Inorg. Chem. **2001,** *40,* 1833−1836 **1833**

Kinetics and Mechanism of Catalytic Decomposition and Oxidation of Chlorine Dioxide by the Hypochlorite Ion

Viktor Csordás,[†] Bernie Bubnis,[‡] István Fábián,*[,†] and Gilbert Gordon[§]

Department of Inorganic and Analytical Chemistry, University of Debrecen, P.O.B. 21,
Debrecen H-4010, Hungary, Novatek, A Division of EBB, Inc., Oxford, Ohio, and
Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio

Received October 4, 2000

The oxidation of ClO_2 by $OCl^-$is first order with respect to both reactants in the neutral to alkaline pH range: $-d[ClO_2]/dt = 2k_{OCl}[ClO_2][OCl^-]$. The rate constant ($T = 298$ K, $\mu = 1.0$ M $NaClO_4$) and activation parameters are $k_{OCl} = 0.91 \pm 0.02$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 66.5 \pm 0.9$ kJ/mol, and $\Delta S^{\ddagger} = -22.3 \pm 2.9$ J/(mol K). In alkaline solution, pH > 9, the primary products of the reaction are the chlorite and chlorate ions and consumption of the hypochlorite ion is not observed. The hypochlorite ion is consumed in increasing amounts, and the production of the chlorite ion ceases when the pH is decreased. The stoichiometry is kinetically controlled, and the reactants/products ratios are determined by the relative rates of the production and consumption of the chlorite ion in the ClO_2/OCl^- and $HOCl/ClO_2^-$ reactions, respectively.

Introduction

The reactions between oxychlorine species are very sensitive to the conditions applied and exhibit a very rich and complex redox chemistry. As a consequence, chlorine may be stabilized in different oxidation states, depending on the absolute and relative reactant concentrations, pH, temperature, etc. Chlorine dioxide quantitatively decomposes into the chlorite and chlorate ions in alkaline solution, but it is reasonably stable in acidic aqueous solutions.[1] The stability of the hypochlorite ion[2] is also pH-dependent. The overall third-order rate of decomposition goes through a maximum at pH 7.10 (25 °C) and produces Cl^- and ClO_3^- in a 2:1 ratio.[3]

Under acidic conditions, ClO_2 was reported as a final product in the $HOCl-ClO_2^-$ reaction,[4−9] acid and metal ion catalyzed decomposition of chlorite ion and related systems.[10−19] This implies that redox side reactions do not occur between chlorine dioxide and other oxychlorine species. Deviations from this general pattern were reported only in a few cases. The reaction between the hypochlorite ion and chlorine dioxide was studied earlier,[20] and it was proposed recently that a direct redox reaction may occur between chlorine dioxide and the chlorite ion coordinated to mercury(II) in the $Hg(II)-ClO_2^--ClO_2$ system.[18]

The formation and subsequent decay of small amounts of ClO_2 were found in the reaction of HOCl with ClO_2^- at pH 8.82, but a detailed interpretation of these observations was not given.[21] It was concluded that the slow loss of chlorine dioxide could be caused either by impurities or by a reaction with HOCl. According to our preliminary studies, the transient concentration of chlorine dioxide can be increased and systematically varied by selecting appropriate experimental conditions. When OCl^- is in excess over ClO_2^-, the decay of ClO_2 is orders of magnitude faster than the base-catalyzed disproportionation of ClO_2.[1] In agreement with previous reports, this is a further piece of evidence that HOCl either is involved in a direct redox reaction with chlorine dioxide or somehow catalyzes its decomposition.

Flis and co-workers reported the following rate law for the $HOCl-ClO_2$ reaction:[20]

$$-\frac{d[ClO_2]}{dt} = k_I[ClO_2][HOCl] + k_{II}[ClO_2] \qquad (1)$$

This study was limited to relatively narrow concentration and pH ranges, and the constraints of the applicability of the rate law were not given. It was proposed that the second term in eq 1 corresponds to the decomposition of chlorine dioxide into Cl_2 and O_2. While this reaction is one of the possible fragmentation

---

* To whom correspondence should be addressed.Phone: +36 52 512-900, extension 2378. Fax: +36 52 489 667. E-mail: ifabian@delfin.klte.hu.
[†] University of Debrecen.
[‡] Novatek, A Division of EBB, Inc.
[§] Miami University.

