Metal-ion Oxidations in Solution. Part XI.† Malic Acid with Cerium(IV) in Perchlorate Media

By **Zahid Amjad** and **Alexander McAuley,*** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

The redox reaction between cerium(IV) ions and malic acid (HL) proceeds *via* an inner-sphere mechanism and has been investigated at an ionic strength of 1·50M over the temperature range 10·6—25 °C using the stopped-flow method. Two intermediate complexes have been identified [equation (i)], the reactive species $[CeL]^{3+}$

$$[Ce(HL)]^{4+} \underset{}{\overset{K_3}{\rightleftharpoons}} H^+ + [CeL]^{3+} \xrightarrow{k_\beta} Ce^{III} + L^{\cdot} \qquad (i)$$

being somewhat more stable; $K_3 = 11 \pm 4$ mol l^{-1} at 25 °C. Formation constants for the complexes have been obtained both from initial optical-density changes and kinetic data. Activation parameters for the intramolecular electron transfer involving the complex $[CeL]^{3+}$ have been derived; $k_\beta = 0{\cdot}52 \pm 0{\cdot}06$ s^{-1} at 25 °C with $\Delta H^\ddagger = 20{\cdot}6 \pm 1{\cdot}5$ kcal mol^{-1} and $\Delta S^\ddagger = 9{\cdot}5 \pm 5$ cal K^{-1} mol^{-1}. The first hydrolysis constant for cerium(IV) [equation (ii)] has been redetermined; $K_h = 0{\cdot}2 \pm 0{\cdot}02$ mol l^{-1} at 25 °C with $\Delta H = 5{\cdot}2 \pm 0{\cdot}7$ kcal mol^{-1} and $\Delta S =$

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

$14{\cdot}3 \pm 4$ cal K^{-1} mol^{-1}, and compared with other values. Possible paths for the rapid decomposition of the radical formed in the redox step are discussed.

THE oxidation of inorganic and organic substrates by cerium(IV) ions in perchlorate media has been the subject of much recent interest and comment.[1-4] Unlike the comparable reactions in sulphate media which are generally slower,[5-8] and where there may be competition between the SO_4^{2-} ion and other ligands for positions in the primary co-ordination sphere of the metal ion, in the presence of perchlorate ions it should be possible to identify any intermediate complexes in solution and so substantiate an inner-sphere mechanism.[9] Evidence for such a route has been obtained previously mainly from Michaelis–Menten kinetic treatments [2,3,9] and only in a few instances has direct complex formation been observed.[10] The situation is more confused in that there are available in the literature several values for the hydrolysis constant [11-13] for the cerium(IV) aqua-ion which differ by almost two orders of magnitude.

In the present paper we present the results of a study where it is possible from optical-density changes (occurring within the first few milliseconds of reaction) to confirm the nature of the complexes involved and to compare the equilibrium constants obtained with those derived in a separate kinetic treatment of the subsequent redox reaction.

EXPERIMENTAL

Materials.—Cerium(IV) was prepared electrolytically by oxidation of cerium(III) perchlorate solutions.[4] Such solutions (*ca.* 0·025M-Ce^{IV} in 4M-$HClO_4$) were prepared by acidification of cerium(IV) hydroxide with excess of perchloric acid followed by treatment with a slight excess of H_2O_2 to reduce the metal ion to oxidation state III.‡ It was shown [4] recently that electrochemical oxidation yields solutions containing monomers, whereas stock solutions prepared from reaction of the metal hydroxide with perchloric acid contain appreciable amounts of polymeric ions. Monomeric cerium(IV) has also been prepared by dissolution of ammonium cerium(IV) nitrate [1] in perchloric acid, and use of such solutions gave results identical in all respects to those with the electrolytically prepared stock. The ionic strength was maintained constant at 1·5M using sodium perchlorate (Fluka, puriss p.a.) and perchloric acid (AnalaR), and it was considered that the small (*ca.* 10^{-3}—10^{-4}M) concentrations of NH_4^+ and NO_3^- ions present when the nitrate salt was used had no effect on the nature of the reagents. In the latter case, the concentration of cerium(IV) nitrato-complexes [14] would represent $<1\%$ of the total metal ion. All solutions were prepared with distilled water obtained from an all-glass still. Cerium(IV) concentrations were determined titrimetrically using ammonium iron(II) sulphate, and $HClO_4$ concentrations using both standard base and weighed samples of disodium tetraborate.

