solid by adhering liquid solution. That this contamination is not due to a solid solution is shown by the fact that equal or larger amounts of HCl and H_2SO_4 are found with the solid phases although these solutes yield normal K_f values (Table I).

The inescapable conclusion of the results of this work is that nitric acid does indeed exist in dimeric form in eutectic perchloric acid[1] at least in the experimental range investigated (temperature around −60° and molalities of 0.02-0.03). Two questions remain unanswered. (a) What is the structure of the nitric acid dimer? (b) Does it exist in solution at higher temperatures? Results of Raman and uv spectra indicate that new species of nitric acid appear in eutectic perchloric acid solutions which are not found in aqueous or perchlorate-salt solutions. However, these spectra were taken at room temperature and the spectral changes observed may be due to monomeric species formed in the eutectic solution at room temperature such as undissociated HNO_3 and do not necessarily belong to a nitric acid dimer. The dimer exists at −60° but not necessarily at room temperature. A detailed investigation of Raman spectra may reveal the structure of the species and the temperature range in which they exist. No detailed structure of the dinuclear nitric acid species can be offered at present since cryoscopic behavior cannot be used to distinguish between different structural formulas of the dimer $H_2N_2O_6$. Furthermore, it cannot distinguish between the dimer $H_2N_2O_6$ and dinuclear species such as $HN_2O_6^-$, $N_2O_6^{2-}$, etc. Even the nitric acid anhydride N_2O_5 is not ruled out by the cryoscopic data, although its existence as a solution containing 59% water by weight is highly improbable.

Registry No. $HClO_4$, 7601-90-3; $Mg(ClO_4)_2$, 10034-81-8; $Cu(ClO_4)_2$, 13770-18-8; $Zn(ClO_4)_2$, 13637-61-1; $Ni(ClO_4)_2$, 13637-71-3; $Mn(ClO_4)_2$, 13770-16-6; $Fe(ClO_4)_2$, 13933-23-8; HCl, 7647-01-0; H_2SO_4, 7664-93-9; HNO_3, 7697-37-2; $Hg_2(ClO_4)_2$, 13932-02-0.

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65201

Reduction of Bromate Ion by Chlorous Acid in Acid Perchlorate Solution

RICHARD C. THOMPSON

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The stoichiometry of the reduction of bromate ion by chlorous acid in acid perchlorate solution is $[(2-n)/4]BrO_3^- + HClO_2 = nClO_2 + (1-n)\,ClO_3^-$ provided allyl alcohol is present to scavenge a hypobromous acid intermediate. The value of n is 0.667 with large excesses of chlorous acid; otherwise it is smaller. The reaction scheme shown below is

$$BrO_3^- + HClO_2 + H^+ \overset{k_a}{=} BrO_2 + ClO_2 + H_2O$$

$$BrO_2 + HClO_2 \overset{k_b}{=} HBrO_2 + ClO_2$$

$$BrO_2 + ClO_2 + H_2O \overset{k_c}{=} HBrO_2 + ClO_3^- + H^+$$

$$HBrO_2 + HClO_2 \overset{k_d}{=} HOBr + ClO_3^- + H^+$$

proposed to accommodate the stoichiometric and kinetic data. The hydrogen ion and temperature dependence of the rate parameter k_a is presented. It was also possible to determine k_c/k_b. The results are comparable to earlier predictions for the reduction of bromate ion by bromous acid.

Introduction

Studies of the reduction of bromate ion by several weak, one-electron reducing agents have led to the conclusion that the reaction proceeds not *via* a direct interaction of the reactants but instead by the sequence

$$BrO_3^- + HBrO_2 + H^+ = 2BrO_2 + H_2O \tag{1}$$

$$BrO_2 + R + H^+ = HBrO_2 + O_x \tag{2}$$

$$2HBrO_2 = BrO_3^- + HOBr + H^+ \tag{3}$$

where R is the reducing agent and O_x its oxidized form.[1-3] An induction period is observed in these systems during which, presumably, a steady-state concentration of the bromous acid intermediate is established. A paradoxical feature is that reaction 1 accomplishes a direct, one-electron reduction of bromate ion by the weak reductant bromous acid and is postulated to not exhibit an induction period. Buxton and Dainton have published results of a radiolysis study of bromate ion in which they conclude that the reverse of reaction 1 occurs in basic solution through the intermediate formation of Br_2O_4.[4] Thus, one resolution of the paradox is that bromous acid is an unusual weak, one-electron reducing agent in that it can react directly with bromate ion in acidic solution to form Br_2O_4 which rapidly dissociates into bromine dioxide as summarized in (1). A direct study of (1) would be of interest in this context but is infeasible experimentally owing to the rapid disproportionation of bromous acid in acidic solution.[3,5] However, a related system is amenable to study if one is willing to

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(1) R. C. Thompson, *J. Amer. Chem. Soc.*, **93**, 7315 (1971).