(1) Gordon, G.; Kieffer, R. G.; Rosenblatt, D. H. *Prog. Inorg. Chem.* **1972**, *15*, 201.
(2) The hypochlorite ion and hypochlorous acid are in fast protolytic equilibrium, and their concentration ratio is determined by the pH. In this paper, the two species will not be distinguished unless it is required by the clarity of presentation.
(3) Adam, L. C.; Fábián, I.; Suzuki, G.; Gordon, G. *Inorg. Chem.* **1992**, *31*, 3534.
(4) Taube, H.; Dodgen, H. *J. Am. Chem. Soc.* **1949**, *71*, 3330.
(5) Tang, T. F.; Gordon, G. *Environ. Sci. Technol.* **1984**, *18*, 212.
(6) Emmenegger, F.; Gordon, G. *Inorg. Chem.* **1967**, *6*, 633.
(7) Aieta, E. M.; Roberts, P. V. *Environ. Sci. Technol.* **1986**, *20*, 50.
(8) Peintler, G.; Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 2954.
(9) Jia, Z.; Margerum, D. W.; Francisco, J. S. *Inorg. Chem.* **2000**, *39*, 2614.
(10) Launer, H. F.; Tomimatsu, Y. *J. Am. Chem. Soc.* **1954**, *76*, 2591.
(11) Launer, H. F.; Wilson, W. K.; Flynn, J. H. *J. Res. Natl. Bur. Stand.* **1953**, *51*, 237.
(12) Gordon, G.; Feldman, F. *Inorg. Chem.* **1964**, *3*, 1728.
(13) Kieffer, R. G.; Gordon, G. *Inorg. Chem.* **1968**, *7*, 235.
(14) Schmitz, G.; Rooze, H. *Can. J. Chem.* **1981**, *59*, 1177.
(15) Schmitz, H.; Rooze, H. *Can. J. Chem.* **1985**, *63*, 975.
(16) Fábián, I.; Gordon, G. *Inorg. Chem.* **1991**, *30*, 3994.
(17) Fábián, I.; Gordon, G. *Inorg. Chem.* **1992**, *31*, 2144.
(18) Fábián, I.; Szűcs, D.; Gordon, G. *J. Phys. Chem. A* **2000**, *104*, 8045.
(19) Tóth, Z.; Fábián, I. *Inorg. Chem.* **2000**, *39*, 4608.
(20) Flis, I. E.; Mischenko, K. P.; Salnis, K. U. *Russ. Appl. Chem.* **1959**, *32*, 284.
(21) Gordon, G.; Tachiyashiki, S. *Environ. Sci. Technol.* **1991**, *25*, 468.

10.1021/ic001106y CCC: $20.00

channels in condensed-phase photolysis of chlorine dioxide,[22−29] it does not seem to be feasible in the thermally induced decomposition. In support of this statement, it should be remembered that slightly acidic solutions of chlorine dioxide can be stored in the dark without apparent concentration loss for several months.

In the present paper we report a pH- and temperature-dependent kinetic study on the hypochlorite ion−chlorine dioxide reaction. Our goal is to explore the exact kinetic role of the hypochlorite ion in the decay of ClO_2. The results are also expected to contribute to a better understanding of the mechanism of the $HOCl-ClO_2^-$ reaction and other reactive systems in which HOCl and ClO_2 are present simultaneously.

