749. *The Kinetics of the Oxidation of Glycollic Acid by Ceric Sulphate*

By A. McAuley

Kinetic data for the oxidation of glycollic acid by ceric sulphate over a temperature range from 25 to 50° are reported. The effect of ionic strength and of sulphuric acid concentration on the reaction rate have been examined. The entropy and energy of activation have been found at 25° in 1M-sulphuric acid.

THE reactions of transition-metal ions with organic acids have been the subject of several recent studies. Waters *et al.*[1-3] have examined reactions involving the oxidation of α-hydroxy-acids with manganese(III), vanadium(V), and cerium(IV) as oxidant and have postulated mechanisms based on the formation of complexes between the metal species and the organic acid, which decompose to yield organic radicals. Further support for this mechanism has come from an investigation [4] of the differing rates of reaction of mandelic and α-deuteromandelic acids. Krishna and Tewari [5] examined the oxidation of mandelic, lactic, and DL-malic acids by ceric ions at 25°, and also studied the rate-dependence of the reaction on sulphuric acid concentration. No detailed study has been made of the reaction between ceric ion and glycollic acid, and little is known about the temperature-dependence of ceric oxidations.[6] The present investigation was undertaken to furnish this information and to study the effect of ionic strength on the reaction rate.

EXPERIMENTAL

The materials were of the highest purity available. AnalaR grade hexanitratoammonium cerate was dissolved in dilute sulphuric acid, and ceric hydroxide was precipitated on addition of concentrated ammonium hydroxide. In one series of solutions the precipitate was washed free from ammonium and nitrate ions, filtered, and dried at 150° for 48 hr. The oxide was then dissolved in sulphuric acid and the solutions diluted to the required ceric concentration with distilled water. Another series of stock solutions was prepared from the washed hydrated ceric oxide by immediate dissolution in sulphuric acid followed by dilution to the required concentration. No difference could be detected between the results given by the different stock solutions. The ceric content was estimated by titration against weighed portions of arsenic trioxide [7] (previously dried at 120°) with barium diphenylaminesulphonate as indicator. The sulphuric acid content was found by addition of 1—2 g. of sodium oxalate to a portion of the

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[1] A. Y. Drummond and W. A. Waters, *J.*, 1953, 435, 440.
[2] P. Levesley and W. A. Waters, *J.*, 1955, 217.
[3] J. S. Littler and W. A. Waters, *J.*, 1959, 1299.
[4] T. J. Kemp and W. A. Waters, *J.*, 1964, 1192.
[5] B. Krishna and K. C. Tewari, *J.*, 1961, 3097.
[6] K. P. Bhargawa, R. Shanker, and S. N. Joshi, *J. Sci. Ind. Res. India*, 1962, **216**, 573.
[7] A. I. Vogel, " Textbook of Quantitative Inorganic Analysis," Longmans, Green & Co., London, 1953.

stock solution. When the solution was heated, the ceric ion reacted with the oxalate [8] and was reduced to the colourless cerous species. Titration against standard sodium hydroxide then gave the amount of sulphuric acid present.

Glycollic acid (L. Light and Co.) was recrystallised three times from anhydrous ether. Excess of ether was removed under reduced pressure, and the material was heated in an air oven at 70° to remove any residual moisture (Found: C, 32·1; H, 5·5. Glycollic acid requires C, 31·6; H, 5·3%). Perchloric acid, sulphuric acid, and ferrous ammonium sulphate were of AnalaR grade.

Rate studies were made by allowing solutions of sulphuric acid and glycollic acid of the required concentrations to come to equilibrium for 1 hr. in a thermostatted bath controlled to ±0·1°. The reaction was started by rapid addition of ceric sulphate, and mixing was achieved by air bubbling. At intervals, 10 ml. portions of the reaction mixture were withdrawn and quickly transferred to a flask containing an excess of ferrous ammonium sulphate and cooled in ice. The excess of ferrous ion was then back-titrated against standard ceric sulphate. No attempt was made to exclude light, since previous oxidation studies with ceric ions [9] have shown that reaction rates are unaffected by light.