(2) (a) R. M. Noyes, R. J. Field, and R. C. Thompson, *J. Amer. Chem. Soc.*, **93**, 7315 (1971); (b) R. J. Field, E. Koros, and R. M. Noyes, *ibid.*, **94**, 8649 (1972).

(3) G. C. Knight and R. C. Thompson, *Inorg. Chem.*, **12**, 63 (1973).

(4) G. V. Buxton and F. S. Dainton, *Proc. Roy. Soc., Ser. A*, **304**, 427 (1968).

(5) A. Massagli, A. Indelli, and F. Pergola, *Inorg. Chim. Acta*, **4**, 593 (1970).

tolerate the substitution of chlorous acid for bromous acid. The rate of disproportionation of chlorous acid is slow enough[6] to not substantially interfere with its oxidation by bromate ion. This communication presents results of a kinetic study of the bromate-chlorous acid reaction in acid perchlorate solution. An additional interest in this system is the elucidation of intermediates formed in bromate oxidations.[7-10]

Experimental Section

Reagents. Previously described sources and assays of sodium chlorite,[6] sodium bromate,[3] lithium perchlorate,[8] hypobromous acid,[8] allyl alcohol,[8] chlorine dioxide,[11] and water[3] were utilized. G. F. Smith ceric perchlorate solution was used. The molar extinction coefficients for chlorine dioxide (ϵ 1242 M^{-1} cm^{-1} at 3600 Å and ϵ 98.5 M^{-1} cm^{-1} at 2800 Å) were taken from the literature[6,11] and were determined for cerium(IV) in 2 M $HClO_4$ (ϵ 476 M^{-1} cm^{-1} at 3600 Å and 1980 M^{-1} cm^{-1} at 2800 Å). All other reactants and products either absorbed negligibly or their slight absorbance was corrected for at the wavelengths utilized.

Procedures. A Zeiss PMQ-11 spectrophotometer equipped with a thermostated (±0.1°), rapid mixing (mixing time <1 sec) sample compartment was used. The production of chlorine dioxide was monitored at 3600 Å. In some of the stoichiometric experiments it was necessary to determine the chlorous acid concentration at the conclusion of the reaction. This was determined by means of a cerium(IV) "quench" monitored at 2800 Å in which the chlorous acid was oxidized quantitatively and rapidly to chlorine dioxide.

The volatility of chlorine dioxide from the reaction solutions was negligible in the more rapid reactions at the concentrations used. Tightly stoppered cells with minimal dead volume were employed for the slower reactions.

It was necessary to determine the derivative $d[(ClO_2)/[HClO_2]_0]/dt$ in the kinetic experiments with excess bromate. This was accomplished graphically by means of a derivimeter purchased from the Gerber Scientific Co. The derivatives or rates obtained are not highly accurate but are at least reproducible (±2%).

Results and Discussion

Stoichiometry. Chlorine dioxide and chlorate ion are the oxidation products of the bromate-chlorous acid reaction. Figure 1 illustrates the type of kinetic results obtained when chlorine dioxide is monitored under conditions of stoichiometric excesses of the bromate reactant. Allyl alcohol is present in the reaction mixture to scavenge the hypobromous acid intermediate.[12] In the absence of allyl alcohol the kinetic results are much more complicated, due in part to the additional reaction between bromate ion and bromide ion (the latter is produced *via* a hypobromous acid-chlorous acid reaction if no scavenger is present).[13] Two important features of Figure 1 are (1) there is no detectable induction period in the bromate-chlorous acid reaction, and (2) the production of chlorine dioxide reaches a maximum value, followed by what we consider to be an induction period prior to the bromate-chlorine dioxide reaction.[14] The latter portion of Figure 1 obtains if chlorine dioxide is reacted with bromate ion; an induction period is observed followed by a kinetic trace superimposable over that shown under identical experimental conditions.

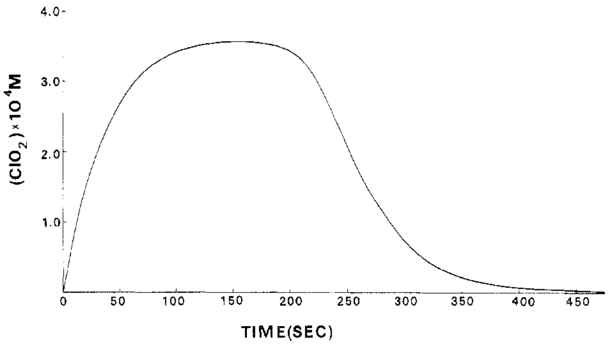

Figure 1. Chlorine dioxide concentration as a function of time in the bromate-chlorous acid reaction with excess bromate ion. Conditions were $[BrO_3^-]_0 = 5.14 \times 10^{-3}$ M, $[HClO_2]_0 = 6.91 \times 10^{-4}$ M, $[CH_2{=}CHCH_2OH]_0 = 2.71 \times 10^{-3}$ M, $[HClO_4] = 1.00$ M, and $T = 25.0°$.

