Metal-ion Oxidations in Solution. Part 17.[1] The Kinetics and Mechanism of the Oxidation of Malonic Acid by Cerium(IV) in Perchloric Acid Media

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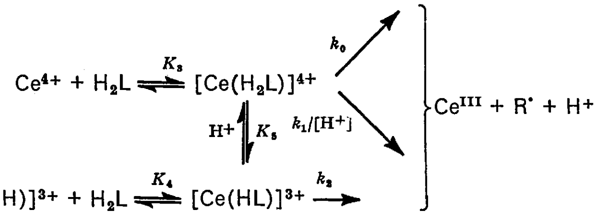
The redox reaction between Ce^{IV} and malonic acid (H_2L) proceeds *via* an inner-sphere mechanism. Using stopped-flow methods, the oxidation has been investigated over the range 2.4—35 °C. A notable feature of the reaction is that, whilst at low temperatures there is kinetic and spectroscopic evidence for intermediate complex formation, at higher temperatures (30 and 35 °C) the reaction order changes to unity with respect to the reductant concentration. The reaction is catalysed by hydrogen ions. The data are rationalized in terms of the following reaction scheme



in which the principal path involves reaction of $[Ce(H_2L)]^{4+}$ ($K_5 < 1$ mol dm^{-3}). The significance of the relative magnitudes and temperature dependences of the equilibrium constants is discussed and the incorporation of the kinetic term k_2 provides a general mechanism for cerium(IV) oxidations. Flow e.s.r. techniques have been used to characterize the radical $R^{\bullet}$, and its stability compared with radical intermediates from the oxidation of other substrates is discussed.

THE diversity of hydrogen-ion dependences of the rates of reaction and the nature and role of intermediate complexes represent two of the more interesting aspects of the oxidation of organic and inorganic substrates by cerium(IV). In both sulphuric[2] and perchloric acid[1,3] media an increase in $[H^+]$ produces a decrease in the rate of oxidation of α-hydroxycarboxylic acids. A similar effect is observed in the reaction with hydrazine.[4] In contrast, the corresponding reactions with alcohols[5-8] and carboxylic acids[9] increase in rate with increasing $[H^+]$. The oxidation of malonic acid exhibits a similar dependence.[10] The latter system is also of interest in that, whilst in sulphuric acid media there is a second-order dependence of the rate, in perchlorate solutions at low temperature there is evidence for an intermediate complex. At higher temperatures, however, the order in ligand concentration reverts to unity.

In this paper we present a treatment of the data in which a single scheme is proposed for oxidations by Ce^{IV} in perchlorate solutions which accounts for the observed differences in rate with hydrogen-ion concentration.

EXPERIMENTAL

Stock solutions of Ce^{IV} were prepared either electrolytically or from ammonium cerium(IV) nitrate.[3,11] In each case these reagents, which were used within 12 h of preparation, were stored at 0 °C to prevent any slow oxidation of the solvent. Malonic acid (B.D.H) was twice recrystallized from methanol–water (1 : 1 v/v), the purity being confirmed by elemental analysis (Found: C, 34.6; H, 3.90. Calc.: C, 34.6; H, 3.85%). The ionic strength was maintained constant at 1.50 mol dm^{-3} using $HClO_4$-(AnalaR)–$Na[ClO_4]$ (Fluka, puriss) mixtures, as described previously.[12] Stock solutions of Ce^{III} were made from the nitrate salt (B.D.H.). All the solutions were prepared using distilled water from an all-glass still.

Kinetics.—Kinetic studies were made under conditions of excess of ligand using stopped-flow spectrophotometers described previously.[13,14] Typical first-order plots to at least 85—90% completion of reaction confirmed the first-order dependence on oxidant concentration, and kinetic traces were analysed using a Nova 2000 computer. Rate constants were reproducible to ±2%, no changes in rate being detected over the wavelength range 330—400 nm. Basic kinetic data are to be found in Supplementary Publication No. SUP 21918 (9 pp.).§

For the stopped-flow experiments in aqueous solution, a Varian E-65 *X*-band e.s.r. spectrometer was equipped with an all-quartz two-entry T-mixing chamber (Varian model E-249) having a mixing volume of 0.002 5 cm^3. The flat sample cell is an integral part of the device, providing a total reacting volume at the point of observation of 0.08 cm^3. Flow rates for the reactant solutions (10 cm^3 min^{-1}) were generated by gravity feed and controlled by a water aspirator applied to the exit tubing. A Gilmont flow meter (no. 13) was inserted into each stream. The *g* factors are quoted relative to diphenylpicrylhydrazyl (dpph), $g =$ 2.003 6, using a Varian E-232 dual-cavity assembly in which the field shift between the cavities had been deter-

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§ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[1] Part 16, Z. Amjad, A. McAuley, and U. D. Gomwalk, *J.C.S. Dalton*, 1977, 82.

