with nitrogen coming largely from the two atoms in trioxodinitrate, at least in its early stages. None of the other reactions appears to involve radical intermediates, at least if (4) is properly identified as the radical catalysis reaction. We are considerably puzzled about reaction 3 but do not believe our results can be explained as disproportionation; hence some such postulate is necessary. With respect to this and the other reactions, interpretation is inhibited by the fact that we are not wholly certain of the products other than gas products. For example, one can imagine more than one mechanism in which nitrate would be produced as a solution product; we have examined solutions after reaction at pH 4.9 for nitrate, both by spectrophotometry and by sensitive spot tests. While we have not detected it, its production is not ruled out because of the low concentration levels and the known difficulty of detection at such levels.

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Kinetic Study of the Cerium(IV)–Bromous Acid Reaction in Acid Sulfate Solution. Implications for the Belousov–Zhabotinskii Oscillating Reaction[1]

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A kinetic study of the cerium(IV)–bromous acid reaction in acid sulfate solution using stopped-flow techniques is reported. The empirical rate expression is $-d[Ce(IV)]/dt = k_{HBrO_2}[Ce(IV)][HBrO_2]$. The values of k_{HBrO_2} are very sensitive to the distribution of cerium(IV) among various sulfato complexes; $Ce(SO_4)_3^{2-}$, the predominant species in 1.5 M H_2SO_4, appears to be unreactive relative to disproportionation of bromous acid. The implications of this study for the Belousov–Zhabotinskii oscillating reaction are discussed. The results of a brief kinetic investigation of the cerium(IV)–chlorous acid reaction are summarized.

Introduction

Considerable effort has been devoted to the elucidation of the mechanism of the Belousov–Zhabotinskii oscillating reaction. An elegant reaction scheme was proposed by Noyes and co-workers[3] and has been refined to the extent that computer simulations of the reaction and various component processes have been reported.[3b,4] These computer analyses appear to be quite successful. However, as Edelson, Field, and Noyes have stated:[3b] "The values of the rate constants for the reactions of cerium(III) and cerium(IV) with the various oxybromine compounds involve considerable speculation". The current scheme for this component process is[4] given in eq 1–7.

$$2H^+ + Br^- + BrO_3^- \rightleftarrows HOBr + HBrO_2 \qquad (1)$$

$$k_1 = 2.1\ M^{-3}\ s^{-1},\ k_{-1} = 10^4\ M^{-1}\ s^{-1}$$

$$H^+ + Br^- + HBrO_2 \rightleftarrows 2HOBr \qquad (2)$$

$$k_2 = 2 \times 10^9\ M^{-2}\ s^{-1},\ k_{-2} = 5 \times 10^{-5}\ M^{-1}\ s^{-1}$$

$$H^+ + Br^- + HOBr \rightleftarrows Br_2 + H_2O \qquad (3)$$

$$k_3 = 8 \times 10^9\ M^{-2}\ s^{-1},\ k_{-3} = 110\ s^{-1}$$

$$H^+ + HBrO_2 + BrO_3^- \rightleftarrows 2BrO_2 + H_2O \qquad (4)$$

$$k_4 = 10^4\ M^{-2}\ s^{-1},\ k_{-4} = 2 \times 10^7\ M^{-1}\ s^{-1}$$

$$H^+ + BrO_2 + Ce^{3+} \rightleftarrows Ce^{4+} + HBrO_2 \qquad (5)$$

$$k_5 = 6.5 \times 10^5\ M^{-2}\ s^{-1},\ k_{-5} = 2.4 \times 10^7\ M^{-1}\ s^{-1}$$

$$Ce^{4+} + BrO_2 + H_2O \rightleftarrows 2H^+ + BrO_3^- + Ce^{3+} \qquad (6)$$

$$k_6 = 9.6\ M^{-1}\ s^{-1},\ k_{-6} = 1.3 \times 10^{-4}\ M^{-3}\ s^{-1}$$

$$2HBrO_2 \rightleftarrows H^+ + HOBr + BrO_3^- \qquad (7)$$

$$k_7 = 4 \times 10^7\ M^{-1}\ s^{-1},\ k_{-7} = 2 \times 10^{-10}\ M^{-2}\ s^{-1}$$

The main features of the oxidation of cerous ions by bromate ions in sulfuric acid medium are indeed consistent with this scheme. However, the large number of parameters that are required and the uncertainty in the values of many of the rate constants justify efforts to determine directly those rate constants amenable to investigation.