The value of $R \equiv [ClO_2]_{max}/[HClO_2]_0$ was determined to be $0.48_2 \pm 0.01_3$ from 11 independent experiments (each in duplicate) conducted in 1.9 M $HClO_4$ at 25° over the range $[BrO_3^-]_0 = (1.70\text{-}7.90) \times 10^{-3}$ M, $[HClO_2]_0 = (0.65\text{-}8.56) \times 10^{-4}$ M, and $[CH_2{=}CHCH_2OH]_0 = (1.34\text{-}5.36) \times 10^{-3}$ M. There is a significant increase in the ratio as the perchloric acid concentration is lowered. For example, $R = 0.53_8$ in 0.95 M $HClO_4$ and 0.58_1 in 0.33 M $HClO_4$. R decreases slightly as the temperature is lowered over the range 25-5°. No significant influence of ionic strength on the value of R was found in the range $I = 0.19\text{-}3.20$ M.

The following type of experiment indicates that the concentration of chlorine dioxide formed is not affected by the accumulation of the allyl alcohol-hypobromous acid addition product produced during the reaction. Reaction solutions containing chlorous acid, allyl alcohol, and large excesses of bromate ion were allowed to react until no chlorine dioxide was detected. A small volume of sodium chlorite solution sufficient to regenerate the initial chlorous acid concentration in the first experiment was then injected into the spent reaction mixture. The values of R obtained were identical, and the kinetic traces in the two experiments were superimposable.

A number of experiments were performed with large excesses of chlorous acid at a hydrogen ion concentration $\geqslant 1.90$ M. A smooth production of chlorine dioxide was observed with the ratio $R' \equiv [ClO_2]_{max,cor}/[BrO_3^-]_0 = 2.00 \pm 0.06$ over the range $[HClO_2]_0 = (0.32\text{-}1.26) \times 10^{-2}$ M, $[BrO_3^-]_0 = 1.05 \times 10^{-4}$ M, $[CH_2{=}CHCH_2OH]_0 = 5.26 \times 10^{-3}$ M, and $T = 25\text{-}5°$. These studies are complicated by the concomitant production of chlorine dioxide *via* the disproportionation of chlorous acid.[6] However, the amount of chlorine dioxide produced in this side reaction is considerably less in the presence of allyl alcohol.[15] Blank experiments identical with those described above in the determination of R' except in the absence of bromate ion were performed. $[ClO_2]_{disproportionation} \equiv [ClO_2]_{disp}$ values

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[6] R. G. Kieffer and G. Gordon, *Inorg. Chem.*, 7, 239 (1968).

[7] R. C. Thompson, *Inorg. Chem.*, 10, 1892 (1971).

[8] R. C. Thompson, *Inorg. Chem.*, 8, 1891 (1969).

[9] R. H. Betts and A. N. MacKenzie, *Can. J. Chem.*, 29, 655 (1951).

[10] (a) W. C. Bray and H. A. Liebhafsky, *J. Amer. Chem. Soc.*, 57, 51 (1935); (b) M. Schlar and S. C. Reisch, *ibid.*, 58, 667 (1936); (c) C. N. Hinshelwood, *J. Chem. Soc.*, 694 (1947).

[11] R. C. Thompson, *J. Phys. Chem.*, 72, 2642 (1968).

[12] References 7, 8, and 10b demonstrate the remarkable scavenging ability of allyl alcohol for hypobromous acid. Data consistent with the formation and effective scavenging of hypobromous acid in the present system are presented in this paper (*vide infra*).

[13] We have briefly studied the reactions of hypobromous acid with chlorous acid and chlorine dioxide. The results show that hypobromous acid oxidizes chlorous acid much more rapidly than bromate ion, with a significant production of chlorine dioxide. The hypobromous acid-chlorine dioxide reaction is very slow.

[14] The plateau region in Figure 1 continues much longer if smaller excesses of bromate ion are used. The absence of any chlorous acid at the plateau was demonstrated by the cerium(IV) technique described later in the text.

[15] See E. B. Grimley, R. Buchacek, and G. Gordon, *Inorg. Chem.*, 10, 873 (1971). These authors found that phenol effectively blocks the formation of chlorine dioxide in a number of systems through the presumed scavenging of a Cl_2O_2 intermediate (which is also produced in the disproportionation of chlorous acid). Our results indicate that allyl alcohol is also an effective scavenger for this intermediate.

were measured at times corresponding to infinite times in the parent experiments. $[\mathrm{ClO_2}]_{\mathrm{max,cor}} = [\mathrm{ClO_2}]_{\mathrm{max,obsd}} - [\mathrm{ClO_2}]_{\mathrm{disp}}$ was used in the computation of R'. $[\mathrm{ClO_2}]_{\mathrm{disp}}$ never exceeded $0.15[\mathrm{ClO_2}]_{\mathrm{max,obsd}}$.

