Kinetics and Mechanism of Redox Reactions in Aqueous Solution. Part 1. Silver(I)-catalysed Oxidation of Cerium(III) by Peroxodisulphate Ion

By **Aditya Prakash, Raj Narain Mehrotra,*** and **R. C. Kapoor,*** Department of Chemistry, University of Jodhpur, Jodhpur-342001, India

The kinetics of the silver(I)-catalysed oxidation of Ce^{III} by $[S_2O_8]^{2-}$ in 0.5 mol dm^{-3} sulphuric acid have confirmed a zero-order dependence on $[Ce^{III}]$ and a first-order dependence on $[Ag^I]$. However, the order with respect to $[S_2O_8{}^{2-}]$ is less than one and the reaction is retarded by both hydrogen sulphate ions and sulphuric acid. The probable mechanism of the reaction is discussed.

THE quantitative oxidation of cerium(III) to cerium(IV) by peroxodisulphate, $[S_2O_8]^{2-}$, ion in the presence of silver(I) is of analytical significance.[1] The kinetics of the silver(I)-catalysed reaction in 1 mol dm^{-3} sulphuric acid indicated first-order dependences on the concentrations of peroxodisulphate and silver(I) ions. The effect of sulphuric acid on the reaction rate was, however, not investigated and no mechanism was suggested.[2] A complex dependence on $[Ce^{III}]$ was reported in the uncatalysed oxidation with ammonium peroxodisulphate in perchloric acid.[3] The silver(I)-catalysed reaction [4] was reported to have a zero-order dependence on $[Ce^{III}]$ and a first-order dependence on $[S_2O_8{}^{2-}]$ and $[Ag^+]$. However, the values of the rate constant, *k*, defined in equation (1), differed by a factor of two in the two investigations [2,4] and is thought to be due to a change in the acid concentration. The redox kinetics with $[NH_4]_2[S_2O_8]$ are complicated by the presence of Ag^I because of the formation and decomposition of a silver ammine complex and of the oxidation of ammonium ion by $[S_2O_8]^{2-}$.[3,5]

$$d[Ce^{IV}]/dt = k[Ag^+][S_2O_8{}^{2-}] \qquad (1)$$

A reinvestigation of the kinetics of this reaction is thus desirable. The preliminary study in 0.5 mol dm^{-3} sulphuric acid indicated that the uncatalysed reaction is quite slow and thus unsuitable for a kinetic study. Since the completion of this work, a report has appeared on the photo-oxidation of cerium(III) sulphate by $[S_2O_8]^{2-}$ in 0.4 mol dm^{-3} sulphuric acid.[6] It is thus interesting to compare our results on the thermal oxidation with those on the photo-oxidation.

EXPERIMENTAL

The reactant solutions were thermostatted in a water-bath at the desired temperature. The required weight of potassium peroxodisulphate (E. Merck, G.R. grade) was first dissolved in a mixture of Ce^{III} and sulphuric acid of the desired concentration in a known volume. The reaction was then initiated by introducing the required volume of silver(I) sulphate solution. This procedure was adopted so as to minimise both the thermal dissociation and hydrolysis of $[S_2O_8]^{2-}$.[7] The reaction was carried out in blackened iodine flasks (Corning glass) to avoid any photochemical reaction.[5] No attempt was made to exclude oxygen either from the reaction vessel or from the distilled water, since preliminary investigations indicated that the reaction velocity was not affected by replacing atmospheric oxygen by nitrogen. This observation is consistent with the study of Matthews and Sworski.[6]

The solutions were prepared in water which had been twice distilled in an all-glass unit in the presence of potassium permanganate. The stock solution of $Ag_2[SO_4]$

---

[1] A. I. Vogel, ' A Text-book of Quantitative Inorganic Analysis,' Longmans, London, 1962, p. 325.

[2] W. H. Cone, *J. Amer. Chem. Soc.*, 1945, **67**, 78.

[3] S. Fronaeus and C. O. Ostman, *Acta Chem. Scand.*, 1955, **9**, 902.

[4] S. Fronaeus and C. O. Ostman, *Acta Chem. Scand.*, 1956, **10**, 320.

