tained from d.m.e. data in various media are compared in Table IV.

TABLE IV

COMPARISON OF CALCULATED AND DIRECTLY MEASURED RATES IN VARIOUS MEDIA

Medium	Av. $k/(H^+)$ in (mmole/l.) $^{-1}$ sec. $^{-1}$ Calcd.	Directly measd.	Ratio
0.5 M Cl^-	0.044	0.175	4.0
2.0 M Cl^-	.49	.80	1.3
0.4 M ClO_4^-	.028	.098	3.5
3.8 M ClO_4^-	.89	1.81	2.0

The fact that the calculated rate constants are low by a factor varying from 4.0 to 1.3 suggests the possibility of improving the relationship contained in equation (16) by the introduction of an empirically determined factor provided a similar discrepancy is found in the study of other disproportionation rates. The present results do however show that equation (16) is essentially correct and that disproportionation rates can be determined to the correct order of magnitude. These results also show that it is incorrect to attempt reaction rate calculations by the arbitrary assumption of a few ångström units as the thickness of the effective reaction volume at the d.m.e.

It is of course possible that the observed discrepancies may be fundamentally more serious and reflect the fact that the calculated disproportionation rate is characteristic of reactions occurring at the surface of the drop where conditions may be quite different from those obtaining in the body of the solution. Because of this aspect of the problem the real significance of any reaction rates calculated from d.m.e. data is open to some question.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Rate Law and Mechanism for the Reaction of Cerium(IV) and Bromide Ion in Aqueous Sulfate Media[1,2]

BY EDWARD L. KING AND MARY L. PANDOW

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Cerium(IV) and bromide ion react in aqueous acidic sulfate media to form cerium(III) and bromine at a conveniently measurable rate. The reaction has been studied spectrophotometrically at 25°; the rate of reaction conforms to the rate equation $-[d(Ce^{IV})/dt] = [(Ce^{IV})/(SO_4^{=})]\{k_{12}'(Br^-)^2 + k_{11}'(Br^-)\}$. Since the dominant species of cerium(IV) in the solutions under consideration contains three sulfate ions and no bromide ions, the two important activated complexes have the compositions $(Ce(SO_4)_2Br_2^{=}$ and $Ce(SO_4)_2Br^-$. Activated complexes involving fewer than two sulfate ions are also important at the low end of the sulfate ion concentration range. Chloride ion catalysis is observed; an activated complex of the composition $Ce(SO_4)_2ClBr^{=}$ is important in chloride media. The presence of lithium ion accelerates the reaction noticeably. In the reaction of cerium(IV) and iodide ion in sulfate media with a pH value of approximately 3, a fraction of the oxidation, which increases with increasing acidity, occurs very rapidly; the remainder of the oxidation proceeds very slowly In such solutions there appears to be present some colloidal cerium(IV) species; it is assumed that it is this species which is responsible for the slow part of the reaction.

Equilibrium in the reaction of cerium(IV) and bromide ion to yield cerium(III) and bromine (or tribromide ion) in sulfuric acid media greatly favors the products. Using the oxidation potential values summarized by Latimer,[3] one calculates the value 7×10^{11} for the equilibrium quotient for the reaction

$$2Ce^{IV} + 2Br^- = 2Ce^{III} + Br_2(aq.)$$

in one molar sulfuric acid.[4] The rate of this unidirectional reaction is conveniently measurable at 25° over a wide range of concentration conditions. It has been possible to represent the rate data by a relatively simple rate law and this has been interpreted in terms of a reasonable mechanism.

Experimental Techniques and Results

Equipment and Reagents.—All spectrophotometric determinations were made using a Beckman Model DU spectrophotometer. The absorption of light by the reaction mixture was determined in cells with ground glass stoppers to prevent the loss of bromine. A thermostating arrangement for the cells was used. The temperature of the solutions was measured at the termination of each experiment. The average values of this temperature for the experiments of each series with the average deviation of the temperature in the several runs from this average value for each series were: 1, 25.4 ± 0.4°; 2, 25.1 ± 0.2°; 3, 25.0 ± 0.2°; 4, 25.0 ± 0.1°; 5, 25.3 ± 0.3°; 6, 25.0 ± 0.2°; 7, 25.0 ± 0.3°; 8, 24.6 ± 0.2°; 9, 24.4 ± 0.2°; 10, 25.0 ± 0.1°; 11, 25.0 ± 0.2°; 13, 25.3 ± 0.3°; 14, 25.9 ± 0.4°. Although the temperature control was not as good as might be desired, there was no evidence that the temperature variation was the most important source of error in this work.

All solutions were prepared using doubly distilled water; the second distillation was from an alkaline permanganate solution. The source of each reagent and the method of determination of its concentration is as follows: reagent grade sodium or potassium bromide was recrystallized and the stock solutions were standardized using silver nitrate; reagent grade sodium sulfate was recrystallized and standardized using a gravimetric barium sulfate determination; three different types of sources of ammonium sulfate were used, reagent grade material was weighed directly, reagent grade material was recrystallized and standardized gravimetrically, and a solution was prepared using ammonia and sulfuric acid solution; reagent grade lithium perchlorate was recrystallized once, twice, or three times and was standardized by conversion of an aliquot of the stock solution to the sulfate for direct weighing; reagent grade sodium perchlorate was recrystallized once or twice and determined by direct weighing of an aliquot of solution which had been heated to dryness; reagent grade sodium chloride was weighed directly or recrystallized and standardized using silver nitrate; the solution of cerium(IV) perchlorate in perchloric acid obtainable from G. F. Smith Chemical

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[1] Presented before the 123rd meeting of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

[2] This work has been supported in part by a grant from the U. S. Atomic Energy Commission.

