squares yields the equations

$$1/\Phi_{\mathrm{Ce}^{+++}} = 31.2 + 0.730(\mathrm{Ce}^{+++})/(\mathrm{Tl}^{+}) \qquad \text{(I)}$$

$$1/\Phi_{\mathrm{Ce}^{+++}} = 20.5 + 0.495(\mathrm{Ce}^{+++})/(\mathrm{Tl}^{+}) \qquad \text{(II)}$$

Equation I is obtained from the data with 2×10^{-2} *M* cerous ion solutions while eq. II is obtained from the data with 10^{-2} *M* cerous ion solutions.

From eq. I and II, k_3/k_2 is evaluated by division of the intercept by the slope. From eq. I, k_3/k_2 is equal to 31.2/0.73 or 42.7. From eq. II, k_3/k_2 is equal to 20.5/0.495 or 41.4. The average value of 42 is in excellent agreement with the value of 38 measured[8] for the radiation chemistry of the same chemical system using cobalt-60 γ-radiation.

This comparison of the photochemistry with the radiation chemistry of ceric ion–cerous ion–thallous ion mixtures thus yields convincing evidence for the postulated formation of OH radical in the photoreduction of ceric ion in sulfuric acid solutions.

Let us assume that OH is an intermediate in perchloric acid and that OH radical can reduce[6] ceric ion in perchloric acid. Then, the following kinetic relationship can be derived

$$\frac{1}{\Phi_{\mathrm{Ce}^{+++}}} = \frac{1}{x\Phi_{\mathrm{OH}}} + \frac{k_2(\mathrm{Ce}^{+++})}{x\Phi_{\mathrm{OH}}k_y(\mathrm{Ce}^{4+})}$$

The value of x would be either 2 or 4 and k_y would be either k_6 or k_7 depending whether ceric ion oxidized OH radical according to reaction 6 or reaction 7

$$\mathrm{Ce}^{4+}\cdot\mathrm{H_2O} + \mathrm{OH} \longrightarrow \mathrm{Ce}^{+++} + \mathrm{H}^{+} + \mathrm{H_2O_2} \qquad (6)^{6}$$

$$\mathrm{Ce}^{4+} + \mathrm{OH} \longrightarrow \mathrm{Ce}^{+++} + \mathrm{H}^{+} + {}^{1}/{}_{2}\mathrm{O_2} \qquad (7)$$

Heidt and Smith[5] report that for 1.1×10^{-2} *M* ceric ion solutions in perchloric acid $1/\Phi_{\mathrm{Ce}^{+++}} = 5 + 670(\mathrm{Ce}^{+++})$. Thus, k_y/k_2 would have a value of 0.68. Whether reaction 6 or reaction 7 occurs could be determined if Φ_{OH} were known. This would have required a study of the effect of added solutes, such as reported here, which was not investigated by Heidt and Smith.[5]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TOLEDO]

A Study of the Kinetics of the Reaction between Oxalate Ion and Cerium(IV) in Aqueous Sulfuric Acid Solution

BY VANCE H. DODSON AND ARTHUR H. BLACK

RECEIVED FEBRUARY 7, 1957

The kinetics of the reaction between cerium(IV) and oxalate ion, bioxalate ion and oxalic acid in aqueous sulfuric acid has been studied over the temperature range of 19 to 35°. The reaction appears to be second order, and the rate of the reaction is dependent upon the concentration of sulfuric acid. The experimental energy of activation is 16.5 ± 0.4 kcal./mole in 0.5, 1.0 and 2.0 *M* sulfuric acid solutions.

Kinetic studies of the reactions between cerium(IV) and tin(II),[1] arsenic(III)[2] and oxalic acid[3] have been reported in the literature. In a recent examination of the reaction between cerium(IV) and oxalate ion[4] in aqueous sulfuric acid, it was noted that the rate of the reaction decreased as the concentration of the sulfuric acid was increased. Since the previously published work[3] merely established the order of the reaction, it was of interest to re-examine the kinetics of the reaction and attempt to establish a mechanism for it.