[2] A. McAuley, *J. Chem. Soc.*, 1965, 4054; A. McAuley and C. H. Brubaker, jun., *J. Chem. Soc. (A)*, 1966, 960.

[3] Z. Amjad and A. McAuley, *J.C.S. Dalton*, 1974, 2521.

[4] J. I. Morrow and G. W. Sheeres, *Inorg. Chem.*, 1972, **11**, 2606.

[5] M. Ardon, *J. Chem. Soc.*, 1957, 1811.

[6] M. Rangaswamy and M. Santappa, *Indian J. Chem.*, 1969, **7**, 473.

[7] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1970, **66**, 679.

[8] D. Benson, 'Mechanisms of Oxidation by Metal Ions,' Elsevier, Amsterdam, 1976, p. 50.

[9] C. F. Wells and M. Husain, *J. Chem. Soc. (A)*, 1971, 380.

[10] M. Ignaczak, *Soc. Sci. Lodz. Acta Chim.*, 1972, **17**, 135 (*Chem. Abs.*, 1973, **78**, 34427).

[11] H. G. Offner and D. A. Skoog, *Analyt. Chem.*, 1966, **38**, 1520.

[12] A. G. Lappin and A. McAuley, *J.C.S. Dalton*, 1975, 1560.

[13] K. J. Ellis and A. McAuley, *J.C.S. Dalton*, 1973, 1533.

[14] J. P. McCann and A. McAuley, *J.C.S. Dalton*, 1975, 783.

mined. Hyperfine splitting constants were measured to ± 0.25 G using Fremy's salt (a_N 13.0 G) as a standard.[15,*]

Stoicheiometry.—Under the conditions of the kinetic experiments (excess of ligand), malonic acid is oxidized to formic acid.[10,16] Attempts to determine volumetrically the amount of this product [17] were unsuccessful owing to the interference of malonic acid present. A stoicheiometry of 6.1 ± 0.1 (four determinations) mol of oxidant per mol of reductant was derived, however, when an excess of metal ion was present. The concentration of Ce^{IV} remaining was determined within a few minutes of completion of the reaction. Any reduction of Ce^{IV} by formic acid would be negligible under these conditions.[9] The overall oxidation may thus be written as in (1).

$$6Ce^{IV} + CH_2(CO_2H)_2 \xrightarrow{H_2O} 6Ce^{III} + 6H^+ + 2CO_2 + HCO_2H \qquad (1)$$

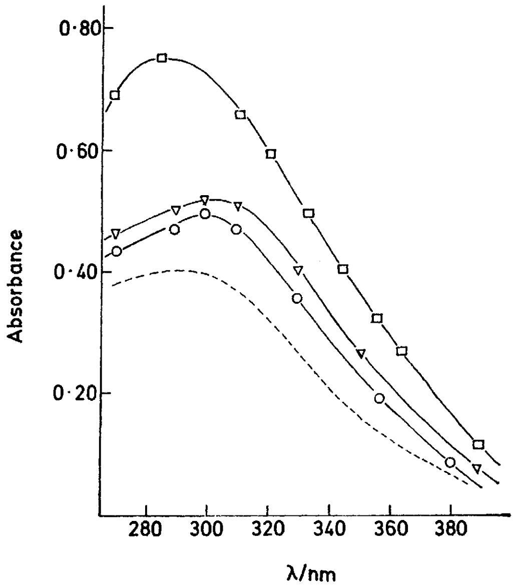

FIGURE 1 Spectra of intermediate complexes: (□), malonic acid (2.5×10^{-2} mol dm^{-3}), [H$^+$] = 0.3 mol dm^{-3}, 7.4 °C; (▽), acetic acid (3.25×10^{-2} mol dm^{-3}), [H$^+$] = 1.00 mol dm^{-3}, room temperature (r.t.); (○) formic acid (2.8×10^{-2} mol dm^{-3}), [H$^+$] = 1.00 mol dm^{-3}, r.t.; (— — —), Ce^{IV} (2.5×10^{-4} mol dm^{-3}), [H$^+$] = 0.60 mol dm^{-3}, r.t. This concentration of metal ion was also used in solutions with the organic acid present. In the case of malonic acid, complex formation is complete to the extent of *ca.* 20%