In this communication we summarize the results of a kinetic study of the oxidation of bromous acid by cerium(IV) in acid sulfate media. The value determined for k_{-5} is in serious disagreement with the estimated value. We conclude that this reaction plays a negligible role under the experimental conditions for the oscillating reaction.

Experimental Section

Preparation and Analysis of Barium Bromite. The synthesis and stability of bromite salts and solutions have been reported.[5] The details of the preparations are scant, and claims of the stability of the solid samples and solutions are conflicting. This situation is in part due to the proprietary nature of bromite, which has extensive commercial applications, and the difficulty in analyzing mixtures of bromate, bromite, hypobromite, and bromide. In our hands, the direct synthesis of pure barium bromite was unsuccessful. Commercial sources of bromite salts have been used by previous investigators but apparently are not available currently.

The Olin Research Center in New Haven, Conn., kindly supplied us with an impure, concentrated solution of sodium bromite sold commercially under the registered trademark Preptone desizing preparation. This solution was found to contain approximately 0.57 M $NaBrO_2$ plus NaOBr (mostly $NaBrO_2$), 0.30 M $NaBrO_3$, and considerable NaBr. Our goal was to isolate from this solution a solid sample of $Ba[BrO_2]_2$, which is reported to be stable, as free as possible from Br^-, OBr^-, and BrO_3^- salts. In a typical preparation, 300 mL of Preptone sodium bromite solution was vigorously stirred with 100 g of $BaCl_2{\cdot}2H_2O$ for 30 min. The slurry was centrifuged and the supernatant was discarded. The solid obtained was extracted with ice cold 0.08 M NaOH. The solution recovered after centrifugation contained little BrO_3^- due to the low solubility of $Ba(BrO_3)_2$ and was moderately stable due to the base present. The solution was concentrated at 35 °C by rotary evaporation, and the pale yellow solid that formed was collected after filtration. In preliminary experiments this solid was mixed with 0.08 M NaOH that contained sufficient Na_2SO_4 to precipitate the Ba^{2+}, and the solution collected after centrifugation was used as a bromite stock. The kinetic results obtained with this solution were similar to those reported here with purer preparations. In principle the pale yellow solid isolated by this procedure should be fairly pure $Ba(BrO_2)_2$ due to the much higher solubility of $BaCl_2$, $BaBr_2$, and $Ba(OBr)_2$.[5a] In practice, however, it was found to be grossly contaminated with inorganic salts, presumably owing to considerable adsorption of foreign ions on the surface of the flocculent $Ba(BrO_2)_2$. A purified sample (preparation A) was obtained by dissolving the solid in a minimum of 0.08 M NaOH, filtering, concentrating in a rotary evaporator, and repeating this cycle with the pale yellow solid that formed and was collected by filtration. A purer sample (preparation B) was obtained by repeating this cycle with a sample of preparation A and accepting a low yield. Both solids were thoroughly dried and stored under vacuum over anhydrous calcium chloride. Decomposition of bromite in these solids was ca. 1% per month.

The results of elemental analysis (Galbraith Laboratories) were as follows. Anal. Calcd for $Ba(BrO_2)_2$: Ba, 38.03; Br, 44.25; O, 17.72. Found (preparation A): Ba, 39.43; Br, 21.81; Cl, 16.23; O, 11.67; Na, 7.46; C, 0.62; H, 0.56; N, 0.008. Found (preparation B): Ba, 46.36; Br, 22.58; O, 13.62; Cl, 12.31; Na, 2.13; C, 0.64; H, 0.58; N, 0.015.

The solids were analyzed for (BrO_2^- + OBr^-) and BrO_3^- by separate titrations. An aliquot was added to pH 4 buffer (potassium acid phthalate) or pH 5 buffer (acetic acid–sodium acetate) containing excess iodide, and the iodine liberated was titrated with standardized thiosulfate to give (BrO_2^- + OBr^-). Another aliquot was added to 0.1 M $HClO_4$ containing excess iodide and molybdate catalyst; this titer gave (BrO_3^- + BrO_2^- + OBr^-). On the assumption that no OBr^- was present, preparation A was found to contain 39.0% $Ba(BrO_2)_2$ and 4.6% $Ba(BrO_3)_2$, while preparation B contained 50.0% $Ba(BrO_2)_2$ and no BrO_3^-. These results correspond to a calculated percent Br in the solids of 19.1 and 22.1, respectively. A comparison with the elemental analysis results indicates that preparation A was contaminated with bromide and/or hypobromite salts, while preparation B was rather free from these impurities.