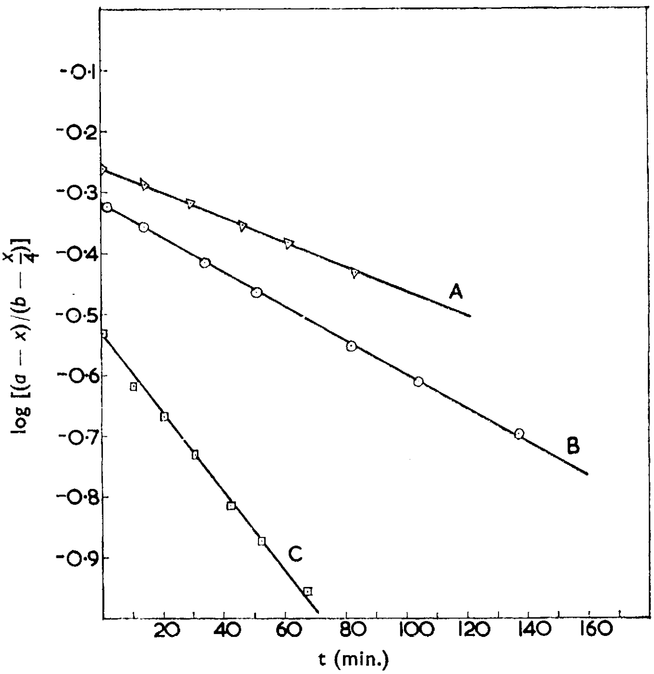

FIGURE 1. Typical rate data
Curve A; Run 4, $T = 50°$.
Curve B; Run 6, $T = 25°$.
Curve C; Run 7, $T = 35°$

The stoicheiometry of the reaction was determined by allowing reaction mixtures containing a large excess of ceric ion to stand for 4 days at 80°. The excess of ceric ion was then estimated as described previously. Duplicate experiments showed that 4·00 moles of ceric ion reacted per mole of glycollic acid.

RESULTS AND DISCUSSION

Rate studies were made at 25, 35, and 50°, and the reaction was found to be of first order for each reactant. The second-order rate constant, k_0, was derived from plots of log $[(a - x)/(b - \frac{x}{4})]$ against t, where a and b are the initial concentrations of ceric ion and glycollic acid, respectively, and x is the amount of cerium(IV) that has reacted after time t. Typical results are plotted in Figure 1 and duplicate experiments agreed to within ±3%. Kemp and Waters [4] give a value for the rate constant for this reaction of $1{\cdot}0 \times 10^{-4}$

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[8] V. H. Dodson and A. H. Black, *J. Amer. Chem. Soc.*, 1957, **79**, 3657.

[9] C. H. Brubaker and A. McAuley, unpublished results.

mole^{-1} sec.$^{-1}$ in 1·66M sulphuric acid at 26·6° Interpolation in the present results yields a value of 1·1 × 10^{-4} mole^{-1} sec.$^{-1}$, in good agreement under these conditions.