The final stoichiometry with sufficient excess chlorous acid at hydrogen ion concentrations ⩾1.9 *M* can be summarized

$$0.333\mathrm{BrO_3^-} + \mathrm{HClO_2} = 0.667\mathrm{ClO_2} + 0.333\mathrm{ClO_3^-} \quad (4)$$

With excess bromate ion, the stoichiometry at the point of maximum chlorine dioxide production (see Figure 1) can be summarized

$$[(2-n)/4]\mathrm{BrO_3^-} + \mathrm{HClO_2} = n\mathrm{ClO_2} + (1-n)\mathrm{ClO_3^-} \quad (5)$$

In 2.0 *M* perchloric acid, the value of n is 0.482 at 25°.

Both of these stoichiometric equations assume that each reacting bromate ion accepts four electrons before being scavenged by allyl alcohol. This assumption was tested experimentally. It was found that cerium(IV) reacts rapidly and quantitatively with chlorous acid to produce chlorine dioxide but reacts much more slowly with any of the other reactants or products of the bromate-chlorous acid reaction. Therefore, a solution containing 7.219×10^{-4} *M* $[\mathrm{HClO_2}]_0$, 2.246×10^{-4} *M* $[\mathrm{BrO_3^-}]_0$, and 2.67×10^{-3} *M* $[\mathrm{CH_2{=}CHCH_2OH}]_0$ in 2.0 *M* $[\mathrm{HClO_4}]$ at 25° was allowed to react completely as judged by the cessation of chlorine dioxide production at 3600 Å. A small known excess of cerium(IV) was injected at 2800 Å and the $[\mathrm{HClO_2}]_\infty$ in the reaction mixture was determined. The ratio $R'' = [\mathrm{BrO_3^-}]_0/([\mathrm{HClO_2}]_0 - [\mathrm{HClO_2}]_\infty)$ was calculated to be 0.355 ± 0.004. Since $[\mathrm{ClO_2}]_\infty/([\mathrm{HClO_2}]_0 - [\mathrm{HClO_2}]_\infty)$ in the reaction mixture was 0.562 ± 0.003, the theoretical value of R'' should be 0.365 on the basis of each bromate ion accepting a total of four electrons from the oxychlorine species prior to being scavenged by allyl alcohol. We consider this agreement sufficient to justify the stoichiometric assumption, particularly in view of supporting evidence found in related systems.[7,8,10b]

The one perturbation that most significantly alters the stoichiometry is the initial presence of chlorine dioxide in the bromate-chlorous acid reaction with excess bromate ion concentration. The results of a number of experiments designed to test this point are summarized in Table I.

Kinetics and Reaction Scheme. We will confine our interpretation of the kinetic results to the entire reaction when considerable excesses of chlorous acid are present but only up to the point of maximum chlorine dioxide production with excess bromate ion (see Figure 1). Despite considerable effort, we have been unable to determine the rate expression for the bromate-chlorine dioxide reaction. The kinetic analysis is more easily understood if we depart from the usual convention and first present a proposed reaction scheme that is consistent with nearly all of the experimental results.

$$\mathrm{BrO_3^-} + \mathrm{HClO_2} + \mathrm{H^+} \overset{k_\mathrm{a}}{=} \mathrm{BrO_2} + \mathrm{ClO_2} + \mathrm{H_2O} \quad \text{(I)}$$

$$\mathrm{BrO_2} + \mathrm{HClO_2} \overset{k_\mathrm{b}}{=} \mathrm{HBrO_2} + \mathrm{ClO_2} \quad \text{(II)}$$

$$\mathrm{BrO_2} + \mathrm{ClO_2} + \mathrm{H_2O} \overset{k_\mathrm{c}}{=} \mathrm{HBrO_2} + \mathrm{ClO_3^-} + \mathrm{H^+} \quad \text{(III)}$$

$$\mathrm{HBrO_2} + \mathrm{HClO_2} \overset{k_\mathrm{d}}{=} \mathrm{HOBr} + \mathrm{ClO_3^-} + \mathrm{H^+} \quad \text{(IV)}$$

$$\mathrm{HOBr} + \mathrm{CH_2{=}CHCH_2OH} = \text{products}$$

The stoichiometric results are semiquantitatively predictable from this scheme. (1) With a sufficient excess of chlorous acid, reaction III is negligible and the stoichiometry becomes (4). (2) With excess bromate ion of any amount, the ratio $[\mathrm{ClO_2}]_{\mathrm{max}}/[\mathrm{HClO_2}]_0$ should be less than 0.667 but independent of initial concentrations of reactants.