Many methods have been reported for the analysis of BrO_2^- and OBr^- individually, but none appear to be very satisfactory. We chose the following procedure. The $[I_2]$ formed in pH 4 or pH 5 buffer was taken as $(2[BrO_2^-]_0 + [OBr^-]_0)$. A separate aliquot was added to excess 0.01 M $HClO_4$, where the anticipated reactions are $2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$, $H^+ + Br^- + HOBr \rightarrow Br_2 + H_2O$, and $H^+ + Br^- + HBrO_2 \rightarrow 2HOBr$. The $[I_2]$ formed upon addition of excess buffer containing iodide ion was determined. In the absence of any bromide contaminant the resulting $[I_2] = {}^1/_2[BrO_2^-]_0 + [OBr^-]$. In this way, preparation B was shown to contain at least 92% BrO_2^- relative to OBr^-, while preparation A contained at least 85% BrO_2^- relative to OBr^-. Any bromide contamination would raise these percentages to an extent not calculable from these experiments. In practice, the bromite concentration of stock solutions was accepted as that calculated from the iodometric titration in pH 4 or 5 buffers assuming no hypobromite contamination. Any error thus introduced into the kinetic results will be small.

Aside from impurities such as $Ba(OH)_2$, $BaCO_3$, and NaOH which for our purposes are innocuous, the principal remaining impurity to consider is chloride ion. In basic solution, chloride is unreactive toward bromite, but in the acidic reaction mixtures of the kinetic experiments, Jacobs and Epstein[6] have estimated a rate constant of ca. 10^7–10^8 $M^{-2}\ s^{-1}$ for the reaction

$$H^+ + Cl^- + HBrO_2 \rightarrow HOCl + HOBr \tag{8}$$

If this estimate is correct, the preparations described would be unsuitable for our purposes, since the $[Cl^-] = 1.25[BrO_2^-]$ in preparation B would be sufficient to consume much of the bromous acid. It will be shown, however, that even a $[Cl^-]_0 = 11[BrO_2^-]_0$ is without kinetic effect in the bromous acid–cerium(IV) reaction in acid sulfate solution.

Other Reagents. A 0.107 M cerium(IV) stock solution in 0.5 M H_2SO_4 was prepared from reagent grade $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$. This solution was found to contain no detectable Ce(III) and was assayed iodometrically. Reagent grade sodium chlorite was obtained from Matheson Coleman and Bell. Sodium perchlorate was obtained from the reaction of perchloric acid and sodium carbonate and was recrystallized three times. Laboratory distilled water was redistilled first from alkaline permanganate and then from a dichromate solution in sulfuric acid. Other chemicals were commercial products of reagent grade.

Kinetic Studies. The kinetic studies were conducted on a Durrum stopped-flow spectrophotometer interfaced with a Xerox Sigma V computer. The wavelength monitored was 317 nm, an absorption maximum for cerium(IV) in 1.5 M H_2SO_4 (ϵ 5.45 × 10^3 $M^{-1}\ cm^{-1}$). Interference from the other reagents and products was negligible. All kinetic data were collected with presumably a pseudo-order excess of bromous acid.

The A_t,t data from each kinetic experiment were treated by a nonlinear least-squares routine, fitted to the first-order rate equation

$$A_t = (A_0 - A_\infty) \exp(-k't) + A_\infty \tag{9}$$

where A_0, A_∞, and k' are adjustable parameters. Each experiment was monitored to at least 80% of completion; 800–950 A_t,t data pairs were collected per experiment. Except in solutions containing ≥0.75 M H_2SO_4 or $[Ce(III)]_0/[Ce(IV)]_0 > 19$, $A_0 - A_\infty$ corresponded to the value calculated on the basis of $[Ce(IV)]_0$ and ϵ, with a 20-mm path length. Reaction mixtures were always checked for initial absorption after mixing (ca. 2 ms) by using a fast, 20–50-ms full sweep rate; in every case the agreement with the calculated value was satisfactory.

The bromite stock solution for a kinetic series was prepared by dissolving the barium bromite in 0.10 M NaOH containing sufficient Na_2SO_4 to precipitate the Ba^{2+} introduced. The solid that formed was removed by centrifugation, and the solution was assayed for bromite. These solutions were stable for at least 24 h. Separate BrO_2^- solutions for individual kinetic experiments were prepared by dilution of aliquots of this stock with the final $[OH^-]$ adjusted to 0.02 M. Thus the bromite solutions remained basic until mixed with the acidic cerium(IV) reactant on the stopped-flow apparatus.