Kinetics.—Kinetic studies were made under conditions of excess of ligand on a stopped-flow instrument described previously.[15] Comparison of blank solutions at (357 nm), in which cerium(IV) was rapidly diluted with acid perchlorate solution, with those where ligand was present indicated formation of a complex within the time of mixing. The subsequent redox reaction was monitored at the same wavelength and from photographs of the oscilloscope traces the decrease in optical density as a function of time was calculated using a Nova 1200 computer. First-order plots were linear to at least 85—90% completion of reaction and replicate experiments gave identical rate constants to within ±2%. Using the initial optical-density change (ΔD) at various wavelengths it was possible to construct the

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‡ 1M = 1 mol dm^{-3}.

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spectrum of the transient. The curve was fairly similar to that derived previously for the interaction of Ce^{IV} with alcohols.[2]

Stoicheiometry.—Differing values for the stoicheiometry of this reaction were derived in sulphate media,[6,16] possibly as a result of the presence of excess of oxidant in the determinations. In order to overcome this problem we used experimental conditions similar to those in the kinetic runs and determined quantitatively the amount of formic acid produced in the presence of excess of reductant.[17] In this method, formic acid was oxidised to CO_2 in the presence of $HgCl_2$ and the mercury(I) chloride formed was then determined using an iodine–thiosulphate titration. Small corrections were made using blank comparisons in the presence of malic acid. The reaction was found to be quantitative only in buffered solutions and the perchloric acid in the reacted solutions was first neutralised to pH *ca.* 6. Four determinations gave a stoicheiometry of 9·5 ± 0·2 mol cerium(IV) reacting per mol reductant, consistent with (1).

$$10Ce^{IV} + HO_2C{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H \xrightarrow{H_2O} 10Ce^{III} + 10H^+ + HCO_2H + 3CO_2 \quad (1)$$

RESULTS AND DISCUSSION

(a) *The First Hydrolysis Constant of the Cerium*(IV) *Aqua-ion*.—Several values for this constant have been reported and many authors have cited the data of Hardwick and Robertson.[11] The results in this paper, however, are acknowledged to involve very small optical-density changes and data are presented at only three hydrogen-ion concentrations, being the minimum required for calculation. Also, deviations from Beer's law are reported at 1·00M-H^+ for metal-ion concentrations $<2 \times 10^{-3}$M. A more recent study[13] yielded a considerably smaller K_h value with no variation in the absorption coefficient under the above acidity conditions in the region up to *ca.* 6×10^{-3}M-Ce^{IV}. Using a Unicam SP 800 spectrophotometer, with scale-expansion accessory, we reinvestigated the situation both at 300 nm, the wavelength used previously, and 357 nm, the wavelength used in the present studies. Using both the perchlorate and hexanitrato-complexes in the range $2{\cdot}5 \times 10^{-4}$—15×10^{-4}M, we found no evidence for dimer formation.

If $[Ce^{IV}]_T$ represents the total cerium(IV) concentration present in solution, the measured absorbance of a cerium(IV) solution may be written as (2), and if no

$$D = \varepsilon_{Ce}[Ce^{4+}] + \varepsilon_{CeOH}[Ce(OH)^{3+}] \quad (2)$$

hydrolysis takes place the absorbance $D_0 = \varepsilon_{Ce}[Ce^{IV}]_T$. Introducing the hydrolysis constant, K_h, the observed absorption coefficient, ε_{obs}, at different $[H^+]$ may be expressed as (3) so that $\varepsilon_{obs} = \{(\varepsilon_0 - \varepsilon_{obs})[H^+]/K_h\} +$

$$\varepsilon_{obs} = (\varepsilon_{Ce} + \varepsilon_{CeOH}K_h[H^+]^{-1})/(1 + K_h[H^+]^{-1}) \quad (3)$$