TABLE 1

Dependence of rate constant on sulphuric acid concentration

Run	10^3[Ce^{IV}] (M)	10^3[Glycollic] acid (M)	[H_2SO_4] (M)	10^4k_0 (mole^{-1} sec.$^{-1}$)	Run	10^3[Ce^{IV}] (M)	10^3[Glycollic] acid (M)	[H_2SO_4] (M)	10^4k_0 (mole^{-1} sec.$^{-1}$)
$T = 25°$									
1	7·304	7·926	1·00	3·15 ± 0·06	5	7·440	15·627	0·270	42·2
2	7·304	15·627	1·00	3·08 ± 0·05	6	7·568	15·780	0·182	74·9
3	14·500	24·500	1·00	3·03 ± 0·05	7	13·275	16·010	0·143	98·0
4	13·229	15·400	0·493	13·4	8	7·885	15·950	0·0894	199·0
$T = 35°$									
1	13·890	31·880	1·26	6·9	6	9·979	25·531	0·597	22·0
2	13·618	24·784	1·00	11·9 ± 0·05	7	10·817	37·176	0·384	72·5
3	5·771	30·362	1·00	13·7 ± 0·03	8	8·559	28·727	0·296	115·1
4	9·121	23·100	1·00	11·0 ± 0·02	9	14·259	23·780	0·196	232·0
5	14·621	21·277	0·815	18·3	10	7·565	25·266	0·104	591·0
$T = 50°$									
1	13·890	25·280	1·45	35·8	6	14·621	16·778	0·543	254
2	14·034	24·500	1·00	77·5 ± 1·6	7	13·229	30·361	0·491	308
3	14·034	25·535	1·00	77·9 ± 0·9	8	14·935	17·140	0·354	543
4	7·304	15·627	1·00	80·1 ± 1·8	9	12·078	13·860	0·246	946
5	19·843	22·771	0·737	139					

The reaction rate is dependent on the sulphuric acid concentration and the results of studies made at varying acid strengths are given in Table 1. Previous investigations of α-hydroxy-acid oxidations by cerium(IV) ions [5,6] have shown the rates to be inversely proportional to the square of the sulphuric acid concentration, the retardation being presumably due to competition between sulphate ions and the organic acid as ligands for the cerium(IV). Plots of k_0 against [H_2SO_4]$^{-2}$ were made at each temperature and these are shown in Figure 2. A linear relationship is seen at high acid concentrations, but at higher pH values there are marked deviations. The present experimental conditions are somewhat different from those in previous investigations, in that a wider range of acid concentrations was used. No attempt was made, however, to keep the ionic strength constant.

The significance of ionic strength was demonstrated in a series of reactions at 35°, where sulphuric acid concentrations were similar to those above, but where sodium perchlorate or sodium chloride was present to maintain an ionic strength of 2·0M. These experiments were only partially successful in that results from only the first 10% (in time) of the runs could be used. As the runs proceeded beyond this point, a yellow crystalline precipitate was seen to form. It had an infrared spectrum corresponding to sodium tetrasulphatocerate.

In their study, Krishna and Tewari [5] derived the dependence of the reaction rate on [H_2SO_4]$^{-2}$ from the equilibria

$$\mathrm{Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^-} \qquad (1)$$

$$\mathrm{HCe(SO_4)_3^- + HSO_4^- \rightleftharpoons H_2Ce(SO_4)_4^{2-}} \qquad (2)$$

Hardwick and Robertson,[10] however, have shown that ceric ions associate with bisulphate to form ceric sulphate complexes according to the equilibria

$$\mathrm{Ce^{4+} + HSO_4^- \overset{K_1}{\rightleftharpoons} Ce(SO_4)^{2+} + H^+} \qquad (3)$$

$$\mathrm{Ce(SO_4)^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} Ce(SO)_4)_2 + H^+} \qquad (4)$$

$$\mathrm{Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_3^{2-} + H^+} \qquad (5)$$

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[10] T. J. Hardwick and E. Robertson, *Canad. J. Chem.*, 1951, **29**, 828.

the values for the equilibrium quotients K_1, K_2, and K_3 being $3{\cdot}5 \times 10^3$, 2×10^2, and 2×10^1, respectively, at an ionic strength of 2·0M.