Table I. Stoichiometry with Added Chlorine Dioxide and Excess Bromate[a]

$[\mathrm{HClO_2}]_0/[\mathrm{ClO_2}]_0$	$[\mathrm{ClO_2}]_0/[\mathrm{ClO_2}]_\infty$	$\Delta[\mathrm{ClO_2}]_{\mathrm{rxn}}/[\mathrm{HClO_2}]_0$ [b]
17.2[c]	0.106	0.489 ± 0.001
5.15[c]	0.301	0.451 ± 0.003
3.27[c]	0.429	0.408 ± 0.005
1.68[c]	0.614	0.373 ± 0.004
1.10[c]	0.730	0.335 ± 0.003
11.2[d]	0.139	0.553 ± 0.002
3.69[d]	0.341	0.523 ± 0.003
2.13[d]	0.494	0.482 ± 0.001
1.02[d]	0.688	0.443 ± 0.001
0.606[d]	0.814	0.377 ± 0.001
10.8[e]	0.139	0.574 ± 0.001
2.23[e]	0.448	0.550 ± 0.004
1.01[e]	0.658	0.519 ± 0.001
0.80[e]	0.714	0.499 ± 0.002
0.514[e]	0.806	0.468 ± 0.003

[a] Initial concentrations: $[\mathrm{BrO_3^-}]_0 = (0.22\text{–}2.13) \times 10^{-2}$ *M*, $[\mathrm{HClO_2}]_0 = (1.29\text{–}6.74) \times 10^{-4}$ *M*, $[\mathrm{ClO_2}]_0 = (0.39\text{–}4.34) \times 10^{-4}$ *M*, and $[\mathrm{CH_2{=}CHCH_2OH}]_0 = 2.69 \times 10^{-3}$ *M*. All experiments at 25.0° and $I = 2.0$ *M* ($\mathrm{LiClO_4}$). [b] $\Delta[\mathrm{ClO_2}]_{\mathrm{rxn}} = [\mathrm{ClO_2}]_{\mathrm{max}} - [\mathrm{ClO_2}]_0$ (see Figure 1). Uncertainties are average deviations of replicate experiments. [c] $[\mathrm{HClO_4}] = 2.00$ *M*. [d] $[\mathrm{HClO_2}] = 0.60$ *M*. [e] $[\mathrm{HClO_4}] = 0.20$ *M*.

The following rate expression results from (I-IV) with sufficient excesses of chlorous acid

$$-\mathrm{d}[\mathrm{BrO_3^-}]/\mathrm{d}t = k_\mathrm{a}[\mathrm{BrO_3^-}][\mathrm{HClO_2}]_0 \quad (6)$$

where $[\mathrm{BrO_3^-}] = [\mathrm{BrO_3^-}]_0 - 0.50[\mathrm{ClO_2}]_\mathrm{m}$. ($[\mathrm{ClO_2}]_\mathrm{m} = [\mathrm{ClO_2}]_{\mathrm{obsd}} - [\mathrm{ClO_2}]_{\mathrm{disp}}$, where values of $[\mathrm{ClO_2}]_{\mathrm{disp}}$ are measured in a blank experiment as discussed earlier.) k_a is the rate parameter associated with reaction I. The integrated form of eq 6 correlated the experimental data very well for at least 90% reaction in $[\mathrm{HClO_4}] \geqslant 1.9$ *M*. The values of k_a as obtained from a least-squares treatment of the data are presented in Table II. The standard deviations associated with the rate parameter were ⩽1.0% at the higher acidities but became progressively larger as the perchloric acid concentration was decreased. In the latter case the competitive disproportionation reaction of chlorous acid becomes increasingly significant compared to the rate of the bromate-chlorous acid reaction.[16] The success of the rate expression (6) requires that the stoichiometric eq 4 be maintained throughout the reaction.

The kinetic analysis under conditions of excess bromate ion is much more complicated. The following expressions can be derived from the reaction scheme (I-IV) under the steady state assumption for the bromine dioxide and bromous acid intermediates.

$$\mathrm{d}[\mathrm{ClO_2}]/\mathrm{d}t = 2k_\mathrm{a}[\mathrm{HClO_2}][\mathrm{BrO_3^-}]/(1 + (k_\mathrm{c}/k_\mathrm{b})[\mathrm{ClO_2}]/[\mathrm{HClO_2}]) \quad (7)$$

$$\mathrm{d}[\mathrm{HClO_2}]/\mathrm{d}t = (-3k_\mathrm{a}[\mathrm{HClO_2}][\mathrm{BrO_3^-}] - (2k_\mathrm{a}k_\mathrm{c}/k_\mathrm{b})[\mathrm{ClO_2}][\mathrm{BrO_3^-}])/(1 + k_\mathrm{c}/k_\mathrm{b})[\mathrm{ClO_2}]/[\mathrm{HClO_2}]) \quad (8)$$

Neither expression is directly usable, since a knowledge of the measured chlorine dioxide concentration during the re-

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(16) The system is even more complicated under these conditions. Values of $[\mathrm{ClO_2}]_\infty/[\mathrm{HClO_2}]_0$ significantly less than 0.667 were found. This indicates to us at least one oxybromine species is reacting with an intermediate produced in the disproportionation of chlorous acid, presumably $\mathrm{Cl_2O_2}$.