Results

Bromous acid is very unstable with respect to disproportionation in strongly acidic solution, but bromite solutions in dilute base are moderately stable. Thus, by mixture of a sulfuric acid solution containing the cerium(IV) with a slightly basic solution of bromite, the system is amenable to study by the stopped-flow technique. However, a mismatch between the ionic strength of the two reactant solutions then exists (unless a neutral salt such as sodium perchlorate is added to the bromite). Operationally, we found that ca. 0.60 M H_2SO_4 solutions represented the maximum acid concentration that could be mixed with the very dilute bromite solutions without appreciable complications due to Schlieren effects.

Reaction solutions containing a $[HBrO_2]_0/[Ce(IV)]_0$ ratio ≥3.6 in 0.30 M H_2SO_4 yielded kinetic profiles that were in excellent accord with the empirical rate expression

$$-d[Ce(IV)]/dt = k'[Ce(IV)] \tag{10}$$

Values of k' determined over a variety of experimental conditions are summarized in Table I. Several kinetic traces and the calculated curves based on eq 9 are given in Figure 1.

Table I. Kinetic Results in 0.30 M H_2SO_4[a] at 25 °C

expt	$[HBrO_2]_0$, M	other reagents	k',[b] s^{-1}	k_{HBrO_2},[c] $M^{-1}\ s^{-1}$
1	1.91×10^{-5}		1.15 ± 0.06	6.0×10^4
2	3.66×10^{-5}		2.25 ± 0.05	6.2×10^4
3	3.82×10^{-5}		2.25 ± 0.07	5.9×10^4
4[d]	4.61×10^{-5}		2.71 ± 0.07	5.9×10^4
5	7.64×10^{-5}		4.50 ± 0.15	5.9×10^4
6	3.66×10^{-5}	4×10^{-4} M Cl^-	2.23 ± 0.03	6.1×10^4
7	3.82×10^{-5}	8.22×10^{-6} M Ce(III)	2.17 ± 0.11	5.7×10^4
8	3.82×10^{-5}	3.29×10^{-5} M Ce(III)	2.07 ± 0.06	5.4×10^4
9	3.66×10^{-5}	9.86×10^{-5} M Ce(III)	1.58 ± 0.02	4.3×10^4
10	3.66×10^{-5}	2.96×10^{-4} M Ce(III)	(0.75 ± 0.01)[e]	
11	3.66×10^{-5}	9.86×10^{-4} M Ce(III)	(0.32 ± 0.01)[f]	
12	3.66×10^{-5}	0.30 M H_2SO_4, 0.30 M $NaClO_4$	2.02 ± 0.03	5.5×10^4
13	3.66×10^{-5}	0.75 M H_2SO_4, 0.75 M $NaClO_4$	(0.53 ± 0.01)[g]	
14	3.82×10^{-5}	1.50 M H_2SO_4, 1.50 M $NaClO_4$	*h*	

[a] Unless otherwise indicated (experiments 12–14). $[Ce(IV)]_0 = 5.35 \times 10^{-6}$ M. [b] Entries are average values of six replicate experiments. Uncertainties are average deviations. [c] $k_{HBrO_2} = k'/[HBrO_2]_0$. [d] Purified $Ba(BrO_2)_2$ used. [e] 75% consumption of Ce(IV). [f] 28% consumption of Ce(IV). [g] 58% consumption of Ce(IV). [h] No consumption of Ce(IV) over a 60-s time period.

Table II. Effect of Bisulfate and Sulfate Ion Concentrations on the Rate Parameter k_{HBrO_2}[a]

expt	$[Na_2SO_4]$[b]	$[HClO_4]$[b]	$[NaClO_4]$[b]	$[H^+]$[c]	$[HSO_4^-]$[c]	$[SO_4^{2-}]$[c]	k_{HBrO_2},[d] $M^{-1}\ s^{-1}$
15	0.333	0.384		0.149	0.235	0.0982	4.19×10^4
16	0.270	0.337	0.245	0.147	0.190	0.0800	5.93×10^4
17	0.200	0.297	0.323	0.154	0.142	0.0580	6.72×10^4
18	0.100	0.148	0.676	0.0892	0.0588	0.0412	15.2×10^4
19	0.100	0.280	0.585	0.203	0.0765	0.0235	13.6×10^4
20	0.050	0.230	0.689	0.192	0.0377	0.0123	34.0×10^4
21	0.020	0.220	0.764	0.205	0.0153	0.00468	99.8×10^4

[a] $[Ce(IV)]_0 = 5.35 \times 10^{-6}$ M, $[HBrO_2]_0 = (3.66–4.06) \times 10^{-5}$ M, $\mu = 1.0$ M ($NaClO_4$), $T = 25$ °C. [b] Formal concentrations. [c] Computed as described in ref 7. [d] Entries are average values of six replicate experiments.