[5] D. A. House, *Chem. Rev.*, 1962, **62**, 185.

[6] R. W. Matthews and T. J. Sworski, *J. Phys. Chem.*, 1975, **79**, 681.

[7] H. Palme, *Z. anorg. Chem.*, 1920, **112**, 97.

(B.D.H.) was stored in a black Polythene bottle. The stock solution of cerium(III) sulphate (Fluka, Purum grade) was similarly prepared and stored. It was standardised by oxidising it to Ce^{IV} with $[S_2O_8]^{2-}$ in the presence of Ag^{I}.[1] Having noted the unsuitability of $[NH_4]_2[S_2O_8]$, discussed earlier, $K_2[S_2O_8]$ (E. Merck, G.R. grade) was used and care was taken to use the same sample throughout.

The progress of the reaction was followed by measuring the absorption of cerium(IV) sulphate at 320 nm in a Beckman DU spectrophotometer with cells of unit path length. The reactant concentrations were adjusted to give an excess of $[S_2O_8]^{2-}$ in the reaction mixtures. Plots of the increasing cerium(IV) concentration against time were linear beyond three half-lives. Zero-order rate constants, k_0, with respect to the appearance of Ce^{IV} were calculated from the gradients of these plots using the method of least squares. Values from replicate runs agreed to within ±2%.

RESULTS

The reaction rates were measured at 35 °C unless stated otherwise. A variation in the concentrations of potassium sulphate, potassium nitrate, zinc sulphate, and aluminium sulphate in the range 0.01—0.05 mol dm^{-3} did not affect the rate of the reaction.

Dependence on the Cerium(III) *Concentration.*—The results obtained at various concentrations of Ce^{III} are presented in Table 1. The zero-order rate constant, k_0, was constant, confirming a zero-order dependence on $[Ce^{III}]$. The earlier findings of Cone,[2] and of Fronaeus and Ostman,[3,4] are thus confirmed.

TABLE 1

Effect of initial cerium(III) concentration on the rate constant k_0. $[S_2O_8^{2-}] = 0.02$, $[H_2SO_4] = 0.5$, $[Ag^{I}] = 5 \times 10^{-5}$ mol dm^{-3}; 35 °C

$10^4[Ce^{III}]$/mol dm^{-3}	0.56	1.12	2.24	2.8	3.36	4.48	5.60
10^8k_0/mol dm^{-3} s^{-1}	0.91	0.92	0.91	0.90	0.91	0.91	0.91

Dependence on the Silver(I) *Concentration.*—The dependence of the rate on the initial silver(I) concentration was investigated over a ten-fold range (Table 2). The rate constant k_0 increased proportionately with the increasing $[Ag^{I}]$ confirming a first-order dependence on $[Ag^{I}]$ and the findings of previous workers.[2-4] A plot of k_0 against $[Ag^{I}]$ was linear and passed through the origin, indicating the absence of any reaction between $[S_2O_8]^{2-}$ and Ce^{III} at the optimum temperature.

TABLE 2

Effect of initial silver(I) concentration on k_0. $[S_2O_8^{2-}] = 0.02$, $[H_2SO_4] = 0.5$, $[Ce^{III}] = 2.8 \times 10^{-4}$ mol dm^{-3}; 35 °C

$10^4[Ag^{I}]$/mol dm^{-3}	0.5	1.0	1.5	2.0	2.5	3.5	5.0
10^8k_0/mol dm^{-3} s^{-1}	0.90	1.80	2.72	3.65	4.56	6.30	8.87

Dependence on the Peroxodisulphate Concentration.—The results obtained with a ten-fold change in $[S_2O_8^{2-}]$ are presented in Table 3. The rate constant k_0 did not increase proportionately with the increasing $[S_2O_8^{2-}]$ and a plot of k_0^{-1} against $[S_2O_8^{2-}]^{-1}$ was linear. This indicates that the order with respect to $[S_2O_8^{2-}]$ is less than one and as such does not confirm the earlier observations [2-4] of a first-order dependence.