ε_{CeOH}, where $\varepsilon_0 = \varepsilon_{Ce}$ and represents the absorption coefficient of the unhydrolysed cerium(IV) ion. The coefficient ε_0 may be calculated from three absorbance readings at three different $[H^+]$ values. From measurements on eight solutions in the range $[H^+] = 0{\cdot}08$—$0{\cdot}92$M ($[Ce^{IV}]_T = 1{\cdot}01 \times 10^{-3}$M), eight differing combinations of ε_{obs} and $[H^+]$ yielded ε_0 values to within ±1%. A plot of $[H^+](\varepsilon_0 - \varepsilon_{obs})$ against ε_{obs} should be linear with gradient K_h^{-1} and intercept ε_{CeOH}. The data at 20·0 °C are presented in this way in Figure 1, from which $K_h = 0{\cdot}17 \pm 0{\cdot}01$ mol l^{-1}. Similar experiments at 15·5 °C and 322 nm gave a value of $0{\cdot}13_5 \pm 0{\cdot}010$ mol l^{-1}. These data may be compared with K_h values of 0·18 (25 °C) and 0·11 mol l^{-1} (5 °C) obtained by Offner and Skoog at $I = 1{\cdot}33$M.[13] At 300 nm, the absorption coefficients $\varepsilon_{Ce} = 8{\cdot}50 \times 10^2$ and $\varepsilon_{CeOH} = 1{\cdot}87 \times 10^3$ l mol^{-1} cm^{-1} may be compared with those derived previously[13] at 305 nm where the corresponding values are $7{\cdot}50 \times 10^2$ and $1{\cdot}74 \times 10^3$ l mol^{-1} cm^{-1} respectively.

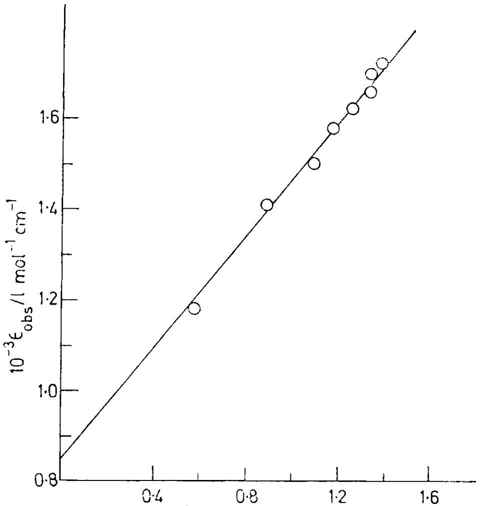

FIGURE 1 Plot of ε_{obs} against $[H^+]$ $(\varepsilon_0 - \varepsilon_{obs})$ at 20·0 °C, 300 nm, $[Ce^{IV}] = 1{\cdot}014 \times 10^{-3}$, $I = 1{\cdot}50$, and $[H^+] = 0{\cdot}0848$—$0{\cdot}9328$M

It is of interest to note that the lower value of K_h derived in these studies is much closer to that for other M^{4+} aqua-ions. The present value may be compared with 0·08 mol l^{-1} for Hf^{4+} ($I = 4{\cdot}00$M)[18] and 0·027 mol l^{-1} ($I = 1$M)[19] at 25 °C for the U^{4+} ion.

(b) *Cerium*(IV)-*Malic Acid Complex Formation*.—From initial optical-density changes it was apparent that a complex was formed within the time of mixing of the reactants and both Ce^{4+} and $[Ce(OH)]^{3+}$ are possible complexing agents. There is also the possibility of the anion of the ligand as a reactant, but in the $[H^+]$ range used (0·40—1·50M), since the pK_a values of malic acid are 3·40 and 5·11, the concentration of free anion would be very low.