Experimental Section

Chemicals. Sodium hypochlorite stock solutions were prepared as described earlier.[3,8] Chlorine dioxide was generated by mixing aqueous solutions of potassium persulfate and sodium chlorite.[30] The product ClO_2 was passed into cold, dilute $HClO_4$ solution ($\sim 10^{-4}$ M) with a steady stream of nitrogen gas. Stock solutions of NaOCl and ClO_2 were stored at 5 °C in the dark and were standardized by iodometric titration before use.[31] To minimize loss to vaporization, ClO_2 stock solutions were kept in and dispensed from a shrinking bottle.[19,32] All other reagents were of reagent grade quality and used without further purification. Samples were prepared using doubly deionized and ultrafiltered or deionized and triply distilled water obtained from MILLI-Q RG (Millipore) or Barnstead/NANOpur water purification systems, respectively. With the exception of the temperature-dependent studies, the kinetic measurements were made at 25 ± 0.1 °C and 1.0 M ionic strength set with $NaClO_4$ prepared from perchloric acid and Na_2CO_3. The pH was adjusted with phosphate or carbonate buffers.

Instrumentation and Methods. Iodometric titrations and pH measurements were made with a Metrohm 721 NET Titrino system equipped with Metrohm 6.0420.100 combined platinum and with Metrohm 6.0202.000 combined glass electrodes, respectively. The pH was measured within ±0.003 unit, and it is defined as $-\log[H^+]$ in this paper.

In the stoichiometric experiments, a ClO_2 stock solution was added to a solution of HOCl and buffer in an all-glass, stoppered vessel. The hypochlorite ion was used at least in 2 times excess in these experiments. The reactor was tightly sealed immediately after introducing ClO_2. The experiments were designed such that the headspace above the reaction mixture was always less than 1−2% of the total volume. The reactants were thoroughly mixed with a Teflon stirring bar. The spent reaction mixtures were analyzed typically 2 h after the reaction was triggered. Within this time frame ClO_2 was completely consumed even in the slowest kinetic runs and subsequent reactions of the excess HOCl were negligible.

An aliquot of the reaction mixture was diluted and treated with excess ethylenediamine in order to remove OCl^-.[33,34] The sample was analyzed for ClO_2^- and ClO_3^- by ion chromatography. Another aliquot was acidified to pH 2.0 with 0.5 M H_2SO_4. After addition of excess KI to the sample, the iodine formed was titrated with standardized sodium thiosulfate solution. Under such conditions, ClO_3^- does not react with I^- while HOCl and ClO_2^- generate 2 and 4 equiv of iodine, respectively. The concentration of the unreacted hypochlorite ion was calculated by combining the chromatographic and iodometric data. The concentration of Cl^- was calculated from the mass balance for the chlorine species.

Table 1. Stoichiometric Data for the Chlorine Dioxide−Hypochlorite Ion Reaction[a]

pH	$10^4 \times [ClO_2]_0$ (M)	$\Delta[ClO^-]/[ClO_2]_0$	$[ClO_2^-]/[ClO_2]_0$	$[ClO_3^-]/[ClO_2]_0$
6.34	9.20	0.44	0.04	0.93
6.36	9.20	0.44	0.05	0.92
6.51	3.10		0.03	0.95
6.94	3.10		0.00	0.98
7.25	9.03	0.46	−0.01	0.96
7.26	9.03	0.45	−0.01	0.96
7.35	3.10		0.00	0.99
7.43	9.20	0.49	0.01	0.98
7.45	9.20	0.50	0.01	0.98
7.85	9.20	0.45	0.07	0.91
7.85	9.20	0.44	0.06	0.93
7.86	5.78	0.48	0.08	0.93
8.21	5.78	0.23	0.29	0.70
8.32	3.10		0.30	0.66
8.69	5.78	0.01	0.47	0.52
8.98	9.20	−0.03	0.48	0.50
8.99	9.20	−0.03	0.48	0.49
9.05	5.78	0.02	0.50	0.50
9.42	5.78	−0.08	0.50	0.49
9.95	9.20	0.00	0.49	0.49
10.23	3.10		0.49	0.49
10.49	3.10		0.50	0.49

[a] $[HOCl] = 2.00 \times 10^{-3}$ M. The concentrations of the individual components were determined with an error less than ±3%.

Ion chromatograms were recorded on a Dionex 100DX ion chromatograph equipped with AS9-HC analytical and AG9-HC guard columns and using a conductivity detector. The eluent was 0.7 g/dm^3 Na_2CO_3. To avoid overloading of the analytical column, the ionic strength was lowered to 0.1 M in these experiments.