TABLE 3

Dependence of zero-order rate constant, k_0, on the initial peroxodisulphate concentration. $[Ag^{I}] = 5 \times 10^{-5}$, $[Ce^{III}] = 2.8 \times 10^{-4}$, $[H_2SO_4] = 0.5$ mol dm^{-3}; 35 °C

$[S_2O_8^{2-}]$/mol dm^{-3}	0.01	0.02	0.04	0.06	0.08	0.10
10^8k_0/mol dm^{-3} s^{-1}	0.50	0.93	1.63	2.14	2.59	2.95

Dependence on the Sulphuric Acid Concentration.—The rate decreased (Table 4) with increasing sulphuric acid and seemed to level out at ⩾2 mol dm^{-3} sulphuric acid. The hydrogen-ion concentration at a given concentration of sulphuric acid was calculated by taking into account the first dissociation constant of $[HSO_4]^-$ as reported by Wallace.[8] The linear correlation between k_0^{-1} and $[H^+]$ is illustrated in Figure 2.

TABLE 4

Effect of sulphuric acid on k_0. $[Ag^{I}] = 5 \times 10^{-5}$, $[Ce^{III}] = 2.8 \times 10^{-4}$, $[S_2O_8^{2-}] = 0.02$ mol dm^{-3}; 35 °C

$[H_2SO_4]$/mol dm^{-3}	0.1	0.2	0.5	1.0	1.5	2.0	2.5	3.0
10^8k_0/mol dm^{-3} s^{-1}	2.44	2.10	1.56	1.12	0.85	0.70	0.70	0.70

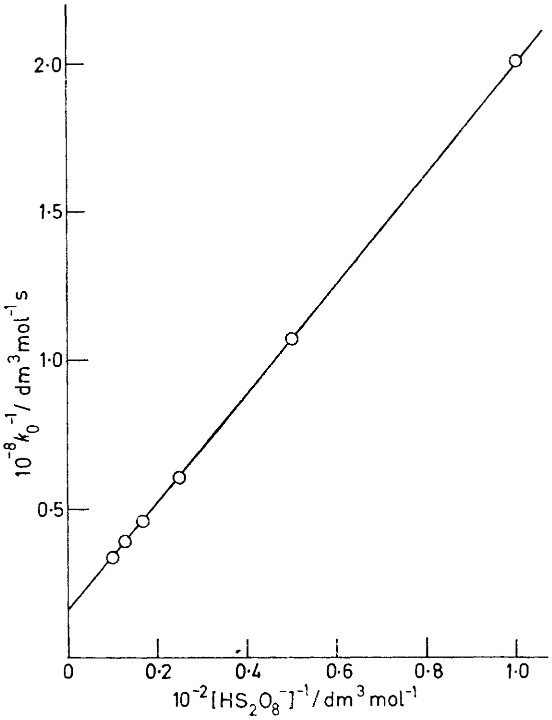

FIGURE 1 Linear dependence of k_0^{-1} and $[HS_2O_8^-]^{-1}$, the total concentration of peroxodisulphate present in the reaction mixture. $[Ce^{III}] = 2.8 \times 10^{-4}$, $[Ag^+]_0 = 5 \times 10^{-5}$, $[H_2SO_4] = 0.5$ mol dm^{-3}; 35 °C

Dependence on the Hydrogensulphate-ion Concentration.—The results in Table 5 indicate that the rate constant k_0 decreased with increasing $[HSO_4^-]$ which was varied by varying the concentration of sodium hydrogensulphate at a given sulphuric acid concentration. A linear correlation between k_0 and $[HSO_4^-]^{-1}$ was found with the plot passing through the origin.

Dependence on the Hydrogen-ion Concentration.—The effect of hydrogen ion, with sulphuric acid as the source, at

---

[8] R. M. Wallace, *J. Phys. Chem.*, 1966, **70**, 3922.

constant $[HSO_4^-]$ was investigated but the effect was obscure because of the more pronounced retardation effect of $[HSO_4]^-$. Replacement of sulphuric by perchloric acid resulted in the precipitation of potassium perchlorate rendering unsuitable the spectrophotometric measurement. The precipitation problem still existed when $Na_2[S_2O_8]$ was used in place of the potassium salt in the presence of perchloric acid. This time the turbidity increased with time.