The variation k' with initial $[HBrO_2]$ is consistent with the rate expression

$$-d[Ce(IV)]/dt = k_{HBrO_2}[Ce(IV)][HBrO_2] \qquad (11)$$

The impurities in the bromite stock solutions do not appear to affect the kinetic results appreciably. Experiment 6 indicates that chloride ion levels far greater than those normally present are without kinetic effect. Also, experiment 4 which used a somewhat purer barium bromite sample yielded a value of k_{HBrO_2} well within the range measured with the usual sample. In preliminary trials, a bromite stock solution even less pure gave results similar to those listed in Table I.

The presence of added Ce(III) in the reaction mixtures has only a minor effect at a level comparable to that ultimately produced during the reaction. Increasing [Ce(III)] gradually lowers the value of the rate constant until incomplete consumption of the Ce(IV) reactant occurs. Reasonable first-order kinetic data were obtained even under this regime.

A mild decrease in k_{HBrO_2} was observed in solutions containing 0.30 M $NaClO_4$ in addition to 0.30 M H_2SO_4. In a 0.75 M H_2SO_4, 0.75 M $NaClO_4$ mixture, however, not only is a substantial reduction in rate seen but also incomplete consumption of the Ce(IV). In a 1.50 M H_2SO_4, 1.5 M $NaClO_4$ mixture, conditions closely approximating those used in the Belousov–Zhabotinskii oscillating reaction, *no reduction of cerium(IV) is observed*!

The distribution of cerium(IV) among such species as $Ce(SO_4)_3^{2-}$, $Ce(SO_4)_2$, $CeSO_4^{2+}$, and Ce(4) (which includes Ce^{4+}, $CeOH^{3+}$, and $Ce(OH)_2^{2+}$) changes dramatically from 0.30 to 1.50 M H_2SO_4.[7] A separate series of experiments were performed to test the influence of changing cerium(IV) species on the rate of oxidation of bromous acid. Various mixtures of sodium sulfate and perchloric acid were used to systematically vary the sulfate and bisulfate concentrations. In addition, the free hydrogen ion concentration was fixed in the range 0.089–0.205 M, and a constant ionic strength of unity was maintained with sodium perchlorate. The results are summarized in Table II, and the approximate fractions of cerium(IV) present as various sulfate complexes and Ce(4) in each experiment are listed in Table III.

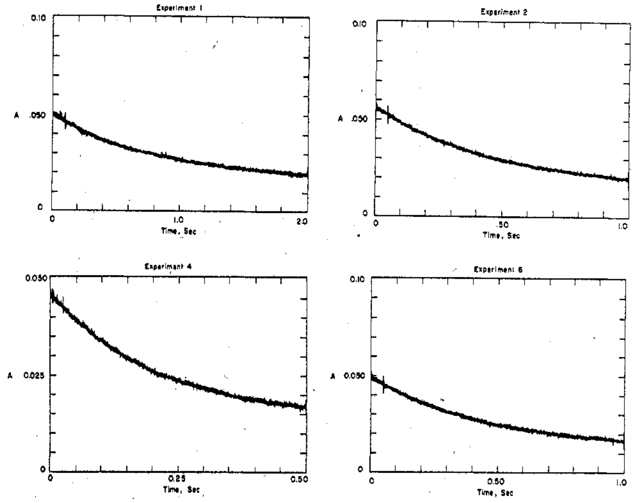

Figure 1. Kinetic traces of the cerium(IV)–bromous acid reaction in 0.30 M H_2SO_4. Conditions: 5.35×10^{-6} M $[Ce(IV)]_0$, $T = 25$ °C, $\lambda = 317$ nm. Solid curves are calculated on the basis of the best fit to eq 9. Experiment 1: $[HBrO_2]_0 = 1.91 \times 10^{-5}$. Experiment 2: $[HBrO_2]_0 = 3.66 \times 10^{-5}$ M. Experiment 4: preparation B used for bromite solution. Experiment 6: $[HBrO_2]_0 = 3.66 \times 10^{-5}$, $[NaCl]_{added} = 4 \times 10^{-4}$ M.