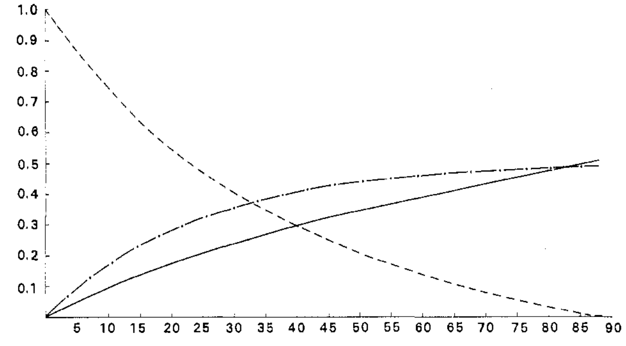

Figure 2. Stoichiometry as a function of time for the bromate–chlorous acid reaction with excess bromate ion: (– – –) curve is $[HClO_2]/[HClO_2]_0$; (– · –) curve is $[ClO_2]/[HClO_2]_0$; and (—) curve is $[ClO_3^-]/[HClO_2]_0$. Conditions were $[BrO_3^-]_0 = 3.16 \times 10^{-3}$ *M*, $[HClO_2]_0 = 6.32 \times 10^{-4}$ *M*, $[CH_2{=}CHCH_2OH]_0 = 2.63 \times 10^{-3}$ *M*, $[HClO_4] = 1.92$ *M*, and $T = 25.0°$.

Table II. Kinetic Results with Large Excesses of Chlorous Acid[a]

$10^3[HClO_2]_0$, *M*	$[HClO_4]$, *M*	k_a, M^{-1} sec^{-1} [b]
1.71	1.94	3.34 ± 0.01
3.37	1.91	3.18 ± 0.04
6.32	1.91	3.28 ± 0.03
6.32	1.42	2.45 ± 0.03
6.33	0.947	1.54 ± 0.02
12.6	0.711	1.21 ± 0.01
3.21[c]	3.58	15.1 ± 0.1
6.32[d]	1.92	1.90 ± 0.03
12.6[e]	1.92	1.17 ± 0.01
12.6[f]	1.92	0.806 ± 0.004

[a] $[BrO_3^-]_0 = 1.05 \times 10^{-4}$ *M* and $[CH_2{=}CHCH_2OH]_0 = 5.26 \times 10^{-3}$ *M*. $T = 25.0°$ and $I = 1.93$ *M* $(LiClO_4]$ unless otherwise indicated. [b] Uncertainties are average deviations of replicate experiments. [c] $I = 3.58$ *M*. [d] $T = 17.0°$. [e] $T = 10.0°$. [f] $T = 5.0°$.

action does not allow the calculation of the chlorous acid concentration. That is, the stoichiometry changes throughout the reaction; eq 5 only represents the final relationship. However, if time is eliminated as an independent variable, two useful differential equations result in which the variables are separable.[17]

$$d[HClO_2]/d[ClO_2] = -{}^3\!/_2 - (k_c/k_b)[ClO_2][HClO_2] \qquad (9)$$

$$d[ClO_2]/d[HClO_2] = -1/({}^3\!/_2 + (k_c/k_b)[ClO_2]/[HClO_2]) \qquad (10)$$

Equation 9 can be integrated (see Appendix I) to yield eq 11 which is in a suitable form for the determination of k_c/k_b from the data listed in Table I

$$2\ln([ClO_2]_0/[ClO_2]_\infty) = \ln[K/(K + 3y_0/2 + y_0^2)] - (1.5/q)\ln[(3y_0 - 2y_0q + 4K)/(3y_0 + 2y_0q + 4K)] \qquad (11)$$

where $K = k_c/k_b$, $y_0 = [HClO_2]_0/[ClO_2]_0$, $q = \sqrt{9/4 - 4K}$, $9/4 - 4K > 0$, and the conditions of excess $[BrO_3^-]$ and added initial ClO_2. The nonlinear least-squares determined values of K at $I = 2.0$ *M* and 25.0° were 0.540 ± 0.021, 0.213 ± 0.007, and 0.112 ± 0.005 at 2.0, 0.60, and 0.20 *M* $[HClO_4]$, respectively. Values of K at other hydrogen ion concentrations were obtained graphically from a ln K *vs.* ln $[H^+]$ plot of these results. According to the reaction scheme (I-IV), K is the ratio of the rate constants for the reduction of bromine dioxide by chlorine dioxide and chlorous acid.