In an endeavour to clarify the position and to investigate the dependence of the reaction rate on the concentration of the sulphuric acid, experiments were performed at constant bisulphate concentration (by using $NaHSO_4$–H_2SO_4 mixtures) and at constant acidity (by using $HClO_4$–H_2SO_4 solutions). The results are shown in Table 2. In the mixtures

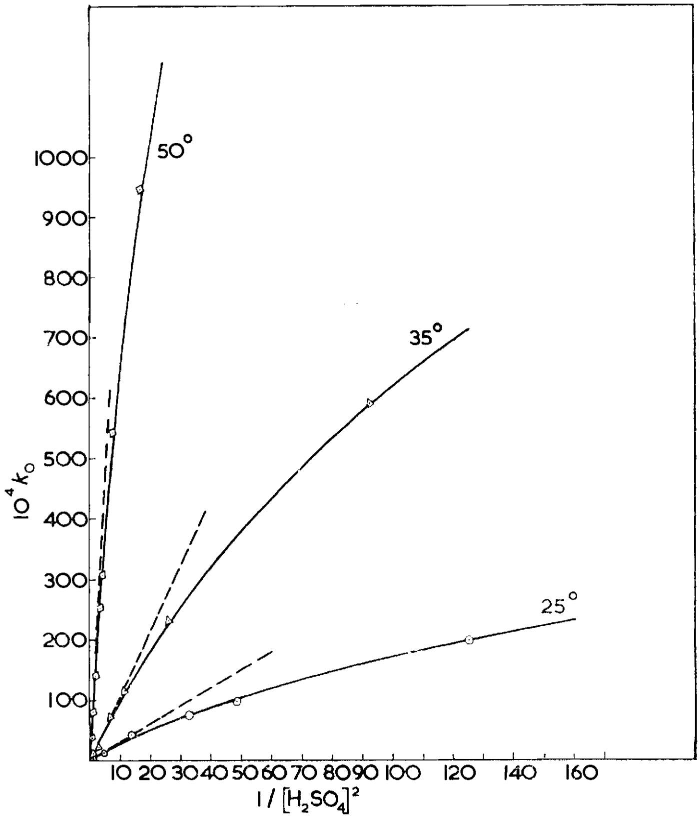

FIGURE 2. Plots of k_0 against $[H_2SO_4]^{-2}$

TABLE 2

Experiments at constant ionic strength, $I = 1{\cdot}0_5$M and $T = 35°$

		$[HSO_4^-] = 1{\cdot}00$M		
10^3 [Ce^{IV}] (M)	10^3 [Glyc] (M)	[$NaHSO_4$] (M)	[H_2SO_4] (M)	10^4k_0 (mole^{-1} sec.$^{-1}$)
8·529	12·388	—	1·00	12·1
8·709	12·648	0·16$_2$	0·83$_8$	9·5$_0$
9·189	13·850	0·31$_9$	0·68$_1$	8·8$_8$
9·145	13·280	0·41$_8$	0·58$_2$	8·0$_7$
9·249	13·850	0·51$_7$	0·38$_3$	7·3$_1$
10·922	13·266	0·84$_2$	0·15$_8$	6·2$_5$

		$[H^+] = 1{\cdot}00$M		
10^3[Ce^{IV}] (M)	10^3[Glyc] (M)	[$HClO_4$] (M)	[H_2SO_4] (M)	10^3k_0 (mole^{-1} sec.$^{-1}$)
8·529	12·388	—	1·00	1·2$_1$
5·479	13·280	0·05$_4$	0·94$_6$	1·6$_0$
8·833	13·020	0·23$_5$	0·76$_5$	2·0$_2$
8·406	13·190	0·44$_6$	0·55$_4$	3·5$_6$
8·869	13·850	0·61$_7$	0·38$_3$	6·9$_2$
5·479	13·280	0·7$_5$	0·25$_0$	14·4$_2$

where the bisulphate concentration is constant, the reaction rate falls with decreasing hydrogen-ion concentration, although no simple relationship is adhered to. This decreasing rate is in the opposite sense to the results obtained in the sulphuric acid experiments (Table 1) and may be due to increasing amounts of hydrolysed ceric species and tetrasulphatocerate ion being present.