[3] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 60, 294.

[4] This calculation is an approximate one since the bromine-bromide potential which was used was the E^0 value and not the value for a one molar sulfuric acid solution.

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS IN RUNS WITH VARYING CONCENTRATION OF BROMIDE ION

Series	No. of runs	Bromide ion concn. range[m]	Stoichiometric concn.[m]			Best empirical rate eq. for k_1[n]	Av. % deviation
			(HSO_4^-)	$(SO_4^=)$	(H^+)		
1[a,b]	16	0.50 – 0.10	0.50	1.00	..	$k_1 = 0.036(Br^-)^2$	11
2[a,c]	8	.50 – .07	.50	0.25	..	$= 0.14(Br^-)^2$	14
3[a,d]	10	.40 – .04	.20	0.10	..	$= 0.31(Br^-)^2$	6.1
4[e]	10	.09 – .01	.30	..	0.75	$= 0.087(Br^-) + 5.7(Br^-)^2$	5.2
5[f]	9	.024 – .001	.20	..	1.81	$= 0.70(Br^-) + 71(Br^-)^2$	2.2
6[g]	5[k]	.0018 – .0004	.10	..	3.0	$= 11.9(Br^-)$	4
7[h]	18	.30 – .033	.50	0.25	..	$= 0.020(Br^-) + 0.14(Br^-)^2$	6.7
8[i]	11	.039 – .0039	1.02	..	0.98	$= 0.33(Br^-) + 1.22(Br^-)^2$	6.3

[a] $((Br^-) + (ClO_4^-)) = 0.50$; principal cations present are ammonium ion and sodium ion. Calculated actual concentrations: [b] $(HSO_4^-) = 0.31$; $(SO_4^=) = 1.19$; $(H^+) = 0.19$. [c] $(HSO_4^-) = 0.30$; $(SO_4^=) = 0.45$; $(H^+) = 0.20$. [d] $(HSO_4^-) = 0.11$; $(SO_4^=) = 0.19$; $(H^+) = 0.09$. [e] $(HSO_4^-) = 0.26$; $(SO_4^=) = 0.037$; $(H^+) = 0.79$. [f] $(HSO_4^-) = 0.18$; $(SO_4^=) = 0.024$; $(H^+) = 1.83$. [g] $(HSO_4^-) = 0.087$; $(SO_4^=) = 0.013$; $(H^+) = 3.01$. [h] $(Cl^-) = 2.0$; principal cations present are ammonium ion and sodium ion. [i] $(Cl^-) = 1.83$; principal cations present are sodium ion and hydrogen ion. [k] In the experiments in this series, the initial concentration of bromide was not extremely high compared to the initial concentration of cerium(IV); therefore, the reaction was not first order under these conditions. The fifteen points in Fig. 1 were determined in five runs, which were made using the second of the spectrophotometic techniques which have been described. [m] All concentrations are expressed in moles/liter. [n] The dimension of k_1 is min.$^{-1}$.

Company was the source of cerium(IV) in most runs, a solution prepared by the electrolysis of a cerium(III) perchlorate solution which had been prepared from recrystallized cerium(III) chloride also was used; reagent grade hydrochloric acid, sulfuric acid and perchloric acid were standardized volumetrically. There was no apparent effect of the source of the several reagents upon the rate of the reaction.

Spectrophotometric Determination of the Rate Constants.—All of the rate constants which have been determined in this work were evaluated spectrophotometrically. The absorption of light by bromine, which is produced, relative to that of cerium(IV), which is consumed, depends upon the bromide ion concentration since it is the bromide ion concentration which determines the relative amounts of bromine and tribromide ion. At the wave lengths studied, tribromide ion absorbs more strongly than bromine. At the highest bromide ion concentration which was studied (0.50 M), 90% of the bromine produced was present as tribromide ion, while at the lowest bromide ion concentration which was studied (4×10^{-4} M), only 0.7% was present as tribromide ion. The value of the equilibrium quotient for the reaction $Br_2(aq.) + Br^- = Br_3^-$ which was used in these calculations was 17.[5] In many of the experiments, the absorption of light by bromine(0) at the wave length 450 mμ is as high as 50% of the absorption of an equivalent amount of cerium(IV). (At shorter wave lengths this fraction is smaller.) Even under the least favorable conditions, however, the absorption of light provided a convenient means of following the reaction.

In most of the experiments which have been performed, the initial concentration of cerium(IV) was very low (5×10^{-4} to 10^{-3} M) compared to the concentration of other substances which influence the rate. Since the reaction was found to be first order with respect to the concentration of cerium(IV), it has been convenient to determine the pseudo-first-order rate constants by a modification[6] of the Guggenheim method.[7] The absorption of light by the reaction mixture at infinite time need not be known in this method. In the experiments followed by this means, the average value of the time interval between the start of the two reaction mixtures was five half-times. No trend in the values of the rate constant with the magnitude of this time interval was observed. In general, each experiment was followed at two wave lengths differing by 10 mμ; the wave length range used in this work was 380 to 450 mμ. The average difference between the two values of k_1, the pseudo-first-order rate constant, was 2.2% if all of the experiments are considered.