A knowledge of the value of K allows the calculation of the chlorous acid, chlorate ion, and bromate ion concentrations at any measured chlorine dioxide concentration during a kinetic experiment. Equation 10 can be integrated (see Appendix II) to yield eq 12

$$[HClO_2]/[HClO_2]_0 = \exp[(-{}^1\!/_2)\ln(1 + ({}^3\!/_2)y + Ky^2) - ({}^3\!/_4q)\ln([3Ky + 4K + 2Kyq]/[3Ky + 4K - 2Kyq])] \qquad (12)$$

where $K = k_c/k_b$, $y = [ClO_2]/[HClO_2]$, $q = \sqrt{9/4 - 4K}$, $9/4 - 4K > 0$, and the conditions of excess $[BrO_3^-]$ and *no* added ClO_2. A table was generated for each K value by means of eq 12 that tabulated values of $[ClO_2]/[HClO_2]_0$, $[HClO_2]/[HClO_2]_0$, $[ClO_3^-]/[HClO_2]_0$, $[BrO_3^-]/[HClO_2]_0$, and expression 13 for 200 input values of y ranging in appropriate

$$2[HClO_2][BrO_3^-]/([HClO_2]_0(1 + K[ClO_2]/[HClO_2])) \equiv \alpha \qquad (13)$$

increments from 0.01 to 1000. A profile of the stoichiometry as a function of time for a typical kinetic experiment is presented in Figure 2.

For each kinetic experiment, a value of α (see eq 13) was read from the tables for various measured value of $[ClO_2]/[HClO_2]_0$. Equation 7 can be transformed into eq 14.

$$\text{rate} \equiv d([ClO_2]/HClO_2]_0)/dt = k_a(\alpha) \qquad (14)$$

Values of the derivative (or rate) were measured manually from a graph of $[ClO_2]/[HClO_2]_0$ *vs.* time (see Experimental Section). Plots of rate *vs.* α were indeed linear, although there was noticeable scatter. Table III lists the values of k_a determined from a least-squares adjustment of the data in terms of eq 14 for all the experiments with excess bromate ion. The maximum standard deviation of k_a was 3.7%; the average standard deviation was 1.3%.

A crucial test of the kinetic analysis and the proposed reaction scheme (I-IV) is a comparison of the k_a values in Tables II and III at equal hydrogen ion concentrations and temperature. We consider the agreement to be remarkably good in view of the extensive range of initial reactant concentrations used and the complexities in the analysis of the kinetic data.

The dependence of k_a at 25° and $I = 1.9$ *M* on the hydrogen ion concentration was analyzed according to the expression

$$k_a = k_0[H^+]^n$$

Using all the appropriate data from Tables II and III. The least-squares value of n was 1.12 ± 0.02. Thus reaction I is predominantly first order with respect to hydrogen ion concentration. The same dependence has been suggested for reaction 1.[3] The rate parameter for reaction 1 was also suggested to be sensitive to ionic strength.[3] k_a varies with ionic strength (see Table III) in a comparable manner, although the effect is not as pronounced. A further prediction that reaction 1 does not exhibit an induction period is in harmony with the present results on reaction I. The apparent activation energy calculated from the temperature dependence of k_a is 11.4 ± 0.3 kcal/mol.

Some further conclusions may be drawn. Reactions 1 and 3, important in other systems, are not operative in the bromate–chlorous acid reaction, apparently due to the remarkable ability of chlorous acid to scavenge bromous acid according to reaction IV. Precedent for the stoichiometry

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(17) See S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, pp 43-46, for a brief discussion of the mathematical procedures developed in this communication.

Table III. Kinetic Results with Excess Bromate[a]

$10^3[BrO_3^-]_0$, M	$[HClO_4]$, M	k_a, M^{-1} sec^{-1} [b]
1.70	1.93	3.31 ± 0.03
3.16	1.92	3.34 ± 0.04
3.16	1.42	2.53 ± 0.01
5.29	0.947	1.55 ± 0.01
3.16	0.947	1.51 ± 0.01
4.24	0.716	1.07 ± 0.02
7.37	0.474	0.719 ± 0.017
7.90	0.332	0.477 ± 0.002
7.90[c]	0.190	0.221 ± 0.001
7.90[d]	0.190	0.203 ± 0.003
7.90	0.190	0.245 ± 0.004
7.90[e]	0.190	0.364 ± 0.002
0.45[f]	3.55	17.2 ± 0.2
3.16[g]	1.92	2.02 ± 0.01
5.29[h]	1.92	1.25 ± 0.01
7.90[i]	1.92	0.856 ± 0.016

