[\text{ClO}_2^-][\text{Cl}_2]$ 

$$Cl_2 + H_2O = HOCl + Cl^- + H^+$$
  $(k_7 = 11 \text{ s}^{-1}; k_{-7} = 1.8 \times 10^4 \text{ M}^{-2} \text{ s}^{-1})$ 

The average deviation of the best fit with this simplified model is 5.1%, and the deviation is systematically greater in HOCl excess. The parameters calculated  $(k_1 = 1.06 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}; k_4 = 3250 \text{ M}^{-2} \text{ s}^{-1}; k_5' = 2200 \text{ M}^{-1})$  are relatively close to those calculated with the four-parameter model. Because the increase in the deviation is not random, but occurs primarily in the curves in excess HOCl (and at higher pH), we conclude that exclusion of the spontaneous hydrolysis of Cl<sub>2</sub>O<sub>2</sub> from the model is not justified.

We also considered whether process C3 can be replaced (at least in part) by process C2. With step C2 instead of (C3) in the model, the best fit achieved was 4.2%, which is almost satisfactory. The calculations, however, reveal the following:

There is complete correlation between  $k_2$  and  $k_6$ ;  $k_2$  can be calculated only if  $k_6$  is fixed.

The ratio of  $k_2$  to  $k_6$  is  $6 \times 10^9$ . Thus if we assume a realistic  $1-10 \text{ s}^{-1}$  rate constant for process C6,  $k_2$  would be essentially at the diffusion-controlled limit for a second-order process. Although Cl<sub>2</sub>O<sub>2</sub> is extremely reactive, it is difficult to see how such a complex reaction could occur with such a high rate.

If we keep both processes C2 and C3 in the model, then computational difficulties arise. It becomes necessary to fix both  $k_7$ and  $k_2$  in order to calculate  $k_3$ . With  $k_7 = 10 \text{ s}^{-1}$ , and  $k_2$  assigned a variety of constant values, we are able to obtain a better fit than 3.46% on minimizing with respect to  $k_3$  only if we assign a negative value to  $k_2$ . We conclude that process C2 does not have a significant effect on the mechanism under our conditions.

# Conclusion

Our results demonstrate convincingly that step C1 is not the only rate-determining step in the reaction of chlorite ion with hypochlorous acid. Process C4 also plays an important (though not exclusive) role in solutions containing excess HOCl. This is the only result of the present study that is in some disagreement with earlier investigations.

All of our results have been obtained in 0.5 M acetate buffer. Under our experimental conditions the ratio of  $[H^+]$  and  $[C-H_3COOH]$  is constant, so that there is no way to distinguish between general and specific acid catalysis, which may be an important factor in determining  $k_1$ .

We have also demonstrated that recent developments in the computational aspects of chemical kinetics make it possible to combine computer simulations of complex reaction mechanisms with rigorous statistical methods that have been used for many years to evaluate complex equilibrium systems. The result is a powerful tool both for assessing the merits of alternative mechanisms and for obtaining quantitative parameter estimates.

The availability of a quantitative model for the generation of ClO<sub>2</sub> in the chlorite-hypochlorous acid reaction should pave the way for mechanistic studies of several chlorite-driven oscillatory systems, including the chlorite-thiosulfate,<sup>5</sup> chlorite-thiourea,<sup>27</sup> chlorite-bromide,<sup>28</sup> and chlorite-thiocyanate<sup>28</sup> reactions.

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Registry No. ClO2\*, 14998-27-7; HOCl, 7790-92-3.

Supplementary Material Available: Tables listing sets of concentration vs time measurements (6-15 per run) for each of the 87 runs used in the data fitting (11 pages). Ordering information is given on any current masthead page.

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