Using the scheme (HL = malic acid) in equations (4)—(7), the observed absorption coefficient, ε_{obs}', of a

$$Ce^{4+} + HL \overset{K_1}{\rightleftharpoons} [Ce(HL)]^{4+} \quad (4)$$

$$[Ce(OH)]^{3+} + HL \overset{K_2}{\rightleftharpoons} [CeL]^{3+} \quad (5)$$

$$Ce^{4+} \overset{K_h}{\rightleftharpoons} [Ce(OH)]^{3+} + H^+ \quad (6)$$

$$[Ce(HL)]^{4+} \overset{K_3}{\rightleftharpoons} [CeL]^{3+} + H^+ \quad (7)$$

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solution containing cerium(IV) and malic acid may be written as (8). This equation may be rearranged to give (9).

$$\varepsilon_{obs}' = \frac{\varepsilon_{Ce} + \varepsilon_{CeOH}K_h/[H^+]^{-1} + \varepsilon_{CeHL}K_1[HL] + \varepsilon_{CeL}K_2K_h[HL][H^+]^{-1}}{1 + K_h/[H^+]^{-1} + K_1[HL] + K_2K_h[HL][H^+]^{-1}} \qquad (8)$$

At the wavelength used for the kinetic measurements (357 nm), $\varepsilon_{Ce} \sim \varepsilon_{CeOH}$ and, from a knowledge of K_h, α can

$$\alpha[HL]^{-1} = \varepsilon_{obs}'(K_1[H^+] + K_2K_h) - (\varepsilon_{CeHL}K_1[H^+] + \varepsilon_{CeL}K_2K_h) \qquad (9)$$

where $\alpha = \varepsilon_{Ce}[H^+] + \varepsilon_{CeOH}K_h - \varepsilon_{obs}'([H^+] + K_h)$

be calculated. Plots of $\alpha[HL]^{-1}$ against ε_{obs}' at fixed $[H^+]$ were linear with positive gradients (G) and negative intercepts (I). The data at 10·6 °C, derived from the initial optical-density changes, are shown in Figure 2.

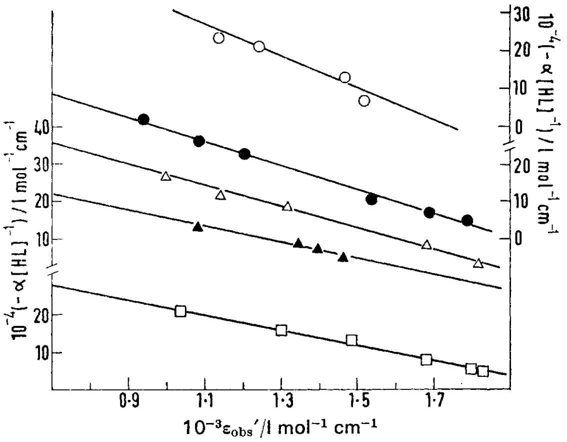

FIGURE 2 Plot of $-\alpha[HL]^{-1}$ against ε_{obs}' [equation (9)] at 10·6 °C, 357 nm, and I = 1·50M. The ordinates have been displaced for clarity: $[H^+]$ = 1·45 (○) and 1·00 (●) (right-hand ordinates); 0·75 (△), 0·25 (▲), and 0·50M (□) (left-hand ordinates)

Similar plots were obtained at other temperatures. From (9) it may be seen that $G = K_1[H^+] + K_2K_h$ and $I = -(\varepsilon_{CeHL}K_1[H^+] + \varepsilon_{CeL}K_2K_h)$, so that plots of G against $[H^+]$ and I against $[H^+]$ yield K_1, K_2K_h, $\varepsilon_{CeHL}K_1$, and $\varepsilon_{CeL}K_2K_h$ from which the absorption coefficients of the complexes may be calculated. The equilibrium constants and absorption coefficients are given in Table 4, whence it is seen that K_1 is relatively small compared with K_2K_h. The errors associated with K_1 were in general too large to allow derivation of any thermodynamic parameters, but ΔH and ΔS values may be calculated for reaction (5). The value of K_1 at 25 °C, 13 ± 5 l mol^{-1}, may be compared with that of 10 l mol^{-1} for the corresponding complex formation with i-propyl alcohol[3] and for other primary and secondary alcohols[2] the corresponding equilibrium constants are in the range 1·5—5 l mol^{-1}.