Cerium(IV) oxidizes chlorous acid much more rapidly than bromous acid. The results of a limited series of experiments with 1.5 M H_2SO_4 plus 1.5 M $NaClO_4$ solutions are summarized in Table IV. A previous study[8] showed that the stoichiometry of this reaction is

$$Ce(IV) + HClO_2 \rightarrow Ce(III) + ClO_2 + H^+ \qquad (12)$$

The present results are consistent with the rate expression

$$-d[Ce(IV)]/dt = k_{HClO_2}[Ce(IV)][HClO_2] \qquad (13)$$

Table III. Approximate Distribution of Cerium(IV) as Sulfato Complexes and Uncomplexed Cerium(IV)[a]

expt	$f_{Ce(4)}$[b]	$f_{CeSO_4^{2+}}$	$f_{Ce(SO_4)_2}$	$f_{Ce(SO_4)_3^{2-}}$
15	1.66×10^{-7}	5.99×10^{-4}	0.113	0.888
16	2.99×10^{-7}	8.79×10^{-4}	0.135	0.864
17	7.45×10^{-7}	1.59×10^{-3}	0.177	0.821
18	1.94×10^{-6}	2.93×10^{-3}	0.232	0.765
19	8.83×10^{-6}	7.64×10^{-3}	0.345	0.648
20	4.62×10^{-5}	2.09×10^{-2}	0.493	0.486
21	4.35×10^{-4}	7.49×10^{-2}	0.673	0.252

[a] Experimental conditions are given in Table II. The calculations are described in ref 7, and the entries are given as the fraction of total [Ce(IV)]. The values are subject to substantial error due to cumulative uncertainties in the equilibrium constants required. The inclusion of three significant figures is arbitrary. [b] Ce(4) = $Ce^{4+} + CeOH^{3+} + Ce(OH)_2^{2+}$.

Table IV. Kinetic Results for the Chlorous Acid-Cerium(IV) Reaction[a]

$[HClO_2]_0$, M	k',[b] s^{-1}	k_{HClO_2},[c] $M^{-1}\ s^{-1}$
2.32×10^{-5}	13.0 ± 0.4	5.60×10^5
4.64×10^{-5}	26.5 ± 0.9	5.71×10^5
9.29×10^{-5}	51.8 ± 2.9	5.58×10^5

[a] $[H_2SO_4] = 1.5$ M, $[NaClO_4] = 1.5$ M, $[Ce(IV)]_0 = 5.35 \times 10^{-6}$ M, and $T = 25$ °C. [b] Entries are average values of six replicate experiments. Uncertainties are average deviations. [c] $k_{HClO_2} = k'/[HClO_2]_0$.

The disproportionation of chlorous acid[9] is slow compared to its oxidation by cerium(IV) under the experimental conditions of this study.

Discussion

Our observation that the kinetics of the cerium(IV)–bromous acid reaction could be conveniently monitored by the stopped-flow technique indicates that the estimated values of k_{-5} and k_7 in eq 1–7 are much too large. For example, in experiment 1 the calculated half-lives for reactions −5 and 7 considered separately are approximately 3.0 and 1.3 ms, respectively. The observed half-life is ca. 650 ms.

Reasonable pseudo-first-order kinetic behavior was observed for experiment 1 even though the ratio $[HBrO_2]_0/[Ce(IV)]_0$ was only 3.6. Even if the disproportionation of bromous acid is not a serious side reaction, this observation is surprising. We suggest that reactions 14 and 15, which predict a stoichiometric

$$Ce(IV) + HBrO_2 \rightarrow Ce(III) + BrO_2 + H^+ \quad {}^1/{}_2k_{HBrO_2} \tag{14}$$

$$H_2O + 2BrO_2 \rightarrow HBrO_2 + BrO_3^- + H^+ \quad k_{-4} \gg k_{HBrO_2} \tag{15}$$

ratio of 2.0 for $\Delta[Ce(IV)]/\Delta[HBrO_2]$, offer an explanation. Noyes and co-workers[3,4] assign a value of $2 \times 10^7\ M^{-1}\ s^{-1}$ to k_{-4} on the basis of the results of pulse radiolysis experiments in neutral and basic solution.[10] We have extended these measurements to 10^{-4} M $HClO_4$ by the pulse radiolysis technique and to 1.0 M $HClO_4$ by flash photolysis[11] and found that this estimate is approximately valid in strongly acidic solution. Again on the assumption that k_7 is much smaller than the estimated value, the net stoichiometry of the title reaction is

$$H_2O + 2Ce(IV) + HBrO_2 \rightarrow 2Ce(III) + BrO_3^- + 3H^+ \tag{16}$$

and the conditions for experiment 1 are nearly pseudo-order in bromous acid.