Stock solutions of the reagents were analyzed by using the same procedures. In these experiments, ClO_2 was purged from the samples with nitrogen gas prior to analysis. The concentrations of the chlorite and chlorate ions were less than 0.5% of the total chlorine in the ClO_2 and OCl^- solutions.

Time-resolved spectra were recorded on a HP-8543 diode array spectrophotometer equipped with an Applied Photophysics RX-2000 rapid kinetics accessory. In agreement with a recent report,[35] the light intensity of the spectrophotometer was found to be strong enough to initiate photochemical decomposition of ClO_2. Such a reaction was not observed when the high-energy UV region of the light beam (<300 nm) was blocked out by inserting a polystyrene cutoff filter between the light source and the sample. Kinetic traces at different wavelengths were consistent with a simple first-order process when OCl^- was applied in large excess over chlorine dioxide. The pseudo-first-order rate constants, which were reproducible within 2%, were determined from kinetic traces at 360 nm. The temperature dependence of the rate constants was studied from 15 to 70 °C. Data fitting was made with the program package SCIENTIST using nonlinear least-squares routines.[36]

Results and Discussion

Stoichiometry. As shown in Table 1, a definite trend was observed in the stoichiometry of the ClO_2/OCl^- reaction as a function of pH. At low pH, the data confirmed earlier results and the main products were Cl^- and ClO_3^-:

---

(22) Mialocq, J. C.; Barat, F.; Gilles, L.; Hickel, B.; Lesigne, B. *J. Phys. Chem.* **1973**, *77*, 742.
(23) Dunn, R. C.; Anderson, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 5307.
(24) Chang, Y. J.; Simon, J. D. *J. Phys. Chem.* **1996**, *100*, 6406.
(25) Pursell, C. J.; Conyers, J.; Denison, C. *J. Phys. Chem.* **1996**, *100*, 15450.
(26) Thørgensen, J.; Jepsen, P. U.; Thomsen, C. L.; Poulsen, J. A.; Byberg, J. R.; Keiding, S. R. *J. Phys. Chem.* **1997**, *101*, 3317.
(27) Esposito, A. P.; Foster, C. E.; Beckman, R. A.; Reid, P. J. *J. Phys. Chem.* **1997**, *101*, 5309.
(28) Foster, C. E.; Reid, P. J. *J. Phys. Chem. A* **1998**, *102*, 3514.
(29) Thørgensen, J.; Thomsen, C. L.; Poulsen, J. A.; Keiding, S. R. *J. Phys. Chem. A* **1998**, *102*, 4186.
(30) Rosenblatt, D. H.; Hayes, A. J. *J. Org. Chem.* **1963**, *28*, 2790.
(31) Vogel, A. I. *Quantitative Inorganic Analysis,* 3rd ed.; Longman: London, 1961.
(32) Silverman, R. A.; Gordon, G. *Anal. Chem.* **1974**, *46*, 178.
(33) Bolyard, M.; Fair, P. S.; Hautman, D. P. *Environ. Sci. Technol.* **1992**, *26*, 1663.
(34) Adam, L. C.; Gordon, G. *Anal. Chem.* **1995**, *67*, 535.
(35) Stanbury, D. M.; Figlar, J. N. *Coord. Chem. Rev.* **1999**, *187*, 223.
(36) *SCIENTIST*, version 2.0; Micromath Software: Salt Lake City, UT, 1995.

$$\mathrm{HOCl + 2ClO_2 + H_2O = 2\,ClO_3^- + Cl^- + 3H^+} \qquad (2)$$

When the pH was increased, ClO_2^- was formed in increasing amounts at the expense of Cl^- formation. At the same time, the consumption of OCl^- and the $[ClO_3^-]_{produced}/[ClO2]_{consumed}$ concentration ratio decreased. Above pH 9.0, the stoichiometry corresponded to the disproportionation of chlorine dioxide and could be approximated by the following equation:

$$\mathrm{2ClO_2 + 2OH^- = ClO_2^- + ClO_3^- + H_2O} \qquad (3)$$

The stoichiometry could be given by the linear combination of eqs 2 and 3 at any intermediate pH.