(c) *Evaluation of Kinetic Data.*—As was previously noted,[7] reactions of cerium(IV) in perchlorate proceed much faster than those in sulphate media and comparison of the present data with those derived previously[5,6] shows an increase in rate of 10^3—10^4 between the two systems. This may reflect either the increased redox potential of the Ce^{IV}–Ce^{III} complex in $HClO_4$[20] or the inability of the α-hydroxyacid to compete successfully as a complexing ligand with the negatively charged sulphate ion. Since in some of the kinetic runs the nitrate complex of cerium(IV) was used, it was necessary to establish whether nitrate ions had any effect on the rate of reaction. The results of experiments carried out in NO_3^- concentrations up to one hundred times that of the oxidant concentration (Table 1) showed no effect on the rate. Similar runs with cerium(III) showed no effect on the observed rate constant up to a fifty-fold excess.

TABLE 1

Effect of nitrate and cerium(III) ions on the reaction rate at 20 °C, I = 1·50M, $[H^+]$ = 1·00M, 357 nm, $[Ce^{IV}]$ = 2·50 × 10^{-4}M, and $[HL]$ = 5·0 × 10^{-3}M

$10^3[Ce^{III}]$/M	k_{obs}/s^{-1}	$10^3[NO_3^-]$/M	k_{obs}/s^{-1}
0·0	1·05 ± 0·01	0·0	1·05 ± 0·01
0·25	1·05 ± 0·01	0·50	1·07 ± 0·02
1·00	1·04 ± 0·01	1·00	1·06 ± 0·01
2·50	1·06 ± 0·02	2·00	1·06 ± 0·02
12·50	1·03 ± 0·03	5·00	1·08 ± 0·01
		25·00	1·04 ± 0·03

The kinetic rate law showed that, whilst the order in oxidant concentration was unity, a non-integral value was obtained for the malic acid, consistent with formation of a complex which undergoes a further intramolecular redox reaction. From the scheme in equations (10) and (11), allowing for the overall stoicheiometry, the

$$\begin{tikzcd}
Ce^{4+} + HL \arrow[r, rightleftharpoons, "K_1"] \arrow[d, rightleftharpoons, "H^+"', "K_h"] & {[Ce(HL)]^{4+}} \arrow[r, "k\alpha"] \arrow[d, rightleftharpoons, "H^+"', "K_3"] & Ce^{III} + HL^{\bullet} \quad (10) \\
{[Ce(OH)]^{3+}} + HL \arrow[r, rightleftharpoons, "K_2"] & {[CeL]^{3+}} \arrow[r, "k\beta"] & Ce^{III} + L^{\bullet} \quad (11)
\end{tikzcd}$$

rate of loss of total cerium(IV) may be expressed as (12)

$$\frac{-d[Ce^{IV}]_T}{dt} = 10k_\alpha[Ce(HL)^{4+}] + 10k_\beta[CeL^{3+}] = \frac{(10k_\alpha K_1[H^+] + 10k_\beta K_2K_h)[Ce^{IV}]_T[HL]}{[H^+] + K_h + (K_1[H^+] + K_2K_h)[HL]} \qquad (12)$$

and the observed first-order rate constant, k_{obs}, as in (13), so that a plot of k_{obs}^{-1} against $[HL]^{-1}$ should be linear.

$$\frac{1}{k_{obs}} = \frac{([H^+] + K_h)}{10(k_\alpha K_1[H^+] + k_\beta K_2K_h)[HL]} + \frac{K_1[H^+] + K_2K_h}{10(k_\alpha K_1[H^+] + k_\beta K_2K_h)} \qquad (13)$$

Treatment of the kinetic data (Table 2) in this way showed excellent linearity (*cf.* Figure 3). From the gradients and intercepts of such plots [equation (13)] an expression similar to that derived previously [equation (9)] for the spectrophotometric measurements is ob-

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TABLE 2

Observed rate constants at varying ligand (HL) and hydrogen-ion concentrations, $I = 1{\cdot}50$M, 357 nm, and $[\mathrm{Ce^{IV}}]_T = 2{\cdot}5 \times 10^{-4}$M. Gradients ($G'$) and intercepts ($I'$) were derived from plots according to equation (13)