A linear dependence of the logarithm of the apparent optical density upon time (modified Guggenheim method[6]) was observed in runs which were followed to as great an extent as 95.4% of completion. The average value of the extent to which the reaction was followed was 63%. With the exception of certain experiments, which will be mentioned, no deviations from first-order behavior were observed. The rate of the reaction must be independent of the concentration of cerium(III) and bromine(0) since the concentrations of these substances changed enormously over the course of most of the experiments.

Another spectrophotometric technique which was used in some experiments involved the measurement of the optical density of a reaction mixture *versus* a water blank. This was useful for experiments in which the light absorption by the products was small compared to the absorption by the colored reactant; this condition prevailed at the lowest bromide ion concentrations which were studied. This method was also preferred to the modified Guggenheim method[6] if the reaction rate was large, since in this method only the absorption of the one solution was changing with time while in the modified Guggenheim method both the "sample" and the "blank" were changing with time. The data obtained in experiments followed by this method conformed to the equation $(D_t - D_\infty) = (\text{const.})e^{-k_1t}$; a graph of log $(D_t - D_\infty)$ *versus* time gave a straight line, from the slope of which the first-order rate constant may be calculated. (The quantities D_t and D_∞ are the optical densities at the times t and infinity, respectively. The value of D_∞ was calculated from the concentration conditions and the known extinction coefficients.)

The numerical values of k which are presented in this paper were calculated by the method of averages.[8] The number of readings taken per experiment ranged from 12 to 40 with an average of 21 for all of the experiments being reported.

Bromide Ion Concentration Dependence.—Six series of experiments have been performed in which the bromide ion concentration has been varied. It has been possible to maintain the rate of the reaction in a conveniently measurable range by using different sulfate ion concentrations in the several series of experiments. (It will be seen that the concentration of sulfate ion influences the rate of the reaction significantly.) The results of these experiments are summarized in Table I. The values of the single parameter, k_{12}, in the empirical rate equation $k_1 = k_{12}(Br^-)^2$ for each of the series 1, 2 and 3 is the average of the values determined for each experiment. The value of the single parameter, k_{11}, in the rate equation $k_1 = k_{11}(Br^-)$ for series 6 is the average of the fifteen values determined in five experiments (see footnote k, Table I). The values of the two parameters, k_{11} and k_{12}, in the empirical rate equation $k_1 = k_{11}(Br^-) + k_{12}(Br^-)^2$ for series 4, 5, 7 and 8 were determined by the method of averages.[8] The average deviations which are listed in Table I are the averages of the percentage differences between the observed values of k_1 and the values calculated using the empirical equation. Both the empirical equations and the experimental points are presented in Fig. 1. It is to be noted that in those series of experiments (1,

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[5] R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

[6] E. L. King, THIS JOURNAL, **74**, 563 (1952).

[7] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

[8] F. Daniels, J. H. Mathews and J. W. Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 369.

2 and 3) in which the bromide ion contributes significantly to the ionic strength, the sum of the concentrations of bromide ion and perchlorate ion was constant. In series 4, 5 and 6, the change in the ionic environment, due to the change of the bromide ion concentration, was not large. It is felt, therefore, that the correlation of data within a particular series (1 through 6) is not subject to any large uncertainty due to a medium effect.

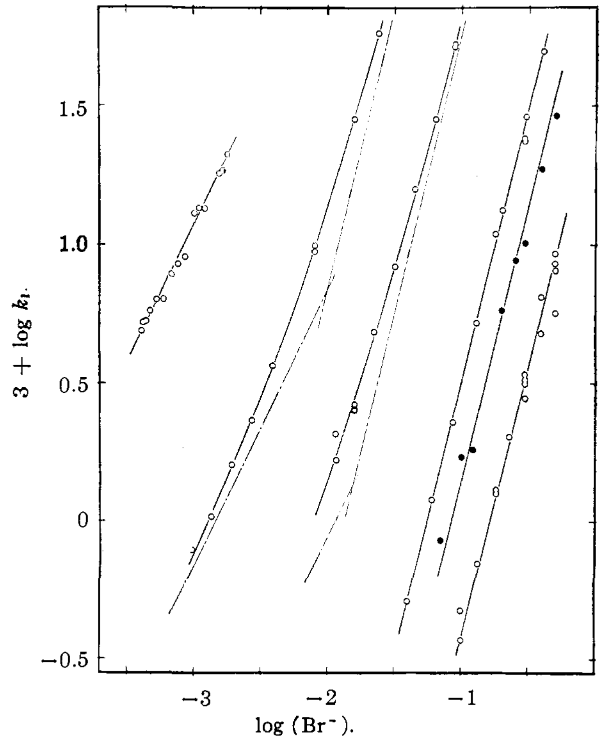

Fig. 1.—Logarithm of k_1 *versus* logarithm of bromide ion concentration. The curves are, from right to left, for series 1, 2, 3, 4, 5 and 6 (see Table I). The solid lines are calculated using the equations given in Table I. The two broken lines for series 4 and 5 have slopes 1 and 2, and are the lines which combine to give the solid lines.