RESULTS AND DISCUSSION

The deepening of the yellow colour of cerium(IV) solutions on addition of malonic acid is indicative of complex formation. This was confirmed from optical-density measurements and the spectrum of the intermediate complex was compiled and is shown in Figure 1. For comparison, the spectra of the complexes with acetic and formic acids are also shown. These spectra are significantly different from those derived for the α-hydroxycarboxylic acids [1] and are consistent with only a weak interaction between malonic acid and Ce^{IV} with little evidence of chelate formation. In fact, optical-density changes at the start of the reaction when compared with a cerium(IV) blank were too small for any realistic determinations of the formation constants of the complexes to be made, as has been done in the case of other cerium(IV) complexes.[1,3]

TABLE 1

Effects of cerium(III) and nitrate ions on the reaction rate at 25 °C, [H$^+$] = 0.60 mol dm^{-3}, 357 nm, [$CH_2(CO_2H)_2$] = 2.5×10^{-2}, [Ce^{IV}] = 2.50×10^{-4}, and I = 1.50 mol dm^{-3}

10^3[Ce^{III}]/mol dm^{-3}	0.0	0.25	1.00	2.50	12.50
$k_{obs.}$/s^{-1}	0.132 *	0.133	0.132	0.133	0.128
10^3[NO_3^-]/mol dm^{-3}	0.0	0.25	1.00	2.52	12.50
$k_{obs.}$/s^{-1}	0.132 *	0.134	0.132	0.133	0.130

* The perchlorate salt of Ce^{IV} was used.

Kinetic measurements were made over a wide range of ligand and hydrogen-ion concentrations. Addition of Ce^{III} to the solutions (up to a 50-fold excess) had no effect on the reaction rate (Table 1), establishing the lack of any back reaction. Similar results were also obtained by adding up to a comparable excess of nitrate ions. In addition, no differences in the observed rate constant, $k_{obs.}$, were found using either cerium(IV) perchlorate or the hexanitrato-complex in perchloric acid. Any cerium(IV) nitrato-complexes,[18] which would be present in very low concentration, are considered to be kinetically unimportant. The values of the rate constants, $k_{obs.}$, at various hydrogen-ion and malonic acid (H_2L) concentrations at two of the temperatures studied are presented in Table 2. At 25 °C, it is seen that the order with respect to the concentration of the organic substrate is virtually unity, whereas at 7.8 °C the order is <1 with the rate tending to a limiting value.

Under the acidity conditions prevailing, malonic acid is essentially undissociated (K_{a1} 1.4×10^{-3} mol dm^{-3}), the amounts of monoprotonated ion, [HL]$^-$, present being *ca.* 0.1—0.4% of the total. Assuming only H_2L to be reactive, the scheme in equations (2)—(9) is consistent with the experimental observations.

$$Ce^{4+} + H_2O \overset{K_h}{\rightleftharpoons} [Ce(OH)]^{3+} + H^+ \qquad (2)$$

$$Ce^{4+} + H_2L \overset{K_3}{\rightleftharpoons} [Ce(H_2L)]^{4+} \qquad (3)$$

$$[Ce(OH)]^{3+} + H_2L \overset{K_4}{\rightleftharpoons} [Ce(HL)]^{3+} + H_2O \qquad (4)$$

$$[Ce(H_2L)]^{4+} \overset{K_5}{\rightleftharpoons} [Ce(HL)]^{3+} + H^+ \qquad (5)$$

$$[Ce(H_2L)]^{4+} \xrightarrow{k_0} Ce^{III} + H^+ + R^\bullet \qquad (6)$$

$$[Ce(H_2L)]^{4+} + H^+ \xrightarrow{k_1} Ce^{III} + 2H^+ + R^\bullet \qquad (7)$$

$$[Ce(HL)]^{3+} \xrightarrow{k_2} Ce^{III} + R^\bullet \qquad (8)$$

$$Ce^{IV} + R^\bullet \xrightarrow{\text{fast}} Ce^{III} + \text{Product(s)} \qquad (9)$$