TABLE 5

Effect of $[HSO_4^-]$ on the k_0 at constant $[H^+]$. $[Ag^I] = 5 \times 10^{-5}$, $[Ce^{III}] = 2.8 \times 10^{-4}$, $[S_2O_8^{2-}] = 0.02$, $[H_2SO_4] = 0.5$ mol dm^{-3}; 35 °C

$[NaHSO_4]$/mol dm^{-3}	0.1	0.2	0.3	0.4	0.6	0.8
$[HSO_4^-]_T$/mol dm^{-3}	0.6	0.7	0.8	0.9	1.1	1.3
$10^8 k_0$/mol dm^{-3} s^{-1}	1.25	1.15	1.03	0.91	0.73	0.62

An indirect approach to the problem was therefore attempted. The rate constant k_0 was computed from the linear plots of k_0 against $[HSO_4^-]^{-1}$ at particular hydrogensulphate-ion concentrations. These values of k_0 were then compared with those obtained at the corresponding sulphuric acid concentrations assuming the acid to be a strong 1 : 1 electrolyte. This comparison indicated that the rate in the presence of sulphuric acid was higher than that in the presence of hydrogensulphate ions of comparable concentration. It could therefore be concluded that the hydrogen ion accelerates the reaction.

Dependence on Temperature.—The rate of the reaction was measured at various temperatures from 35 to 50 °C. The logarithms of the zero-order rate constant k_0 were plotted against $1/T$ and the energy of activation calculated from the linear Arrhenius plot was 9.6 ± 0.5 kcal mol^{-1}.* The entropy of activation was then calculated as -31 ± 2 cal K^{-1} mol^{-1}.

Effect of Radical Scavenger.—The addition of acrylonitrile produced a white curdy precipitate confirming the presence of free radicals in the reaction system. However, the addition of acrylamide did not make the solution heterogeneous and it was possible to follow the reaction spectrophotometrically. The reaction rate was retarded by increasing concentrations of acrylamide. After some time the reaction virtually stopped.

DISCUSSION

Several oxidations by peroxodisulphate do not proceed at a convenient rate at ambient temperature despite the relatively high redox potential, $E = 2.01$ V, of the half reaction (2). This could be due to the high value of the

$$[S_2O_8]^{2-} + 2e^- \longrightarrow 2[SO_4]^{2-} \qquad (2)$$

activation energy, *ca.* 30 kcal mol^{-1}, for the rate-limiting homolysis of $[S_2O_8]^{2-}$,[5] shown in (3). The above con-

$$[S_2O_8]^{2-} \longrightarrow 2[SO_4]^{\cdot -} \qquad (3)$$

sideration explains the failure of the reaction to proceed with a measurable speed in the absence of Ag^I, the catalyst used here. This also indicates that the oxidation of Ce^{III} by $[S_2O_8]^{2-}$ is negligible. The role of the metal catalyst is thus to accelerate reaction (3) to make $[SO_4]^{\cdot -}$ available in sufficient concentration for the oxidation of Ce^{III} in the fast step, because the reaction has a zero-order dependence on $[Ce^{III}]$. Our results are therefore consistent with the report[6] that the quantum efficiency for photo-oxidation of Ce^{III} is independent of the cerium(III) concentration. Peroxodisulphate oxidations are known to be catalysed by Cu^{II} in certain cases,[9] but our investigations indicated that the present oxidation is not catalysed by copper(II) ions.

The absorbance spectra of cerium(III) sulphate in aqueous solution has[10] absorbance maxima at six different wavelengths, *viz.* 201, 211, 221, 239, 253, and 296 nm. These bands are attributed to $4f \rightarrow 5d$ transitions.[11] It is well known that Ce^{III} forms complexes with sulphate ions.[12-14] It is appropriate at this point to consider the equilibria (4) and (5) between Ce^{3+} and its two sulphate complexes, from which (6) may be derived.