The values of k_{HBrO_2} calculated from the pseudo-first-order rate constants are subject to minor error from an uncertainty in $[HBrO_2]_0$ and an unknown but apparently small error that is dependent on the extent of concomitant bromous acid disproportionation.

The absence of kinetic effect of chloride ion even at a level 11 times that of the initial bromous acid concentration suggests that the estimated value (10^7–$10^8\ M^{-2}\ s^{-1}$) of the rate constant for reaction 8 is much too large.[6]

The experiments with added Ce(III) indicate that the Ce(III) produced during the reaction has a minimal effect on the rate behavior. In the presence of sufficient Ce(III), however, the reaction rate is significantly suppressed and incomplete reduction of the Ce(IV) is observed. This feature most likely results from the increasing importance of reactions 5 and 7.[12] The first-order kinetic behavior observed is consistent with an approach to an equilibrium which does not correspond to complete reduction of the Ce(IV) reactant.

The trend from pseudo-first-order kinetic behavior in 0.30 M H_2SO_4, 0.30 M $NaClO_4$ solution to a total absence of cerium(IV) consumption in 1.5 M H_2SO_4, 1.5 M $NaClO_4$ is startling. It is unreasonable to argue that the change in $[H^+]$ is responsible, especially since reactions −5 and 7 are presumably insensitive to $[H^+]$ in this region. Available equilibrium data[7] indicate that at least 99.9% of the cerium(IV) is present as $Ce(SO_4)_3^{2-}$ in 1.5 M H_2SO_4. In 0.30 M H_2SO_4, however, the distribution of cerium(IV) is approximately 2.4×10^{-4}% Ce(4), 0.30% $CeSO_4^{2+}$, 20.0% $Ce(SO_4)_2$, and 79.7% $Ce(SO_4)_3^{2-}$. An examination of the trend in the rate constant k_{HBrO_2} as a function of cerium(IV) complexes (Tables II and III) strongly supports the conclusion that $Ce(SO_4)_3^{2-}$, the overwhelmingly predominant species present in the usual solutions where the Belousov–Zhabotinskii oscillating reaction has been studied, is quite unreactive toward bromous acid. Consequently, in 1.5 M H_2SO_4 solution the major reaction that occurs in a mixture of cerium(IV) and bromous acid is disproportionation of bromous acid with no competitive reduction of the cerium(IV). If this conclusion is correct, then not only is the estimated value of k_{-5} much too large but also reaction −5 can be neglected in the analysis of the oscillating reaction.

It is not unreasonable to predict that chlorous acid is oxidized by cerium(IV) more rapidly than bromous acid. This is speculative, but it has been proposed that bromous acid rapidly oxidizes chlorous acid and BrO_2 rapidly oxidizes chlorous acid.[8] In any case we observe that chlorous acid readily reduces cerium(IV) even in 1.5 M H_2SO_4. Even here, however, the rate constant is ca. 43 times less than that estimated[3] for k_{-5} in eq 5.

The assignment of individual rate constants to each of the cerium(IV) species under our experimental conditions is speculative, due to both the limited kinetic data collected and the uncertainties in the numerous equilibrium constants required. Nevertheless, it is instructive to show that the data in Tables II and III can be crudely correlated if the assumption is made that only $CeSO_4^{2+}$ and $Ce(SO_4)_2$ are reactive toward bromous acid under the stated experimental constraints. A plot of $k_{HBrO_2}/f_{CeSO_4^{2+}}$ vs. $f_{Ce(SO_4)_2}/f_{CeSO_4^{2+}}$ approximates linear behavior (Figure 2), though admittedly with considerable scatter. Such a relationship would be anticipated if expression 17 were valid.