While reaction 3 properly describes the stoichiometry of the ClO_2/OCl^- reaction in the alkaline pH range, it represents only an intermediate stage whenever OCl^- and ClO_2^- are present simultaneously in the reaction mixture. The kinetics and stoichiometry of the reaction between these two species have been extensively studied.[4−9] In alkaline solution it is a slow process that produces ClO_3^- and Cl^- as final products. It follows that the unreacted OCl^- would eventually remove the chlorite ion produced in reaction 3 and the same stoichiometry would prevail in the entire pH region.

Kinetics. The first-order decay of chlorine dioxide at large excess of HOCl over ClO_2 and the linear dependence of the pseudo-first-order rate constant on the total concentration of the hypochlorite ion confirm that the reaction is first order in both reactants:

$$-\frac{\mathrm{d}[\mathrm{ClO_2}]}{\mathrm{d}t} = k[\mathrm{ClO_2}][\mathrm{OCl^-}]_{\mathrm{tot}} \qquad (4)$$

Thorough analysis of the kinetic traces gave no evidence of a second term in the rate law as suggested by eq 1. This strongly suggests that the first-order loss of chlorine dioxide reported by Flis and co-workers[20] was probably caused by some sort of artifact in their experiments. At the high chlorine dioxide concentrations used in that work, slow volatilization of ClO_2 from the reaction vessel could possibly corrupt the data. It was also confirmed in control experiments that the ClO_2/OCl^- reaction was much faster than the decomposition of chlorine dioxide with base over the entire pH region studied. Under alkaline conditions (pH > 9.0), the hypochlorite ion was not consumed (see eq 3) and the reaction could be formally treated as an OCl^--catalyzed decomposition of chlorine dioxide.

The pH dependence of k_{obs} is shown in Figure 1. The characteristic sigmoid shape can readily be associated with the acid−base equilibrium between HOCl and OCl^-. Apparently, chlorine dioxide is oxidized much more quickly by the hypochlorite ion than by the hypochlorous acid. Considering that the acid−base reaction is a fast preequilibrium and taking into account the stoichiometry of the reaction, k_{obs} can be expressed as follows:

$$k_{\mathrm{obs}} = 2\left(\frac{k_{\mathrm{OCl}}}{1 + K_{\mathrm{p}}[\mathrm{H^+}]} + \frac{k_{\mathrm{HOCl}}K_{\mathrm{p}}[\mathrm{H^+}]}{1 + K_{\mathrm{p}}[\mathrm{H^+}]}\right)[\mathrm{OCl^-}]_{\mathrm{tot}} \qquad (5)$$

where K_p, k_{OCl}, and k_{HOCl} are the protonation constant of the hypochlorite ion and the rate constants for the reactions of OCl^- and HOCl, respectively.

Fitting of k_{obs} on the basis of eq 5 gave the following results: $\log K_P = 7.40 \pm 0.02$, $k_{OCl} = 0.91 \pm 0.02$ M^{-1} s^{-1}, and $k_{HOCl} = (1.5 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1}. The value for the protonation constant of OCl^- is the same as the value that was reported on the basis of an independent study before.[3] The HOCl path has a marginal contribution to the reaction, and the fitted value for k_{OCl} practically did not change when the second term was neglected in eq 5.

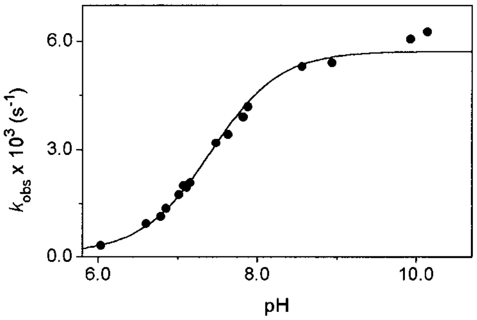

Figure 1. Experimental (●) and fitted on the basis of eq 5 (solid line) pseudo-first-order rate constants, k_{obs}, as a function of pH. $[OCl^-] = 3.13 \times 10^{-3}$ M, $T = 298$ K, $\mu = 1.0$ M $NaClO_4$.