[a] $[HClO_2]_0 = 6.33 \times 10^{-4}$ M and $[CH_2{=}CHCH_2OH]_0 = 2.63 \times 10^{-3}$ M. $T = 25.0°$ and $I = 1.93$ M ($LiClO_4$) unless otherwise indicated. [b] Uncertainties are average deviations of replicate experiments. [c] $I = 0.19$ M. [d] $I = 0.95$ M. [e] $I = 3.06$ M. [f] $I = 3.55$ M. [g] $T = 17.0°$. [h] $T = 10.0°$. [i] $T = 5.0°$.

shown in (IV) comes from a study of the disproportionation of chlorous acid[6] and a variety of evidence that suggests that bromous acid prefers to oxidize in a two-equivalent path whenever possible.[2,7,8,10] Bromate ion also normally acts as a two-equivalent oxidant. Its failure to do so in the present system may result from a facile production of a $BrClO_4$ intermediate in reaction I, analogous to the probable formation of Br_2O_4 in reaction 1.[4] A difficult question to suitably answer, however, is why $BrClO_4$ would dissociate rather than undergo the redox reaction III. It may be that both of these reactions occur, and our reaction scheme is oversimplified.

The result that k_c/k_b is near unity at high acidities is consistent with the assumption that bromine dioxide is a very reactive species and does not discriminate between chlorine dioxide and chlorous acid. However, the hydrogen ion dependence of K is not predictable from reaction scheme I-IV. A possibility is that bromine dioxide reacts much more rapidly with chlorite ion than chlorous acid.

Registry No. BrO_3^-, 15541-45-4; $HClO_2$, 13898-47-0; ClO_2, 10049-04-4; ClO_3^-, 14866-68-3.

Appendix I

Let eq 9 be expressed as

$$d(By)/dB = -{}^3/_2 - K/y$$

where $y = A/B$, $A = [HClO_2]$, $B = [ClO_2]$, and $K = k_c/k_b$. Then, since $A_\infty = 0$ at the plateau (see Figure 1) and $B_0 > 0$ if ClO_2 is added

$$\int_{B_0}^{B_\infty} -d(\ln B) = \int_{y_0}^{0} [y/(K + 3y/2 + y^2)]\ dy$$

This equation can be integrated in closed form and rearranged to yield eq 11.

Appendix II

Let eq 10 be expressed as

$$d(Ay)/dA = -1/({}^3/_2 + Ky)$$

where $y = B/A$, $A = [HClO_2]$, $B = [ClO_2]$, and $K = k_c/k_b$. Then, since $y_0 = 0$ with no added ClO_2 as in the kinetic experiments

$$\int_{A_0}^{A} -d(\ln A) = \int_{0}^{Y} [({}^3/_2 + Ky)/(1 + 3y/2 + y^2)]dy$$

This equation can be integrated and rearranged to yield eq 12. Equations 11 and 12 are valid provided $9/4 - 4K > 0$; this happens to be the case when $[H^+] \leqslant 2.0$ M for the present system. For the experiments conducted in 3.55 M $HClO_4$, $9/4 - 4K < 0$. The integrated expression is then different from eq 12 and involves arctangents. This latter expression was used for those experiments.

Contribution from the Departments of Chemistry, Canisius College, Buffalo, New York 14208, and The State University of New York at Buffalo, Buffalo, New York 14214

Electron Spin Resonance and Optical Spectra of the Hexachloromanganate(IV) Ion

PAUL J. McCARTHY*[1a] and ROBERT D. BEREMAN*[1b]

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The single-crystal optical spectrum of Mn(IV) doped into K_2SnCl_6 has been measured as well as the esr of the polycrystalline Mn(IV) in K_2SnCl_6. The Racah parameter B was evaluated at 584 cm^{-1} and $10Dq$ was shown to be 18,240 cm^{-1}. Variable-temperature studies show that Mn(IV) is thermally unstable in the $SnCl_6^{2-}$ lattice and is reduced to Mn(II), probably through Mn(III). Evidence for Mn(III) in the optical spectrum is discussed.

Introduction

Mn(IV) has a very restricted chemistry and relatively little has been reported on the spectra of its complexes either in solution or in the crystalline state.[2] Most extensively treated has been the MnF_6^{2-} ion, whose absorption and emission spectra have been quite thoroughly investigated.[3-8] Reflectance spectra of the analogous chloro complex have been studied by Moews[9] and by Jezowska-Trzebiatowska and coworkers,[10] who also studied the solution spectrum. No report of the crystal spectrum of $MnCl_6^{2-}$ at low temperature

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[1] (a) Canisius College. (b) State University of New York at Buffalo.

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