The Electrolyte Effect upon the Reaction Rate.—A series of experiments with varying concentrations of sodium perchlorate has been performed; the concentration conditions were 0.29 *M* sodium bromide, 0.50 *M* ammonium bisulfate and 0.25 *M* ammonium sulfate. The values of $10^3 \times k_1$ observed at 0.25, 0.50, 1.00 and 1.50 *M* sodium perchlorate were 10.2, 9.3 (av. of 8.9 and 9.6), 9.3 and 10.6 (av. of 10.0 and 11.1) min.$^{-1}$, respectively. In contrast to this small effect was the effect of lithium perchlorate upon the rate. A series of experiments at the same concentration conditions as those performed to determine the effect of sodium perchlorate was performed with lithium perchlorate. The values of $10^3 \times k_1$ observed at 0.25, 0.50, 1.00 and 1.50 *M* lithium perchlorate were 10.8, 13.3 (av. of 12.4 and 15.1), 15.3 (av. of 14.9, 15.2, 15.5 and 15.6) and 19.6 (av. of 18.4, 19.4, 20.2 and 20.5) min.$^{-1}$, respectively. It appears that the enhancement of the rate by lithium perchlorate compared to sodium perchlorate at the same concentration is approximately proportional to the concentration of the lithium perchlorate ($((k_1)_{LiClO_4} - (k_1)_{NaClO_4})/(LiClO_4) = 8$, 6 and 6 at 0.50, 1.0 and 1.5 *M* lithium perchlorate, respectively).

These experiments have been performed under concentration conditions which make the term $k_{12}(Br^-)^2$ the important one. The electrolyte effect may be rather different under concentration conditions which favor the term $k_{11}(Br^-)$.[8a]

Catalysis by Chloride Ion.—The addition of sodium chloride to the reaction mixture increased the reaction rate significantly under the same bromide ion, bisulfate ion and sulfate ion concentration conditions which existed in the experiments where the effect of sodium perchlorate was small (see preceding section). This effect has been interpreted in terms of a specific catalysis by chloride ion. The dependence of the reaction rate, in the presence of chloride ion, upon the concentration of bromide ion was determined in two series of experiments (series 7 and 8). The results are summarized in Table I and in Fig. 2. First- and second-order dependence of the rate upon the bromide ion concentration was approached at low and high bromide ion concentrations, respectively. It is of interest to note that the coefficient of the term which involves the square of the bromide ion concentration is the same for series 2 and 7. It seems reasonable to interpret the closeness of these two values of k_{12} as an indication that chloride ion is not a catalyst for the reaction path which involves two bromide ions.

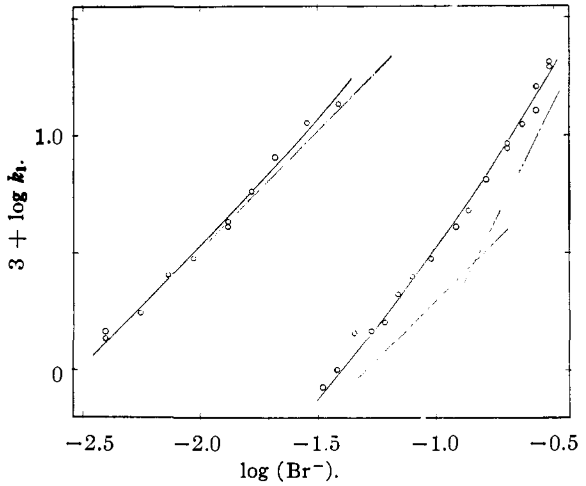

Fig. 2.—Logarithm of k_1 *versus* logarithm of bromide ion concentration for experiments involving solutions containing chloride ion. The curves are, from right to left, for series 7 and 8 (see Table I). The solid lines are calculated using the equations given in Table I. The broken lines for series 7 have slopes 1 and 2, and are the lines which combine to give the solid line. The broken line for series 8 is the line of slope 1 which the solid line is approaching at a low bromide ion concentration.

A series of experiments at constant ionic strength (series 9) involving a varying concentration of chloride ion, at a bromide ion concentration which favors the first-order bromide term, was performed with the purpose of establishing the dependence of the rate upon the concentration of chloride ion. The data are presented in Fig. 3; the solid line in this figure conforms to the equation $10^3 \times k_1 = 5.0(Cl^-) + 5.0$. Since these experiments were carried out at a single concentration of bromide ion, the bromide ion concentration dependence of the term which involved the concentration of chloride ion was not known with certainty; it seemed reasonable, however, to suggest that the dependence was first order with respect to the concentration of bromide ion. The enhancement of the rate in the presence of chloride ion was not due, to any appreciable extent, to the intermediate formation of molecular chlorine. This followed from the fact that the enhancement of the rate of reduction of cerium(IV) in the presence of bromide ion and chloride ion was much greater than the rate of reduction of cerium(IV) by chloride ion under these conditions but in the absence of bromide ion.