$$k_{HBrO_2} = k''f_{CeSO_4^{2+}} + k'''f_{Ce(SO_4)_2} \tag{17}$$

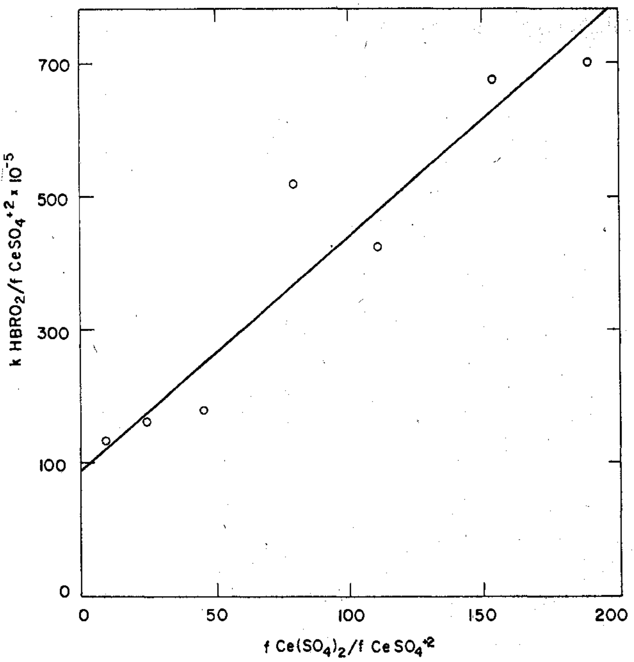

Figure 2. Plot of $k_{HBrO_2}/f_{CeSO_4^{2+}}$ as a function of $f_{Ce(SO_4)_2}/f_{CeSO_4^{2+}}$.

The results of an earlier kinetic study[13] on the reaction of large excesses of cerium(III) with bromate ion in sulfuric acid solution have been questioned[4] as a result of computer simulations using eq 1–7. The present study suggests that results of the latter analysis must be viewed with serious reservations in that the estimated values for the rate constants k_{-5} and k_7 are poor estimates. The present results do not provide evidence that would give rise to reservations concerning the basic mechanism for the Belousov–Zhabotinskii oscillating reaction proposed by Noyes and co-workers. They do reaffirm, however, that computer modeling[4] in which a number of extraneous rate parameters have to be estimated is not a useful procedure for assessing the validity of direct kinetic measurements. If the experimental data are not correct, it is preferable to demonstrate this fact in the laboratory.

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Registry No. Ce^{4+}, 16065-90-0; HBrO$_2$, 37691-27-3; Ba(BrO$_2$)$_2$, 14899-01-5; NaBrO$_2$, 7486-26-2; SO$_4^{2-}$, 14808-79-8; HClO$_2$, 13898-47-0.

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Chloritopentaamminecobalt(III): Synthesis, Decomposition, and Oxidation–Reduction Reactions

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The synthesis and characterization of chloritopentaamminecobalt(III) nitrate are described. In acidic solution the complex decomposes by an internal oxidation–reduction process with the formation of chlorine dioxide and cobalt(II). At 25 °C and $I = 0.50$ M, k(extrapolated) = 8.0×10^{-6} s^{-1}, $\Delta H^{\ddagger} = 25._3 \pm 1._7$ kcal/mol, and $\Delta S^{\ddagger} = 3 \pm 5$ cal/(mol deg). The presence of pentaamminecobalt(III) rather than a proton greatly reduces the rate of oxidation of chlorite. The rate law for the cobalt(III) oxidation of the chlorito complex is $-d[\text{comp}]/dt = k_{\text{comp}}[\text{comp}][\text{Co(III)}]/[\text{H}^+]$, with $k_{\text{comp}} = 9.1$ s^{-1}, $\Delta H^{\ddagger} = 28._1 \pm 0._4$ kcal/mol, and $\Delta S^{\ddagger} = 40 \pm 1$ cal/(mol deg) at 25 °C and $I = 2.1$ M. For the Co^{III}–HClO$_2$ reaction, $-d[\text{HClO}_2]/dt = k_{\text{HClO}_2}[\text{HClO}_2][\text{Co(III)}]/[\text{H}^+]$, with $k_{\text{HClO}_2} = 2.4 \times 10^3$ s^{-1}, $\Delta H^{\ddagger} = 15._5 \pm 0._7$ kcal/mol, and $\Delta S^{\ddagger} = 9 \pm 3$ cal/(mol deg) at 25 °C and $I = 2.0$ M. The stoichiometry of the chromium(II) reduction of the chlorito complex is similar to and compared with that for the corresponding reduction of chlorous acid. Oxygen-18 tracer experiments demonstrate that the cobalt–oxygen bond originally present in the complex is largely retained in the $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ product during reduction with Fe^{2+}, VO^{2+}, and HSO$_3^-$ but is substantially broken during oxidation with cobalt(III).

Introduction

The oxidation–reduction chemistry of oxyhalogen ions and acids is a rich field and has received considerable attention. The reactivity of these species would be expected to be modified upon coordination to substitution-inert metal cations. However, the lack of synthetic techniques for the preparation of such complexes has been a serious obstacle to experimental investigation. To the best of our knowledge, the comparative

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