Two intermediate complexes are involved, $[Ce(H_2L)]^{4+}$ and $[Ce(HL)]^{3+}$, the latter being formed either *via* reactions (3) and (5) or by (4), the paths being kinetically indistinguishable. The electron transfer within the complexes is considered to be the rate-determining step with the formation of a radical. If the pre-equilibrium reactions are rapid compared with the redox reactions,

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* Throughout this paper: 1 G = 10^{-4} T; 1 cal = 4.184 J.

[15] J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.

[16] H. Degn, *Nature*, 1967, **213**, 589.

[17] J. W. Hopton, *Analyt. Chim. Acta*, 1953, **8**, 429.

[18] I. A. Labadev, B. F. Myasoedov, and V. Ya. Frankel, *Russ. J. Inorg. Chem.*, 1973, **18**, 1716.

TABLE 2

Observed rate constants at varying $[H_2L]$ and $[H^+]$, and $[Ce^{IV}]_T = 2.50 \times 10^{-4}$ mol dm^{-3}, $I = 1.50$ mol dm^{-3} $[NaClO_4]$, and 357 nm

$\frac{\theta_c}{°C}$	$\frac{[H^+]}{mol\ dm^{-3}}$	$\frac{10^2[H_2L]}{mol\ dm^{-3}}$	$\frac{10^2k_{obs.}}{s^{-1}}$	G/mol dm^{-3} s	I/s
7.8	0.288	1.00	1.70	0.554	3.14
		1.53	2.57	±0.007	±0.40
		2.00	3.19		
		2.50	4.02		
		3.50	5.23		
		5.00	6.93		
	0.75	1.00	2.46	0.383	2.50
		1.50	3.55	±0.002	±0.098
		2.00	4.62		
		2.50	5.60		
		3.50	7.49		
		5.00	9.90		
	0.50	1.50	3.08	0.45	2.60
		2.00	3.96	±0.005	±0.24
		2.50	4.78		
		3.50	6.48		
		5.00	8.66		
	1.00	2.04	5.48	0.327	1.99
		2.50	6.79	±0.002	±0.53
		3.50	8.77		
		5.00	11.60		
	1.25	1.00	3.35	0.285	1.44
		1.50	4.90	±0.003	±0.23
		2.00	6.28		
		2.50	7.70		
		3.00	10.70		
25.0 *	0.50	1.00	5.09	0.196	
		2.00	9.92	±0.003	
		2.50	12.60		
		3.00	15.40		
		3.50	18.4		
	1.00	1.00	6.05	0.156	
		2.50	15.5	±0.015	
		3.50	21.5		
		5.00	30.6		
	0.60	1.50	7.98	0.182	
		2.00	10.6	±0.003	
		2.50	13.5		
		5.00	26.4		
	1.25	1.00	7.06	0.140	
		1.50	10.8	±0.001	
		2.00	14.4		
		2.50	17.4		
		3.00	20.9		
		3.50	25.4		
		5.00	35.5		

* The perchlorate salt of Ce^{IV} was used; all intercepts, I, <0.02.

the rate of decrease of $[Ce^{IV}]_T$ may be expressed as in (10) and the observed first-order rate constant as in

$$-\tfrac{1}{6}\cdot\left(\frac{d[Ce^{IV}]_T}{dt}\right) = k_0[Ce(H_2L)^{4+}] + k_1[Ce(H_2L)^{4+}][H^+] + k_2[Ce(HL)^{3+}] \quad (10)$$

(11). Two limiting forms of this equation are of interest

$$k_{obs.} = \frac{6(k_0K_3[H^+] + k_1K_3[H^+]^2 + k_2K_4K_h)[H_2L]}{[H^+] + K_h + (K_3[H^+] + K_4K_h)[H_2L]} \quad (11)$$

as they have been observed in other reactions of Ce^{IV}: (*a*) if $([H^+] + K_h) \ll (K_3[H^+] + K_4K_h)[H_2L]$, then equation (11) reduces to (12); (*b*) if $([H^+] + K_h) \gg$

$$k_{obs.} = 6(k_0K_3[H^+] + k_1K_3[H^+]^2 + k_2K_4K_h)/(K_3[H^+] + K_4K_h) \quad (12)$$