Experimental Part

Equipment and Reagents.—Reaction rates were determined by using a Bausch and Lomb Spectronic 20 colorimeter. The solutions were kept in a constant temperature bath, then mixed and immediately transferred to the cell and placed in the instrument. In all of the experiments conducted, the cell and its contents were never in the instrument longer than one minute. Over the temperature range of 19 to 35° this short exposure to the heat of the excitor lamp produced no deviations greater than ±0.1° in the reaction mixtures.

The reagents were prepared by dissolving anhydrous cerium(IV) acid sulfate (G. Frederick Smith Chemical Co.) and C.P. Special Grade anhydrous sodium oxalate (Baker Chemical Co.) in aqueous sulfuric acid of known molarity. The cerium(IV) solutions were standardized with iron(II). Ferrous *o*-phenanthroline was used as the indicator. The concentrations of the oxalate solutions were checked against the cerium(IV) solutions. Reagent grade sulfuric acid and distilled water were used in the preparation of the aqueous acid solutions. A series of 2.0, 1.0 and 0.5 *M* solutions was prepared. These were used as solvents in the cerium(IV) and oxalate solutions and as diluents in the reaction rate measurements. No special precautions were taken to protect the solutions from light and air.[5]

Spectrophotometric Determination of the Rate of Reaction.—The per cent. transmission of the standard cerium(IV) solutions was measured at 425, 450 and 475 mμ and found to obey Beer's law. The calibration curve at 450 mμ over the range of concentrations 0.0055 to 0.00025 *M* was the one most often used in these experiments. No significant variation in per cent. transmission of the cerium(IV) solutions was observed at any of these three wave lengths when the concentration of sulfuric acid was varied from 0.5 to 2.0 *M*.[6]

The following procedure was followed in measuring the reaction rates. The oxalate solution of known concentration, prepared by diluting a portion of the stock solution with sulfuric acid of appropriate molarity, was placed in a stoppered wide-mouth conical flask. The cerium(IV) solution of known concentration (in sulfuric acid of the same molarity as that in the oxalate solution) was placed in a stoppered soft glass test-tube whose bottom had been blown to form a thin-walled bulb. Both the bulb and flask were then placed in the constant temperature bath. At time zero the bulb of cerium(IV) solution was broken in the conical flask and the solutions were mixed by rapid swirling. A portion of the reaction mixture was immediately transferred to the colorimeter cell and per cent. transmission readings were taken at various time intervals.

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[1] C. H. Brubaker, Jr., and A. J. Court, THIS JOURNAL, **78**, 5530 (1956).

[2] J. S. Yates and H. C. Thomas, *ibid.*, **78**, 3950 (1956).

[3] S. D. Ross and C. G. Swain, *ibid.*, **69**, 1325 (1947).

[4] A. H. Black and V. H. Dodson, *J. Chem. Ed.*, **33**, 562 (1956).

[5] H. H. Willard and P. Young, THIS JOURNAL, **51**, 149 (1929).

[6] E. G. Jones and F. G. Soper, *J. Chem. Soc.*, 802 (1935).

The time required by the experimenters to mix the solutions and place them in the instrument varied from eight to ten seconds. The number of readings taken per experiment ranged from three to seven in number. The concentration of unreacted cerium(IV) at the various time intervals was then determined from a plot of the logarithm of per cent. transmission *versus* concentration that had been predetermined from the standard solutions.

Results

The initial concentration of the oxalate ion, bioxalate ion or oxalic acid was varied from 0.007 to 0.005 *M* in the experiments, while that of the cerium(IV) was approximately 0.01 *M*. The reaction was observed to be second order, first order each in cerium(IV) and oxalate, bioxalate or oxalic acid. A graphical treatment of the results of several typical experiments is shown in Fig. 1.