Sulfate Ion, Bisulfate Ion and Hydrogen Ion Dependence.—In the determination of the manner in which the concentrations of these ions influenced the rate of the reaction, certain difficulties were encountered. The ionization con-

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[8a] NOTE ADDED IN PROOF.—The observed electrolyte effect is the resultant of the effect of electrolyte upon the concentration of sulfate ion (the effect of which is discussed elsewhere in this paper) and the electrolyte effect upon the values of k_{11}' and k_{12}'. Since an increase in the concentration of electrolyte increases the concentration of sulfate ion, the observed small effect of sodium perchlorate upon the value of k_{12} indicates that k_{12}' increases with an increase in ionic strength.

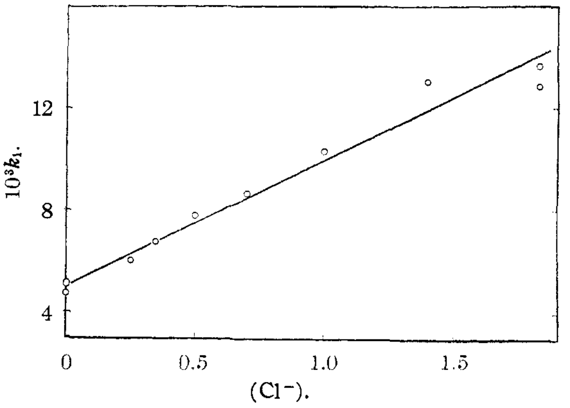

Fig. 3.—k_1 *versus* chloride ion concentration. The solid line conforms to the equation $10^3 k_1 = 5.0 \times (Cl^-) + 5.0$. The concentration conditions for the experiments were: 0.039 *M* sodium bromide, 1.00 *M* sulfuric acid, 0.02 *M* ammonium sulfate and $(2.0 - (Cl^-))$ *M* sodium perchlorate.

stant of bisulfate ion has the value 0.010 at zero ionic strength and 25°[9]; the value of the concentration equilibrium quotient in solutions of an ionic strength greater than zero is expected to be greater than 0.010. Approximate values of the quotient $K = (H^+)(SO_4^=)/(HSO_4^-)$ as a function of the ionic strength were calculated upon the assumption that $K/K^\circ = (y\pm)^2_{NaClO_4}/(y\pm)^3_{Na_2SO_4}$. Although this activity coefficient term has the correct form, the assumption that the K/K° values in the media being studied are equal to the values of the activity coefficient ratio which involves the activity coefficients of sodium perchlorate and sodium sulfate in solutions of only a single electrolyte is very uncertain. In addition, it has been suggested that sodium sulfate is not completely dissociated.[10] If this is true, the choice of its activity coefficient as a model for a strong 1–2 electrolyte was a poor one; no better choice was immediately obvious, however. By a method of successive approximations, the concentrations of the several species were calculated for each of the solutions studied. The concentration of sulfate ion so calculated was as high as five times the stoichiometric concentration of sulfate ion, this extreme being realized in a solution containing a large excess of bisulfate ion. Forty-two experiments (series 10) in which the calculated concentrations of sulfate ion and bisulfate ion were 0.1 to 0.6 *M* and 0.03 to 0.44 *M*, respectively, were performed. The ratio of the extreme values of k_1 which were observed was 5.0, of $k_1 \times (SO_4^=)$ was 1.7, and of $k_1 \times (HSO_4^-)$ was 22. For this complete series of experiments (series 10), in which the bromide ion concentration was 0.30 *M* and the range of the ionic strength was 0.8 to 2.8, the average value of $k_1 \times (SO_4^=)$ was 5.1 moles liters^{-1} min.$^{-1}$ with an average difference of 15% between the observed values of this product and the average value. The scattering of the data was not random, however; in a given set (the same stoichiometric concentration of ammonium sulfate and a varying stoichiometric concentration of ammonium bisulfate), the value of $k_1 \times (SO_4^=)$ increased with an increasing concentration of sulfate ion and bisulfate ion. It is possible that a different assumption regarding the dependence of the ionization quotient for bisulfate ion upon ionic strength would lead to a more completely consistent interpretation. The calculated values of the sulfate ion concentration in the experiments of series 1, 2 and 3 presented in Table I are 1.19, 0.45 and 0.19 *M*, respectively. The values of the product $k_{12} \times (SO_4^=)$ are 43, 62 and 59 moles^{-1} liters min.$^{-1}$, respectively. The value of $k_{12} \times (SO_4^=)$ calculated from the average value of 5.1 for $k_1 \times (SO_4^=)$ in the 42 experiments at 0.30 *M* bromide ion is 5.1/0.09 = 57 moles^{-1} liters min.$^{-1}$. Over the whole range of sulfate ion concentration from 1.25 *M* down to 0.1 *M*, the reaction rate is inversely proportional to the concentration of sulfate ion.

It was observed in a series of experiments (series 11) at a stoichiometric composition of 1 *M* ammonium sulfate, 0.3 *M* sodium bromide and 0.50 to 3.0 *M* ammonium bisulfate that the rate was increased at the higher concentrations of ammonium bisulfate; the increase in k_1 was approximately twofold in going from 1 to 3 *M* ammonium bisulfate. The actual concentration of sulfate ion increased as the ammonium bisulfate concentration increased; this change would decrease the rate. The reason for the increase may be merely an electrolyte environment effect due to the high ionic strength or it may be due to a specific effect of bisulfate ion upon the rate.