$(K_3[H^+] + K_4K_h)[H_2L]$ in equation (11) then we obtain (13). According to equation (12) $k_{obs.}$ should

$$k_{obs.} = 6(k_0K_3[H^+] + k_1K_3[H^+]^2 + k_2K_4K_h)[H_2L]/([H^+] + K_h) \quad (13)$$

be independent of $[H_2L]$ and although this expression has been found to hold in the oxidations of formic acid,[9] isopropyl alcohol,[7] and mandelic acid[1] at very large excesses of reductant and low temperature, no evidence was found for this limiting rate law under the most extreme experimental conditions used in the present study, *i.e.* $[H_2L]$ *ca.* 200 times greater than $[Ce^{IV}]_T$ at 3.4 °C.

At higher temperatures (>25 °C) there is no kinetic evidence for complex formation, suggesting that the equilibrium constants for the intermediates are very small, an observation confirmed by the negligible optical-density changes under these conditions. If such is the case, equation (13) should hold. Typical plots of $k_{obs.}$ against $[H_2L]$ at 30.1 and 35.4 °C are shown in Figure 2. Similar behaviour was observed at other

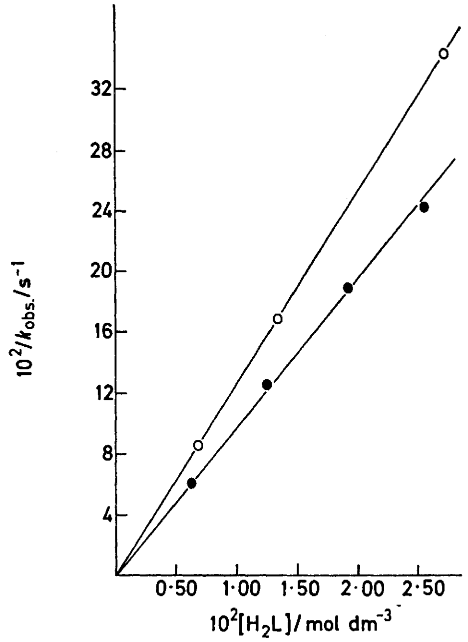

FIGURE 2 Typical plots of $k_{obs.}$ against $[H_2L]$ at 357 nm and $[Ce^{IV}]_T = 2.50 \times 10^{-4}$ mol dm^{-3}; (○) 35.4 °C, $[H^+] = 0.90$ mol dm^{-3}; (●) 30.1 °C, $[H^+] = 1.00$ mol dm^{-3}

$[H^+]$, again with the lines passing through the origin. (It should be pointed out that similar reactions in sulphate media show an identical kinetic behaviour and thus in these solutions the existence of weak complexes with small equilibrium constants comparable with or lower than those in the present study cannot be completely excluded.) From the gradients (α) of these plots and using equation (12) the expression (14) may be

$$([H^+] + K_h)\alpha = 6(k_0K_3[H^+] + k_1K_3[H^+]^2 + k_2K_4K_h) \quad (14)$$

obtained. Using values of α and K_h[3,11] at 30.1 and 35.4 °C, plots of the left-hand side of (14) against $[H^+]$ yielded excellent straight lines passing through the origin (Figure 3). This is indicative of only reaction (6), the decomposition of the complex $[Ce(H_2L)]^{4+}$, as the kinetically important step. If only this path exists then equation (14) reduces to the form (15) so that a

$$\alpha^{-1} = (6[H^+]k_0K_3)^{-1} + (6k_0K_3K_h)^{-1} \quad (15)$$

plot of α^{-1} against $[H^+]^{-1}$ should be linear. Treatment of the data in this manner not only supports the suggested mechanism but also yielded K_h values (0.34 ± 0.016 and 0.29 ± 0.013 mol dm^{-3} at 35.4 and 30.1 °C respectively) which are in reasonable agreement with extrapolated values derived from optical-density data[3,11] (0.32 and 0.255 mol dm^{-3}). Confirmation is thus provided of much lower values for K_h than those determined previously by Hardwick and Robertson.[19]