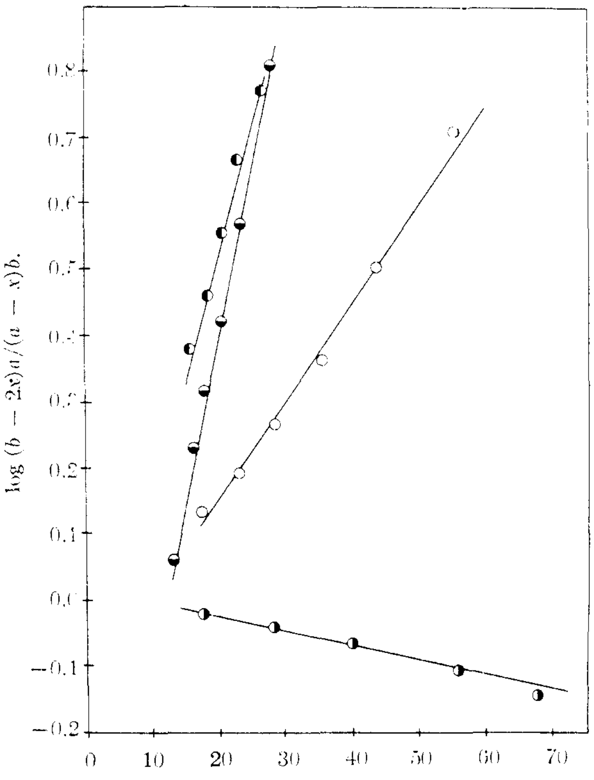

Fig. 1.—Typical second-order rate plots: ◐, a = 0.01045 *M* Ce(IV), b = 0.00613 *M* oxalate, in 1.0 *M* H_2SO_4 at 27°; ◒, a = 0.01045 *M* Ce(IV), b = 0.00750 *M* oxalate, in 1.0 *M* H_2SO_4 at 19°; ○, a = 0.01050 *M* Ce(IV), b = 0.00693 *M* oxalate, in 2.0 *M* H_2SO_4 at 25°; ◑, a = 0.01050 *M* Ce(IV), b = 0.00495 *M* oxalate, in 2.0 *M* H_2SO_4 at 25°.

The second-order rate constants that are reported in Table I were calculated from the slopes of plots similar to those of Fig. 1 and represent the average of several experiments. The deviations reported in Table I are average deviations.

The plots of log k *versus* $1/T$, shown in Fig. 2, for the reactions carried out in the three different concentrations of sulfuric acid have approximately the same slope. The activation energies calculated from the slopes of these plots are 16.9 kcal./mole (in 0.5 *M* acid), 16.7 kcal./mole (in 1.0 *M* acid) and 15.8 kcal./mole (in 2.0 *M* acid) and average 16.5 ± 0.4 kcal./mole.

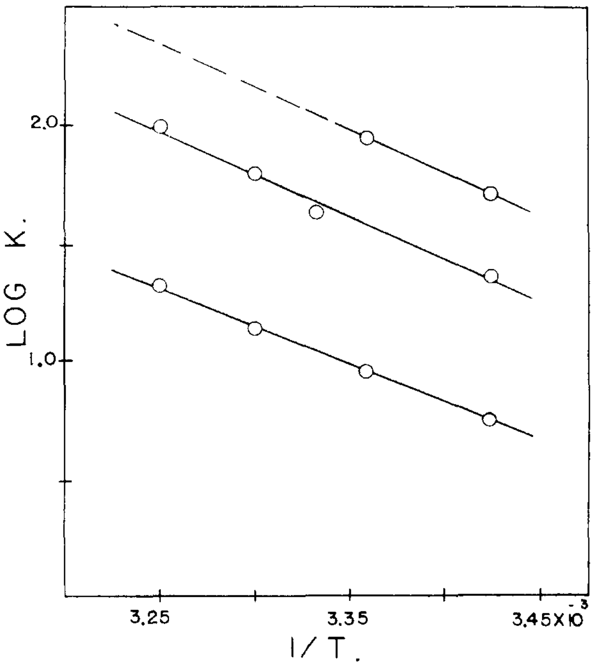

Fig. 2.—Arrhenius plot: upper curve, reactions in 0.5 *M* H_2SO_4; middle curve, reactions in 1.0 *M* H_2SO_4; lower curve, reactions in 2.0 *M* H_2SO_4.