It is at ammonium bisulfate concentrations just below the concentration at which this increase in rate became noticeable that an anomalous behavior was observed. In a number of experiments (series 12) performed using both of the spectrophotometric techniques, the reaction appeared to be slightly less than first order in cerium(IV). The stoichiometric concentrations under which this behavior was observed are: (12a) 0.1 *M* $(NH_4)_2SO_4$, 0.7–2 *M* NH_4HSO_4; (12b) 0.17 *M* $(NH_4)_2SO_4$, 1.0–2 *M* NH_4HSO_4; (12c) 0.25 *M* $(NH_4)_2SO_4$, 1.3–2 *M* NH_4HSO_4; all of the experiments were carried out at 0.3 *M* bromide. No rationalization of this behavior has been devised.

Two series of experiments (series 13 and 14) were performed in which the concentration of bisulfate ion, bromide ion, and the sum of the hydrogen ion and sodium ion concentrations were kept constant while the hydrogen ion concentration was varied. The value of k_1 is proportional to approximately the 1.7 power of the hydrogen ion concentration; this is shown in Fig. 4. This dependence of the rate upon the concentration of hydrogen ion at a constant concentration of bisulfate ion is not consistent with the rate being only inversely proportional to the sulfate ion concentration. The results of the experiments of series 4, 5 and 6, experiments in which the sulfate concentration is low, indicate this trend also. That is, at low sulfate ion concentrations and/or high hydrogen ion concentrations, the reaction rate is proportional to the sulfate ion concentrations raised

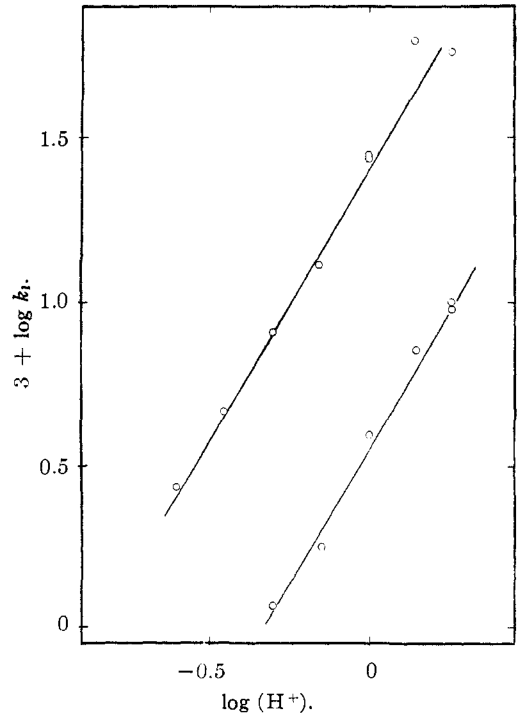

Fig. 4.—Logarithm k_1 *versus* logarithm (H^+). Concentration conditions: both series, 1.8 *M* perchlorate ion, 0.20 *M* bisulfate ion, the sum of the concentration of hydrogn ion and sodium ion equals 2.0 *M*. Upper curve (series 13), 0.024 *M* bromide ion; lower curve (series 14), 8×10^{-3} *M* bromide ion. Both solid lines have a slope of 1.7.

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[9] T. F. Young, I. M. Klotz and C. R. Singleterry, quoted in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 430.

[10] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

to a power more negative than −1 and/or the hydrogen ion concentration raised to a positive power. The experiments have not been extensive enough to establish the form of the rate law which is valid under these concentration conditions.

Since the experiments run at a low bromide ion concentration (series 4, 5, 6, 13 and 14) were the experiments in which this dependence of the rate upon the sulfate ion concentration was not minus first power, one might be led to the conclusion that this new dependence upon the sulfate ion concentration is incorporated only in the rate law term which involves a first-order bromide ion concentration dependence. As will be indicated, this is not true; the rate of the reaction was conveniently measurable only if the runs at low bromide ion concentration were carried out in the presence of a low sulfate ion concentration, and *vice versa*.

In the series 4 and 5, which are summarized in Table I, the rate law includes both terms. If the dependence of the two constants k_{11} and k_{12}, defined in the equation $k_1 = k_{11}(\mathrm{Br}^-) + k_{12}(\mathrm{Br}^-)^2$, upon the concentrations of hydrogen ion, sulfate ion and bisulfate ion were the same, the ratio of k_{12} to k_{11} would be the same in the two series. This ratio has the values 65 and 100 for series 4 and 5, respectively. These values are close enough to one another to suggest that the dependence of k_{11} and k_{12} upon the concentrations of hydrogen ion, sulfate ion and bisulfate ion is the same. This was confirmed by the results in a series of three experiments (series 15) at 1.00 *M* sulfuric acid, 0.02 *M* ammonium sulfate, and 0.013 to 0.07 *M* sodium bromide. The values of k_1 are given by the equation

$$k_1 = 0.025((\mathrm{Br}^-) + 80(\mathrm{Br}^-)^2)$$

in which the ratio of k_{12} to k_{11} is the same as the average of the two values determined in more extensive series of experiments (series 4 and 5).[11]

There is considerably more uncertainty in the establishment of the order of the reaction with respect to sulfate ion, bisulfate ion and hydrogen ion than in the determination of the order with respect to bromide ion. It was possible to maintain the medium approximately constant in the series of experiments in which the bromide ion concentration was varied. This was not possible in the series of experiments in which the sulfate ion concentration varied. In addition to the uncertainties in the value of the concentration of sulfate ion, which have been discussed, a kinetic medium effect due to the presence of divalent anions may exist; this medium effect would not have been disclosed by the studies involving varying concentrations of sodium perchlorate. The principal conclusion that the reaction rate is inversely proportional to the concentration of sulfate ion is felt to be a valid one, however.