At lower temperatures (<25 °C) the situation differs from that described above in that there is both spectrophotometric and kinetic evidence for the presence of intermediate complexes in appreciable concentrations. Under these conditions, equation (11) should hold and plots of $k_{obs.}^{-1}$ against $[H_2L]^{-1}$ were linear at 3.4, 7.8, 10.4, and 18.0 °C (Figure 4). From the gradients (G) [equation (16)] and intercepts (I) [equation (17)] of such

$$([H^+] + K_h)/6(k_0K_3[H^+] + k_1K_3[H^+]^2 + k_2K_4K_h) \quad (16)$$

plots, a marked dependence of I on $[H^+]$ was observed

$$(K_3[H^+] + K_4K_h)/6(k_0K_3[H^+] + k_1K_3[H^+]^2 + k_2K_4K_h) \quad (17)$$

similar to the α-hydroxycarboxylic acid reactions,[1,3] indicating that equilibrium (5) is now also important. It may be shown that expression (18) is applicable and,

$$([H^+] + K_h)(I/G) = K_3[H^+] + K_4K_h \quad (18)$$

using values for G and I derived from kinetic data (Table 2) together with the appropriate values of K_h, the equilibrium constants K_4 and K_3 (Table 3) were obtained from a plot of equation (18). Rate constants were obtained [equation (16)] from the gradients of plots of $k_{obs.}^{-1}$ against $[H_2L]^{-1}$. If there is a negligible contribution to the reaction rate from the complex $[Ce(HL)]^{3+}$ (k_2 small), then a plot of $([H^+] + K_h)/G[H^+]$ against $[H^+]$ should be linear. Treatment of the data in this manner showed good linearity over the range 3.4—18 °C. The rate constants k_0 are presented in Table 3, the errors deriving almost exclusively from inaccuracies in K_3 and K_4. It is unfortunate that these formation constants having low numerical values are not known with greater certainty since the change in the reaction order with temperature is largely dependent on the relative extent of these equilibria. Some reasonably quantitative measurements may, however, be made if the linear Arrhenius plot obtained at low temperatures is extrapolated to 25—35 °C. The composite constant k_0K_3 has been determined experimentally at all temperatures and a plot of log k_0K_3 against T^{-1} showed marked curvature suggesting a non-linear variation of log K_3 with T^{-1}. This behaviour is consistent with a non-zero ΔC_p of complex formation and has been found for other systems of this type.[1,7] Using extrapolated values of k_0 it appears that K_3 varies only by a factor of *ca.* 4 over the range 3.4—35 °C ($\Delta H_f < 10$ kcal mol^{-1}). Also, the composite constant k_1K_3 corresponding to the acid-catalysed path [equation (7)] remains relatively unchanged and so represents a diminishing contribution to the reaction at higher temperatures especially when $[H^+] < 1$ mol dm^{-3}. In contrast to K_3, equilibrium (4) is much more temperature dependent and values of K_4 vary by about three orders of magnitude over the temperature range studied. The change in kinetic order which is observed is thus a consequence of the marked variation of the equilibrium constants and of their similarity at or near 5—10 °C. In the case of the α-hydroxycarboxylic acids, equation (4) is dominant with $K_5 > 1$ and the redox reaction takes place virtually exclusively *via* reaction (8). In the present study, K_5 may be shown to be <0.3 mol dm^{-3} at 3.4 °C decreasing

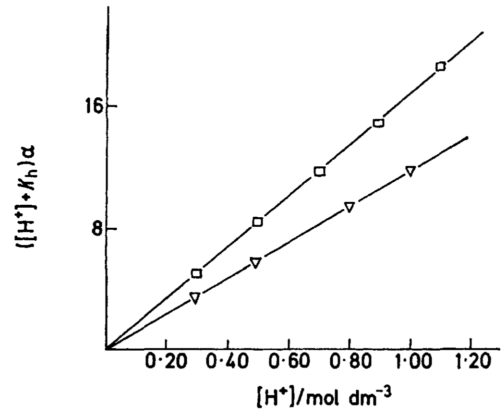

FIGURE 3 Plots of $([H^+] + K_h)\alpha$ against $[H^+]$ [see equation (14)] at 35.4 (□) and 30.1 °C (▽). The K_h values used were 0.29 and 0.24 mol dm^{-3} respectively at the temperatures studied (see text)