TABLE I

RATE CONSTANTS FOR THE OXIDATION OF OXALATE BY CERIUM(IV) AT VARIOUS TEMPERATURES IN AQUEOUS SULFURIC ACID

No. of exp.	Concn. of H_2SO_4, *M*	Temp., °C. ±0.1°	$k_{av.}$, l. × mole^{-1} × sec.$^{-1}$
7	0.5	19.0	49.7 ± 8.7
8		25.0	87.6 ± 7.2
9	1.0	19.0	22.6 ± 0.9
10		27.0	42.8 ± 4.0
10		30.0	62.9 ± 4.3
4		35.0	97.0 ± 10.5
8	2.0	19.0	5.45 ± 0.26
9		25.0	9.02 ± 0.27
6		30.0	13.7 ± 0.7
6		35.0	20.9 ± 1.6

Discussion and Conclusions

The total ionic strength of each of the reaction mixtures examined in this work is extremely large in comparison with that of the reactants; and, as might be expected, the deviations in the reaction rates with changes in concentration of the reactants are not significant. Had there been a noticeable variation, an interpretation would not be entirely justified in view of the high ionic strength of the solutions.[7]

A plot of log k − log k_0 *versus* $\sqrt{\mu}$ is shown in Fig. 3. In this graph, log k_0 is the rate constant at infinite dilution with respect to sulfuric acid, k is the average measured rate constant (Table I), and μ is the total ionic strength of the hydrogen, bisulfate and sulfate ions in solution. The concentrations

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[7] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., New York, N. Y., 1946, Chap. 13.

of these ions were roughly estimated from the dissociation constants of oxalic acid and bisulfate ion.[8] Molar concentrations were converted to molalities and ionic strengths were derived from these latter values. The graph in Fig. 3 shows that the differences between log *k* and log k_0 over the temperature range 19 to 35° are approximately the same for solutions of similar ionic strength (with respect to sulfuric acid). This same conclusion can be reached by comparing the slopes of the curves in Fig. 2. The data plotted in Figs. 2 and 3 indicate that the same species of reactants are involved in the rate-determining step, regardless of the acidity of the reaction medium.

There is considerable evidence that the cerium(IV) ion exists primarily as the trisulfato complex ion in sulfuric acid solutions. This is especially true in acid concentrations such as those employed in this work.[6,9] It is also reasonable to assume that in these strongly acid solutions the oxalate is present mainly as oxalic acid with smaller amounts of bioxalate ion and only traces of oxalate ion. The rate-determining step must then be either (I) or (II)

$$2Ce(SO_4)_3^{-2} + HC_2O_4^{-1} \longrightarrow 2Ce^{+3} + 2CO_2 + 5SO_4^{-2} + HSO_4^{-1} \quad (I)$$

$$2Ce(SO_4)_3^{-2} + H_2C_2O_4 \longrightarrow 2Ce^{+3} + 2CO_2 + 4SO_4^{-2} + 2HSO_4^{-1} \quad (II)$$

Since both reactions I and II produce bisulfate ions, they might be expected to respond to a change in acid concentration. The presence of excess sulfate ions in the reaction medium would also tend to reduce the rate of the reaction. From the standpoint of the concentration of the reactants, an increase in acid concentration would tend to slow down reaction I and speed up reaction II. However, as the concentration of the sulfuric acid solutions is increased from 0.5 to 2.0 *M*, the concentration of bioxalate ion and oxalic acid remains fairly constant. Therefore, the noted effect of the acid on the reaction rates must be due to the excess sulfate, bisulfate and hydrogen ions in solution.