The Reaction of Cerium(IV) and Iodide.—It has been reported[12] that the oxidation of iodide ion and leuco malachite green by cerium(IV) in an ammonium bisulfate–ammonium sulfate buffer with a *p*H of 3 proceeds in two stages. A fraction of the oxidation, which increases with increasing acidity, occurs at too great a rate to measure; the remainder of the oxidation proceeds very slowly. Since this is observed for both reducing agents, Swain and Hedberg suggested that this unusual behavior is a characteristic of the cerium(IV). Experiments involving cerium(IV) and iodide have been carried out in the current work and the observations of Swain and Hedberg have been confirmed. In addition, it has been observed that the apparent extinction coefficient of cerium(IV), $\bar{\epsilon}$ ($\bar{\epsilon} = \log(I_0/I)/(\mathrm{Ce^{IV}})l$, where l is the cell length), decreases very markedly in sulfate media if the *p*H value is increased above approximately 2.5. At a *p*H value of 4, the values of $\bar{\epsilon}$ at 380 and 400 mμ are 17 and 10% respectively, of their values over the *p*H range 1.4 to 2.4, in which range the value of $\bar{\epsilon}$ is approximately constant. It is suggested that in sulfate media of *p*H value greater than 2.5 and a cerium(IV) concentration of approximately 5×10^{-4}, an appreciable fraction of the cerium(IV) is present as a colloidal hydroxide or basic sulfate[13] which is *not* in rapid equilibrium with the solution. The observations of the kinetics of the cerium(IV)–iodide reaction are consistent with this if the reaction rate between the colloidal cerium(IV) species and the reducing agent is low while the rate of the reaction between simply dispersed cerium(IV)–sulfate species and iodide ion is too large to measure.

Discussion

The form of the rate equation for a chemical reaction gives the composition of the activated complex for the reaction. The data in the sulfate ion concentration range 0.1 to 1.2 *M* conform to the rate equation

$$-\frac{\mathrm{d}(\mathrm{Ce^{IV}})}{\mathrm{d}t} = \frac{(\mathrm{Ce^{IV}})}{(\mathrm{SO_4^{=}})}\{k'_{12}(\mathrm{Br}^-)^2 + k'_{11}(\mathrm{Br}^-)\}$$

The two independent terms indicate that activated complexes of two different compositions are important. The one contains one cerium, one *fewer* sulfate ion and two *more* bromide ions than the average number of these ions which are associated with cerium(IV). The other contains one cerium, one *fewer* sulfate ion and one *more* bromide ion than the average number of these ions which are associated with cerium(IV). Therefore, the average number of sulfate ions and bromide ions which are associated with cerium(IV) must be known before the actual compositions of the activated complexes are known.

Using the assumption regarding the dependence of the ionization quotient of bisulfate ion, which has already been discussed, a value of 70 for the equilibrium quotient $(\mathrm{Ce(SO_4)_3^{=}})/(\mathrm{Ce(SO_4)_2})(\mathrm{SO_4^{=}})$ at an ionic strength of 2 is calculated from the value of 20 presented by Hardwick and Robertson[14] for the equilibrium quotient $(\mathrm{Ce(SO_4)_3^{=}})(\mathrm{H^+})/(\mathrm{Ce(SO_4)_2})(\mathrm{HSO_4^-})$. Therefore, at the sulfate ion concentrations now being considered, approximately 90% or more of the cerium(IV) is present as the complex $\mathrm{Ce(SO_4)_3^{=}}$. One would conclude that the two different activated complexes each involve two sulfate ions. It seems very unlikely that cerium(IV) bromide complex ions are present at an appreciable concentration in the presence of sulfate ion at the concentrations which exist in the solutions being studied. (A basis for the suggestion that cerium(IV) bromide complex ions are not present at an appreciable concentration in the solutions containing both sulfate ion and bromide ion is the observed greater tendency for sulfate complex formation than for chloride complex formation with zirconium(IV)[15] and thorium(IV).[16] The

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[11] The concentration conditions for series 15 are like those of series 8 (Table I) except no sodium chloride is present. In contrast to the identical values of k_{12} for series 2 and 7, which differ in this same respect, the values of k_{12} for these two series are 2.0 (series 15) and 1.22 (series 8). This difference is probably due to the difference in the actual concentration of sulfate ion in series 8 and 15 which results because of the change of ionic strength. A given percentage change in the value of the equilibrium quotient for the ionization of $\mathrm{HSO_4^-}$ leads to a larger percentage change in the concentration of sulfate ion under the conditions of series 8 and 15 (high hydrogen ion and bisulfate ion concentrations) than under the conditions of series 2 and 7 (high bisulfate ion and sulfate ion concentrations).