Temperature-dependent data at pH 8.0 were evaluated by considering only the k_{OCl} term in eq 5 and using earlier reported thermodynamic data for the temperature dependence of K_p. The activation parameters were calculated by fitting k_{OCl} on the basis of

$$k_{\mathrm{OCl}} = \frac{kT}{h}\,\mathrm{e}^{\Delta S^{\ddagger}/R}\,\mathrm{e}^{-\Delta H^{\ddagger}/(RT)} \qquad (6)$$

The results are $\Delta H^{\ddagger} = 66.5 \pm 0.9$ kJ/mol and $\Delta S^{\ddagger} = -22.3 \pm 2.9$ J/(mol K).

Mechanism. The unique feature of the ClO_2/OCl^- reaction is that the distinct pH dependence of the stoichiometry is not associated with any change in the rate law as a function of pH. The pseudo-first-order rate constant is strictly proportional to $[OCl^-]$ in the entire pH region, and the corresponding pH profile exhibits an inflection point at the $\log K_p$ of HOCl (pH = 7.40). At the same time, the changeover between the limiting stoichiometries (eqs 2 and 3) occurs in a narrow pH range at around pH 8.1. These features imply that the same initial step is operative regardless of the actual pH and that the stoichiometry is controlled by the rates of subsequent competing reaction steps. In accordance with these considerations, we propose the following mechanism for the interpretation of the results:

$$\mathrm{OCl^- + H^+ = HOCl} \qquad \text{fast equilibrium} \qquad (R7)$$

$$\mathrm{ClO_2 + OCl^- = Cl_2O_3^-} \qquad \text{rate determining} \qquad (R8)$$

$$\mathrm{Cl_2O_3^- + ClO_2 = Cl_2O_3 + ClO_2^-} \qquad (R9)$$

$$\mathrm{Cl_2O_3 + OH^- = HOCl + ClO_3^-} \qquad (R10a)$$

or

$$\mathrm{Cl_2O_3 + H_2O = HOCl + ClO_3^- + H^+} \qquad (R10b)$$

$$\mathrm{ClO_2^- + H^+ = HClO_2} \qquad \text{fast equilibrium} \qquad (R11)$$

$$\mathrm{HOCl + HClO_2 = Cl_2O_2 + H_2O} \qquad (R12)$$

$$\mathrm{Cl_2O_2 + H_2O = ClO_3^- + Cl^- + 2H^+} \qquad (R13)$$

The formation of the $Cl_2O_3^-$ intermediate in the rate-determining step is consistent with the simple second-order rate law, and steps R7−R10 are sufficient to explain the stoichiometry in alkaline solution. The reaction of ClO_2 with HOCl, if it occurs at all, is also expected to generate $Cl_2O_3^-$ via the formation of HCl_2O_3. In this case, an immediate proton loss should follow the rate-determining step.

A simple one-electron-transfer step between the reactants would be an alternative of step R8, but this possibility can be rejected on the basis of the following arguments. The primary products of the electron transfer would be ClO_2^- and ClO. According to earlier studies, ClO is a strong oxidant that would immediately react with ClO_2^- (and excess ClO_2) to form the chlorate and chloride ions.[18,37] However, in this case the chlorite ion would not be stable even at high pH and the mechanism would contradict experimental observations. Furthermore, there is no reason to assume that the oxidation of ClO_2 to ClO_3^- and the reduction of OCl^- to Cl^- in less alkaline solution would occur via respective lower and higher oxidation state intermediate chlorine species. It should be added that very recently it was incorrectly proposed that ClO is capable of reducing ClO_2 to the chlorite ion.[38] Were this reaction step operative, it would predict a very different stoichiometry than was observed experimentally.