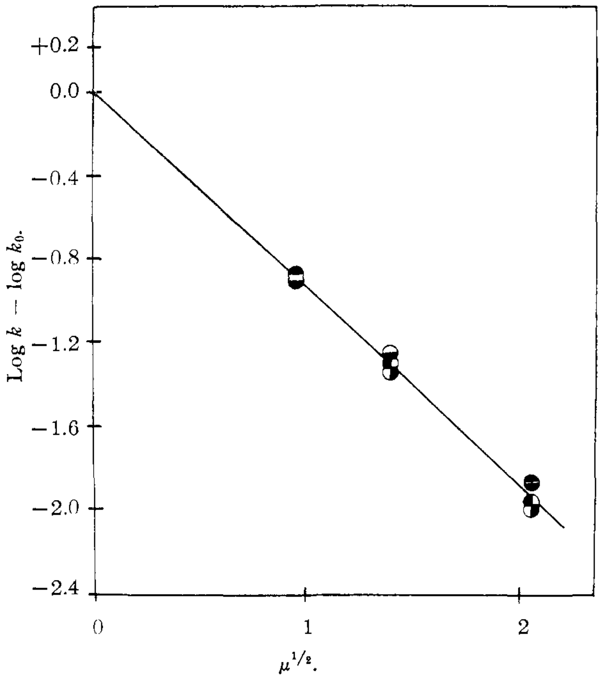

Fig. 3.—Relationship between measured second-order rate constants and ionic strength of acid medium: ◒, 19°; ◓, 25°; ◐, 30°; ◑, 35°.

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[8] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solution," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1949, Chap. 14.

[9] (a) G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938); (b) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AND FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Chemical Properties of Nitrosyl Perchlorate: The Neutralization Equivalent

BY MEYER M. MARKOWITZ, JOHN E. RICCI, RICHARD J. GOLDMAN AND PAUL F. WINTERNITZ

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The quantitative preparation of nitrosyl perchlorate from dinitrogen trioxide and perchloric acid is limited by the subsequent hydrolysis of the product below a minimum acid concentration. The neutralization equivalent weight of nitrosyl perchlorate under defined conditions is $NOClO_4/2$. Some aspects of the thermal behavior of the salt are treated briefly.

Introduction

Interest in the nitric oxide molecule stems from the diversity of bond types into which the group may enter.[1–3] Previous studies concerning nitrosyl perchlorate ($NOClO_4$), as representative of a compound containing a nitric oxide cation (NO^+), have dealt with the electrolytic behavior in anhydrous nitromethane,[4] the Raman spectrum in perchloric acid,[5] the crystallographic structure,[6] the heat of formation,[7] and the thermal decomposition.[8] The material to follow presents lab-

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[1] C. C. Addison and J. Lewis, *Quart. Revs. (London)*, **9**, 115 (1955).

[2] T. Moeller, *J. Chem. Educ.*, **23**, 441, 542 (1946).

[3] E. S. Gould, D. H. Ross and W. A. Fessler in R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 9, Interscience Encyclopedia, Inc., New York, N. Y., 1952, pp. 462–472.

[4] A. Hantzsch and K. Berger, *Z. anorg. allgem. Chem.*, **190**, 321 (1930).

[5] W. R. Angus and A. H. Leckie, *Trans. Faraday Soc.*, **31**, 958 (1935); *Proc. Roy. Soc. (London)*, **A150**, 615 (1935).

[6] L. J. Klinkenberg, *Rec. trav. chim.*, **56**, 749 (1937).

[7] K. Cruse, G. Huck and H. Moeller, *Z. anorg. Chem.*, **259**, 173 (1949); **260**, 295 (1949).

[8] K. Cruse, G. Huck and H. Moeller, *ibid.*, **259**, 159 (1949); K. Gerding and W. F. Haak, *Chem. Weekblad*, **52**, 282 (1956).