It is to be noted that the trend in the value of the ratio of k_{12} to k_{11}, 65 (series 4), 80 (series 15), and 100 (series 5), follows the trend in the ionic strength (i.e., 0.9 (series 4), 1.3 (series 15), and 1.9 (series 5)). This suggests that the value of k_{12}' increases with an increase of ionic strength more than does the value of k_{11}', which is reasonable in view of the values of ΔZ^2 for the reactions of formation of the two different activated complexes.

[12] C. G. Swain and K. Hedberg, THIS JOURNAL, **72**, 3373 (1950).

[13] The *p*H value at which the occurrence of this colloidal material becomes important will be lower the higher the cerium(IV) concentration.

[14] T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

[15] R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

[16] E. L. Zebroski, W. H. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

bromide complex ions would be expected to be even less stable than the chloride complex ions.) The two different activated complexes must involve one and two bromide ions, and must, therefore, have the compositions, $Ce(SO_4)_2Br_2^=$ and $Ce(SO_4)_2Br^-$. The kinetic data do not identify the products of the decomposition of these activated complexes; certain conclusions are reasonable however. The production of a cerium(II) species is *extremely* unlikely, and therefore bromide ion must undergo a one electron oxidation in the rate-determining step. The species formed upon decomposition of the two activated complexes are the bromine atom, possibly hydrated, and the complex species Br_2^-. The species Br_2^- has previously been suggested as an intermediate in various reactions.[17-19] The ratio of the values of k_{12} to k_{11} allows a calculation of the relative amounts of Br_2^- and Br(aq.) formed in the rate-determining steps. It will be recalled that the value of this ratio is approximately $80(Br^-)$. Since the value of 10^4 has been suggested for the equilibrium constant for the reaction[18]

$$Br + Br^- \rightleftharpoons Br_2^-$$

it appears that a smaller amount of Br_2^- relative to Br(aq.) is formed in the rate-determining steps at a particular bromide ion concentration compared to the relative amounts of these two species which are present at equilibrium in a solution of the same bromide ion concentration.

A mechanism which is consistent with this rate law is

$$Ce(SO_4)_3^= + Br^- \rightleftharpoons Ce(SO_4)_2Br^- + SO_4^= \quad (1)$$

$$Ce(SO_4)_2Br^- + Br^- \longrightarrow Ce(SO_4)_2^- + Br_2^- \quad (2)$$

$$Ce(SO_4)_2Br^- + aq. \longrightarrow Ce(SO_4)_2^- + Br(aq.) \quad (3)$$

The first reaction is a rapidly reversible equilibrium which lies far to the left. Reactions 2 and 3 are rate-determining steps; the products formed in these two steps, Br_2^- and Br(aq.), are rapidly converted to bromine. It is seen that the activated complexes in steps 2 and 3 have the compositions demanded by the form of the rate law.

The catalytic activity of chloride ion results from the introduction of an important activated complex of the composition $Ce(SO_4)_2BrCl^=$.[20] A mechanism analogous to that consisting of steps 1 and 2 in which a bromide ion in *either* step 1 *or* 2 is replaced by a chloride ion is consistent with the rate law.

If the only important activated complexes were those containing two sulfate ions, the reaction would become zero order in sulfate ion as the sulfate ion concentration was lowered to the point where the average number of sulfate ions associated with a cerium(IV) in the solution was two. Actually, the data of experiments carried out at a low concentration of sulfate ion (series 4, 5 and 6, and series 13 and 14) indicate that the order with respect to sulfate ion becomes more negative as the sulfate ion concentration is lowered. Therefore, activated complexes containing fewer than two sulfate ions must also play a role in this reaction. Such activated complexes become important, however, only at relatively low concentrations of sulfate ion since their concentrations decrease with increasing sulfate ion concentration.

The increase in rate with an increase in the concentration of bisulfate ion at high concentrations of bisulfate ion (series 11) indicates that activated complexes which involve one or more bisulfate ions probably become important at high concentrations of bisulfate ion.

The absence of any significant contribution to the rate by activated complexes which contain three sulfate ions strongly suggests that the bromide ion and cerium(IV) must come in "contact" for the electron transfer to occur. In order for "contact" to be made, one sulfate ion must be displaced from the first coördination sphere around the cerium(IV) by a bromide ion. It might then be asked why activated complexes containing two fewer sulfate ions than are contained in $Ce(SO_4)_3^=$ are important at low concentrations of sulfate ion. The answer may lie partially in a consideration of the nature of the cerium(III) species which is formed in the rate-determining step. Cerium(III)-sulfate complex ions[21] are much less stable than cerium(IV)-sulfate complex ions.[14] It appears, therefore, that a definite advantage, with respect to the lowering of the free energy of activation, results if some of the sulfate ions which must eventually be dissociated from the cerium are dissociated before the activated complex is formed.

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[17] R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **29**, 386 (1933).

[18] H. Taube, THIS JOURNAL, **70**, 3928 (1948).

[19] P. R. Carter and N. Davidson, *J. Phys. Chem.*, **56**, 877 (1952).

[20] The sulfate ion concentration dependence of the rate was not determined in the presence of chloride ion; it is merely a suggestion, therefore, that the activated complex which contains one chloride ion also contains two sulfate ions.

[21] R. E. Connick and S. W. Mayer, THIS JOURNAL, **73**, 1176 (1951).