$$Ce^{3+} + [HSO_4]^- \overset{K}{\rightleftharpoons} [Ce(SO_4)]^+ + H^+ \qquad (4)$$

$$[Ce(SO_4)]^+ + [HSO_4]^- \overset{K'}{\rightleftharpoons} [Ce(SO_4)_2]^- + H^+ \qquad (5)$$

$$[Ce^{3+}] = \frac{[Ce^{III}][H^+]}{[H^+] + K[HSO_4^-]} \qquad (6)$$

It has been assumed that $(1 + K[HSO_4^-][H^+]^{-1}) \gg KK'[HSO_4^-]^2[H^+]^{-2}$ and the last term has been neglected. Connick and Mayer[13] and Newton and Arcand[14] independently reported the formation constant of $[Ce(SO_4)]^+$ as 60 in 0.5 mol dm^{-3} sodium perchlorate[13] and 33.78 at 25 °C.[14] These workers[13,14] hold the view that the existence of $[Ce(SO_4)_2]^-$ cannot be excluded. Newton and Arcand[14] estimated the formation constant for $[Ce(SO_4)_2]^-$ as 0.2 at 25 °C. The assumption made in deriving equation (6) is thus justified.

The observed retardation in the rate of reaction with increasing hydrogensulphate-ion concentration is now explicable if it is assumed that Ce^{3+} is the reactive cerium(III) species that undergoes oxidation by $[S_2O_8]^{2-}$. In other words the retardation by $[HSO_4]^-$ can be attributed to the increased resistance of $[Ce(SO_4)]^+$ and $[Ce(SO_4)_2]^-$ complexes towards oxidation by $[S_2O_8]^{2-}$. It is therefore difficult for us to support the suggestion of Fronaeus and Ostman[3] that cerium(III) sulphate complexes are oxidised more readily than the free hydrated cerium(III) ion, Ce^{3+}. Our results, the gradual retardation in the rate with increasing concentration of $[HSO_4]^-$ (Table 5), lead to a conclusion which is opposite to that made by Fronaeus and Ostman.[3] The levelling of the reaction rate in $\geqslant 2$ mol dm^{-3} sulphuric acid (Table 4) can also be explained in terms of equilibria (4) and (5). It seems that

---

* 1 cal = 4.184 J.

[9] T. L. Allen, *J. Amer. Chem. Soc.*, 1951, **73**, 3589, and refs. 7, 17, and 139 cited in ref. 5.

[10] L. J. Heidt and J. Berestecki, *J. Amer. Chem. Soc.*, 1955, **77**, 2049.

[11] C. K. Jørgensen and J. Brinen, *Mol. Phys.*, 1963, **6**, 629.

[12] S. Fronaeus, *Svensk kem. Tidskr*, 1952, **64**, 317.

[13] R. E. Connick and S. W. Mayer, *J. Amer. Chem. Soc.*, 1951, **73**, 1176.

[14] T. W. Newton and G. M. Arcand, *J. Amer. Chem. Soc.*, 1953, **75**, 2450.

a steady equilibrium between Ce^{3+} and two cerium(III) sulphate complexes is reached in $\geqslant 2$ mol dm^{-3} sulphuric acid.

In view of the results and discussion given above, reactions (7)—(10) are suggested to explain the kinetics of the present reaction. The assumption made is that peroxodisulphate in the presence of sulphuric acid exists as $[HS_2O_8]^-$ because the first ionisation of $H_2S_2O_8$, a very strong acid, is considered to be complete. The further ionisation of $[HS_2O_8]^-$ is believed to be prevented by the hydrogen ion present in the reaction mixture. The rate

$$[HS_2O_8]^- + Ag^+ \xrightleftharpoons{K_1} [Ag(S_2O_8)]^- + H^+ \qquad (7)$$

$$[Ag(S_2O_8)]^- \xrightarrow{k_2} Ag^{2+} + [SO_4]^{2-} + [SO_4]^{\cdot -} \qquad (8)$$

$$Ce^{3+} + Ag^{2+} \xrightarrow{k_3} Ce^{IV} + Ag^+ \qquad (9)$$

$$Ce^{3+} + [SO_4]^{\cdot -} \xrightarrow{k_4} Ce^{IV} + [SO_4]^{2-} \qquad (10)$$

of the reaction, calculated from equations (7)—(10), is given by equation (11). The rate-limiting step is (8),

$$\frac{-d[Ce^{III}]}{dt} = \frac{d[Ce^{IV}]}{dt}$$

$$= k_0 = \frac{2k_2K_1[Ag^+]_0[HS_2O_8^-][Ce^{3+}]^0}{(1 + K_1[HS_2O_8^-][H^+]^{-1})} \qquad (11)$$