Under conditions of medium acidity, the cerium(IV) is present as a mixture of all three ceric sulphate complexes [10] $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$. If the reactive species is $CeSO_4^{2+}$, then using equations (4) and (5) we may write

$$\frac{-d[Ce^{IV}]}{dt} = [Ce^{IV}][Glyc]\,.\,k\Big/\left\{1 + K_2\frac{[HSO_4^-]}{(H^+)} + \frac{K_2K_3[HSO_4^-]^2}{[H^+]^2}\right\}$$

where [Glyc] is the glycollic acid concentration and k divided by the factor in braces is the observed rate constant k_0. Krishna and Tewari (*loc. cit.*) suggested $Ce(SO_4)_2$ as the reactive species, and that, by using equations (1) and (2), a relationship similar to that given above would result. The experimental evidence as to the species present in solution would, however, tend to argue against this mechanism. From the results at constant hydrogen-ion concentration (Table 2) and the K values quoted above, a plot was made of k_0 against $\{1 + K_2[HSO_4^-] + K_2K_3[HSO_4^-]^2\}^{-1}$ which is shown in Figure 3. The curve should pass through the origin, but the slight positive intercept is probably due to in accuracies in k_0 and to the fact that the K values used were derived at an ionic strength of 2·0M, which is considerably higher than that of the present media.

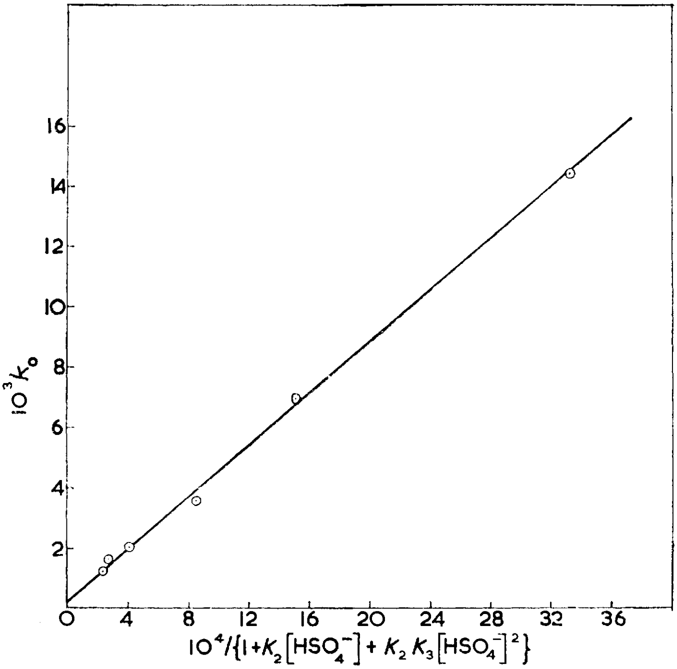

FIGURE 3. Plot of k_0 against $\{1 + K_1[HCO_4^-] + K_2K_3[HSO_4^-]_2\}^{-1}$ at $T = 35°$ and $I = 1{\cdot}0_5$M

From a temperature study [6] of the rate of oxidation of lactic acid by ceric ion, the values of E_a and ΔS^* at 25° were found to be 22·8 kcal./mole and 3·12 e.u., respectively. In this work,[6] however, potassium sulphate was used to maintain a constant ionic strength, and the rate constants obtained differ from those of other workers.[4,5] In the present study, plots of $\log(k_0/T)$ against T^{-1} are linear, indicating that the enthalpy of reaction is constant over the temperature range studied. Activation parameters for the reaction were calculated from the absolute rate equation,

$$'k' = (KT/\boldsymbol{h})\ e\ .\ \mathrm{e}^{\Delta S^*/R}\,\mathrm{e}^{-E_a/RT}$$

the values of E_a and ΔS^* being 10·1 ± 0·8 kcal./mole and —42·1 ± 2 e.u., respectively. Further work on the temperature-dependence of these reactions is at present being undertaken.

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