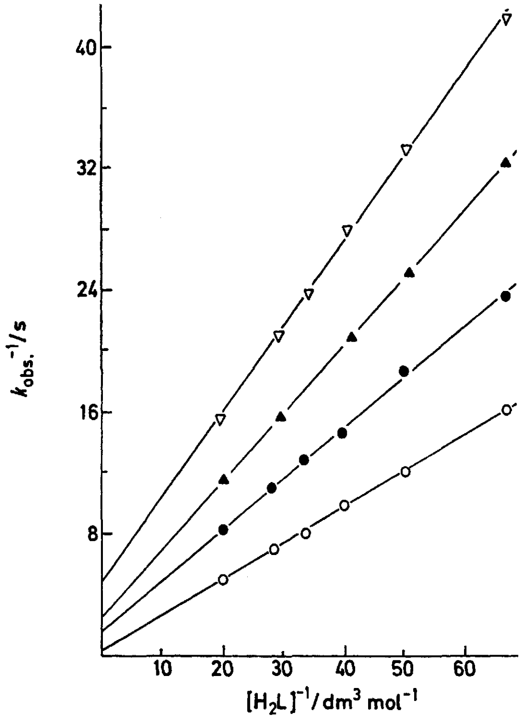

FIGURE 4 Plots of $k_{obs.}^{-1}$ against $[H_2L]^{-1}$ [equation (11)] at various temperatures and hydrogen-ion concentrations: (▽) 3.4 °C, $[H^+] = 0.45$ mol dm^{-3}; (▲) 7.8 °C, $[H^+] = 0.50$ mol dm^{-3}; (●) 10.4 °C, $[H^+] = 0.70$ mol dm^{-3}; (○) 18.0 °C, $[H^+] =$ 0.90 mol dm^{-3}

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[19] T. J. Hardwick and E. Robertson, *Canad. J. Chem.*, 1951, **29**, 818.

Table 3

Rate constants and equilibrium parameters

$\frac{\theta_c}{°C}$	$\frac{k_0K_3}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$	$\frac{k_1K_3}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$	$\frac{K_3}{\text{dm}^3\ \text{mol}^{-1}}$	K_4K_h	$\frac{10^2k_0}{\text{s}^{-1}}$ [a]
3.4	0.289 ± 0.01	0.198 ± 0.02	6.76 ± 0.54	2.04 ± 0.30	4.3 ± 0.3
7.8	0.342 ± 0.03	0.236 ± 0.028	4.78 ± 0.59	1.39 ± 0.56	7.1 ± 1.2
10.4	0.425 ± 0.025	0.267 ± 0.03	4.53 ± 0.58	0.67 ± 0.32	9.4 ± 1.9
18.0	0.608 ± 0.031	0.285 ± 0.035	2.24 ± 0.60	0.32 ± 0.3	27.1 ± 8
25.0	1.07 ± 0.03	0.233 ± 0.035			(50 ± 15) [b]
30.1	1.87 ± 0.05				(90 ± 20) [b]
35.4	2.75 ± 0.08		(2 ± 1) [b]	$(\leqslant 0.01)$ [b]	(150 ± 40) [b]

[a] $\Delta H^\ddagger = 20 \pm 4$ kcal mol^{-1}. [b] Extrapolated.

to $<5 \times 10^{-3}$ mol dm^{-3} at 35 °C where only second-order behaviour is observed.

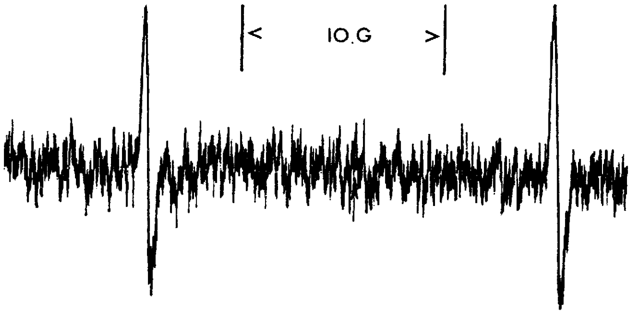
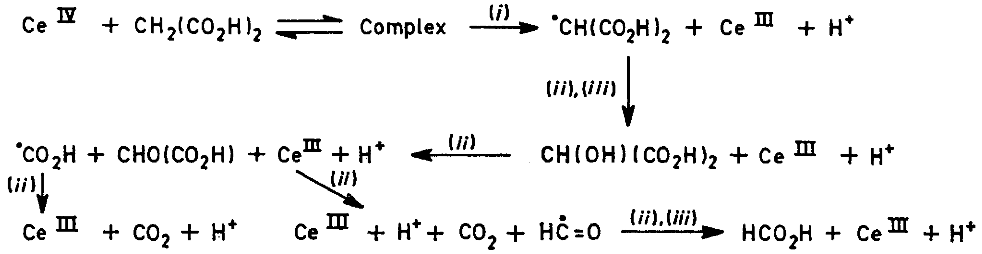