A relatively small negative entropy of activation was found for the initial step. It is unlikely that solvation effects have significant contribution to the activation parameters, and $\Delta S^\ddagger$ is consistent with a weak association between the reactants in the precursor complex. This interaction probably occurs between the negatively charged oxygen atom of OCl^- and the partially positive chlorine atom of ClO_2, implying Cl−O−Cl connectivity for the $Cl_2O_3^-$ intermediate.

According to the mechanism, the chlorite ion is produced in the reaction of $Cl_2O_3^-$ with a second molecule of ClO_2 (step R9). This step is followed by the regeneration of OCl^- and the formation of ClO_3^-. Step R10 is very fast, and with respect to the rate law and overall stoichiometry, it is irrelevant whether it occurs with a solvent molecule or with the hydroxide ion. The two transient species $Cl_2O_3^-$ and Cl_2O_3 are presumably formed in extremely low steady-state concentrations, and direct experimental evidence is not available to confirm their existence. However, our conclusions are corroborated by earlier kinetic studies, which postulated the formation of very similar reactive intermediates in the reactions of oxyhalogen species.[1,3,9,39−43]

The consumption of the chlorite ion is interpreted in terms of the $HOCl/ClO_2^-$ reaction (steps R11−R13). There seems to be a consensus in the literature that this reaction proceeds via the Cl_2O_2 intermediate and produces only ClO_3^- in excess HOCl.[4−9,21] The mechanism postulated here assumes that the stoichiometry of the ClO_2/OCl^- reaction is determined by the interplay of the two reaction paths leading to the formation and consumption of the chlorite ion. The former path is relatively fast in alkaline solution. This, coupled with the slow decay of the chlorite ion, makes possible the accumulation of ClO_2^-.

The rate of the initial step, R2, swiftly decreases as OCl^- is converted to HOCl by decreasing the pH (step R1). In contrast, the rate of the $HOCl/ClO_2^-$ reaction is proportional to $[H^+]^2$ in the alkaline pH range and increases by about 6 orders of magnitude when the pH is decreased from 10.0 to 6.0.[21] Thus, the chlorite ion becomes a reactive intermediate at low pH and it is completely consumed by the end of the ClO_2/OCl^- reaction. The opposite pH dependencies of the two kinetically coupled reaction paths also explain the sharp changeover in the stoichiometry as a function of pH.

In conlusion, the results presented here confirm that the immediate products of the chlorine dioxide−hypochlorite ion reaction are ClO_3^- and ClO_2^-. When OCl^- is used in excess, the chlorite ion is involved in subsequent reactions and the lifetime and transient concentration of this species are kinetically controlled by the competing reaction paths. Perhaps the most important implication of the results is that chlorine dioxide and the hypochlorite ion cannot coexist in aqueous solution for an extended period of time in the neutral to alkaline pH range, and the reaction between these species may explain the enhanced decomposition rate of chlorine dioxide in related systems. The results also imply that under neutral conditions the chlorine dioxide−hypochlorite ion reaction is competitive with the formation of chlorine dioxide in the hypochlorous acid−chlorite ion reaction. Thus, the corresponding mechanism must include the ClO_2/OCl^- path for proper interpretation of the noted decay of ClO_2 in that system.

Acknowledgment. This work was supported by NATO Linkage Grant CRG.LG 973337 and by Grants OTKA T 029568 and M 028244 from the Hungarian National Research Foundation.

Supporting Information Available: Two tables of observed rate constants as a function of OCl^- and ClO_2 concentrations, pH, and temperature and a plot of observed rate constants as a function of $[OCl^-]$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001106Y

---

(37) Buxton, G. V.; Subhani, M. S. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 947.

(38) Horváth, A. K.; Dolnik, M.; Zhabotinsky, A. M.; Epstein, I. R. *J. Phys. Chem. A* **2000**, *104*, 5766.

(39) Beach, M. W.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 1225.

(40) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 1942.

(41) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 2135.

(42) Fábián, I.; van Eldik, R. *Int. J. Chem. Kinet.* **1995**, *27*, 491−498.

(43) Fábián, I.; Gordon, G. *Inorg. Chem.* **1997**, *36*, 2494.