(7) is a fast equilibrium, and (9) and (10) are the fast steps of the mechanism. Here $[Ag^+]_0$ is the total concentration of $Ag_2[SO_4]$ present in the reaction mixture, and $[Ce^{3+}]^0$ denotes zero-order dependence in Ce^{III}. Since the peroxodisulphate was varied at a fixed concentration of hydrogen ion, $K_1[H^+]^{-1}$ could be replaced by another constant K^1 and if one replaces $[Ce^{3+}]$ by $[Ce^{III}]$, the concentration of Ce^{III} present in the reaction mixture [from equation (6)], equation (11) becomes (12).

Equation (12) is consistent with the linear plot of k_0 against $[Ag^+]_0$ which passes through the origin, and with the linear plot (Figure 1) of k_0^{-1} against $[HS_2O_8^-]^{-1}$

$$k_0 = \frac{2k_2K_1[Ag^+]_0[HS_2O_8^-][Ce^{III}]^0}{(1 + K^1[HS_2O_8^-])([H^+] + K[HSO_4^-])} \qquad (12)$$

which has an intercept on the rate axis and, as stated earlier, is different from the earlier reports.[2-4] The present result is also consistent with a similar relation between the observed rate of cerium(III) excitation and $[S_2O_8^{2-}]$ in the photo-oxidation of Ce^{III} by peroxodisulphate in aqueous sulphuric acid.[6] This establishes the parallelism between the thermal oxidation and the photo-oxidation of Ce^{III} by peroxodisulphate in sulphuric acid. If it is assumed that $K[HSO_4^-] \gg [H^+]$, because of the high value[13,14] of K, equation (12) is consistent with a linear plot at constant $[H^+]$ of k_0 against $[HSO_4^-]^{-1}$ which passes through the origin. Equation (12) is also consistent with a linear plot (Figure 2) of k_0^{-1} against $[H^+]$, or $[HSO_4^-]$, when both are varied in the variation of the concentration of sulphuric acid.

Although complex formation has been proposed between Ag^I and peroxodisulphate ion, the absorption spectra of cerium(III) solutions in the presence and absence of $[S_2O_8]^{2-}$ did not provide any evidence for complex formation between Ce^{III} and peroxodisulphate. A similar observation was also reported recently.[6]

The fast step in the mechanism involving sulphate radical ion, $[SO_4]^-$, is based on the fact that the rate constant for the reaction between Ce^{3+} and $[SO_4]^{\cdot -}$ is reported[15] to be 1.43×10^8 dm^3 mol^{-1} s^{-1}. The possibility of the formation of $[SO_4]^{\cdot -}$ through reactions (13) and (14) was excluded, although it could have explained the retarding effect of $[HSO_4]^-$. The evidence

$$[S_2O_8]^{2-} + H_2O \rightleftharpoons [HSO_4]^- + [SO_4]^{\cdot -} + OH^{\cdot} \qquad (13)$$