Figure 5 E.s.r. spectrum of the radical intermediate. $[\text{Ce}^{\text{IV}}]_T = 5 \times 10^{-3}$, $[\text{CH}_2(\text{CO}_2\text{H})_2] = 0.115$, and $[\text{H}^+] = 2.01$ mol dm^{-3}

Using the detailed scheme proposed, and from a knowledge of the relative values of the equilibrium constants, the hydrogen-ion dependence of these oxidations becomes clearer. In systems where K_3 dominates or where K_4K_h is small, the protonated complex is the reactive species and as $[\text{H}^+]$ is increased so the rate of oxidation of the substrate will increase. This behaviour has been observed in the reactions of alcohols.[6,7] In the case of isopropyl alcohol [7] there is some evidence for reactions (6) and (8), and in the reaction of cyclohexanol [6,20] the slight acid dependence is reflected in the almost identical values of k_0 and k_2. If, however, $K_5 > 1$ and the deprotonated complex predominates, an inverse $[\text{H}^+]$ dependence would be expected as has been found for the α-hydroxycarboxylic acids. Also, although the $[\text{H}^+]^{-1}$ dependence found in the oxidation of hydrazine [4] is consistent with the reaction of $[\text{Ce(OH)}]^{3+}$ and $[\text{N}_2\text{H}_5]^+$, so leading to the observed second-order kinetics, the existence of weak intermediate complexes cannot be excluded completely.



Scheme (*i*) Slow, rate determining; (*ii*) Ce$^{\text{IV}}$; (*iii*) water

The stoicheiometry of the reaction may be interpreted if malonic acid is oxidized in a one-electron step to yield Ce$^{\text{III}}$ and a radical which reacts further in a series of steps to give formic acid as product. Using the flow e.s.r. technique, on reacting solutions of 0.01 mol dm^{-3} Ce$^{\text{IV}}$ and 0.230 mol dm^{-3} malonic acid (both in 2.01 mol dm^{-3} HClO_4), the doublet observed (Figure 5), with $g = 2.003\,7 \pm 0.000\,3$ and $a_{\text{H}}^{\alpha} = 20.3 \pm 0.3$ G, is consistent with the radical $^{\bullet}\text{CH(CO}_2\text{H)}_2$. This species has been observed in the radiolysis of the organic acid *in situ* with a high-energy electron beam.[21] The hyperfine coupling constant is in excellent agreement with the value quoted under similar acidity conditions. The *g* value, however, is higher in the present case and may reflect either slight differences in the geometry of the radical or its complex formation with cerium ions.

The mechanism may thus be formulated as in the Scheme. Several aspects are highlighted by the e.s.r. observations. In the presence of O_2, the radical was no longer detectable, consistent with a carbon free-radical formulation. Under these conditions the peroxo-species produced probably reacts with Ce$^{\text{IV}}$ more rapidly than the parent radical. Also, the species $^{\bullet}\text{CH(CO}_2\text{H)}_2$ is more stable than the intermediates [considered to be $R^1R^2\dot{\text{C}}(\text{OH})$] formed in the corresponding reactions with α-hydroxycarboxylic acids.[1] In these systems, although there is evidence from polymerization experiments for a radical being formed, an investigation similar to that described here failed to provide information on the nature of the radical. A possible answer may lie in either the more rapid reaction of Ce$^{\text{IV}}$ with the alcohol intermediates or a greater stability of $^{\bullet}\text{CH(CO}_2\text{H)}_2$ deriving from a p_π-electron delocalization over the entire species.

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[20] H. L. Hintz and D. C. Johnson, *J. Org. Chem.*, 1967, **32**, 556.

[21] K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 1186.