$$2OH^{\cdot} \longrightarrow \tfrac{1}{2}O_2 + H_2O \qquad (14)$$

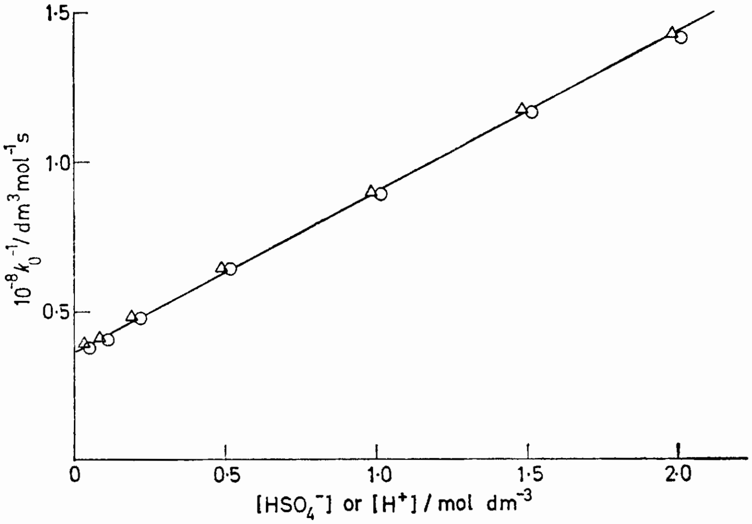

FIGURE 2 Plots of $1/k_0$ against $[H^+]$ (○) and $[HSO_4^-]$ (△) when both concentrations are varied in the variation of the sulphuric acid concentration. $[Ce^{III}] = 2.8 \times 10^{-4}$, $[Ag^+]_0 = 5 \times 10^{-5}$, $[S_2O_8^{2-}] = 0.02$ mol dm^{-3}; 35 °C

---

[15] L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 1967, **71**, 3802.

against these reactions arises from earlier investigations of peroxodisulphate oxidations.[5] In the absence of any exchange of ^{35}S between $[SO_4]^{2-}$ and $[S_2O_8]^{2-}$ under the conditions of the kinetics experiments, no mechanism of decomposition can be proposed which involves an equilibrium between $[S_2O_8]^{2-}$ and $[SO_4]^{2-}$ or $[SO_4]^{\cdot-}$.[5] According to Kolthoff and Miller,[16] the oxygen produced during the decomposition of $[S_2O_8]^{2-}$ in aqueous acidic solutions comes from the peroxodisulphate and not from water as expressed in (14). However, there is still one more possibility for the formation of $OH^\bullet$ radicals as shown in equation (15). The $OH^\bullet$ radicals thus produced

$$OH^\bullet + [HSO_4]^- \rightleftharpoons [SO_4]^{\cdot-} + H_2O \qquad (15)$$

could be considered as an oxidant for Ce^{3+}. The equilibrium quotient $[SO_4^{\cdot-}]/[OH^\bullet][HSO_4^-]$ is *ca.* 50 $dm^3\ mol^{-1}$ in 0.4 mol dm^{-3} sulphuric acid.[17]

Anbar and Neta [18] reported a value of $2.2 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ for reaction (16) and as such one may conclude

$$Ce^{3+} + OH^\bullet \longrightarrow [OH]^- + Ce^{IV} \qquad (16)$$

that Ce^{III} is more likely to be oxidised by $OH^\bullet$ than by $[SO_4]^{\cdot-}$. However, Sworski *et al.*[17] calculated the quotient $[SO_4]/[OH^{\bullet-}]$ as 302 and 15 in 4.0 and 0.4 mol dm^{-3} sulphuric acid respectively, indicating that this ratio increases much more rapidly than the increase in sulphuric acid concentration. The decrease in the $OH^\bullet$ concentration with increasing sulphuric acid is considered to be due to reaction (17) where $OH^\bullet$ radicals react with sulphuric acid to yield $HSO_4^{\cdot-}$ radicals [19] which oxidise [20] Ce^{III}, as shown in (18). Sworski *et al.*[17] therefore

$$OH^\bullet + H_2SO_4 \longrightarrow HSO_4^{\cdot-} + H_2O \qquad (17)$$

$$Ce^{3+} + HSO_4^{\cdot-} \longrightarrow Ce^{IV} + [HSO_4]^- \qquad (18)$$

concluded that most of the oxidation of Ce^{III} is effected by $[SO_4]^{\cdot-}$ radicals as the lower rate of oxidation by them is more than compensated by their greater concentration. Thus the exclusion of equilibrium (13) from the proposed mechanism is justified.

We thank the U.G.C., New Delhi, for support.

[5/188 *Received*, 28*th January*, 1975]

---

[16] I. M. Kolthoff and I. K. Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 3055.

[17] R. W. Matthews, H. A. Mahlman, and T. J. Sworski, *J. Phys. Chem.*, 1972, **76**, 1265.

[18] M. Anbar and P. Neta, *Internat. J. App. Radiation Isotopes*, 1967, **18**, 493.

[19] T. J. Sworski, *J. Amer. Chem. Soc.*, 1956, **78**, 1768.

[20] T. J. Sworski, *Radiation Res.*, 1957, **6**, 645.