θ_c/°C	[H$^+$]/M	10^2[HL]/M	k_{obs}/s^{-1}	$10^3G'$/mol l^{-1} s	I'/s
25·0	0·60[a]	0·25	1·60	1·012 ± 0·03	0·218 ± 0·004
		0·375	2·05		
		0·500	2·39		
		2·50	3·94		
		3·75	3·98		
	0·80[b]	0·50	2·20	1·24 ± 0·03	0·205 ± 0·006
		1·50	3·60		
		2·50	4·02		
		3·75	4·00		
	1·00[b]	1·00	3·59	1·44 ± 0·01	0·209 ± 0·004
		2·50	3·73		
		3·00	3·85		
		3·50	4·00		
		5·00	4·25		
	1·25[b]	0·25	1·07	1·82 ± 0·02	0·211 ± 0·004
		0·50	1·74		
		1·00	2·50		
		1·50	3·04		
		2·00	3·34		
		2·50	3·64		
		3·75	3·73		
	1·45[b]	0·25	0·95	2·06 ± 0·025	0·225 ± 0·005
		0·388	1·31		
		0·50	1·59		
		0·75	2·05		
		1·50	2·76		
		2·50	3·14		
		3·75	3·58		
20·0	0·50	0·312	1·18	1·32 ± 0·03	0·414 ± 0·006
		0·375	1·32		
		0·50	1·49		
		0·75	1·68		
		1·50	2·01		
		2·50	2·12		
	0·75	0·25	0·84	1·86 ± 0·04	0·413 ± 0·008
		0·375	1·10		
		0·50	1·31		
		0·75	1·49		
		1·50	1·90		
		2·50	2·04		
		3·75	2·09		
	1·00	0·25	0·69$_2$	2·46 ± 0·08	0·468 ± 0·018
		0·50	1·03		
		0·75	1·20		
		2·50	1·80		
		3·75	1·94		
	1·25	0·25	0·63	2·80 ± 0·04$_5$	0·468 ± 0·009
		0·375	0·83		
		0·50	0·95$_5$		
		0·75	1·20		
		1·50	1·52		
		2·50	1·71		
		3·75	1·87		
	1·50	0·25	0·54	3·42 ± 0·09$_2$	0·470 ± 0·019
		0·375	0·74		
		0·50	0·87		
		0·75	1·04		
		1·50	1·40		
		3·75	1·86		
16·0	0·30	0·312	0·83	1·48 ± 0·066	0·727 ± 0·013
		0·500	0·97$_5$		
		0·75	1·10		
		1·50	1·20		
	0·90	0·375	0·61$_7$	3·39 ± 0·066	0·722 ± 0·01
		0·50	0·71$_4$		
		0·75	0·84		
		1·50	1·05		
		2·50	1·18		

TABLE 2 (*Continued*)

θ_c/°C	[H$^+$]/M	10^2[HL]/M	k_{obs}/s^{-1}	$10^3G'$/mol l^{-1} s	I'/s
	1·25	0·25	$0{\cdot}38_7$	4·51 ± 0·03	0·771 ± 0·01
		0·375	0·50		
		0·50	0·61		
		0·75	$0{\cdot}72_5$		
		1·50	$0{\cdot}94_3$		
		2·50	1·06		
		3·75	1·09		
	1·50	0·25	$0{\cdot}33_8$	$5{\cdot}44 \pm 0{\cdot}09_4$	$0{\cdot}78 \pm 0{\cdot}01_9$
		0·375	$0{\cdot}45_4$		
		0·50	$0{\cdot}54_5$		
		0·75	0·64		
		1·50	$0{\cdot}89_3$		
		2·50	1·01		
		3·75	1·09		
10·6	0·25	0·25	$0{\cdot}40_8$	2·05 ± 0·19	1·58 ± 0·04
		0·437	$0{\cdot}49_5$		
		0·625	$0{\cdot}54_3$		
		1·25	$0{\cdot}58_1$		
		1·88	0·580		
	0·50	0·25	$0{\cdot}31_9$	$4{\cdot}07_5 \pm 0{\cdot}07_6$	1·41 ± 0·005
		0·437	$0{\cdot}41_7$		
		0·625	$0{\cdot}46_7$		
		1·25	$0{\cdot}55_3$		
		1·83	$0{\cdot}59_5$		
		2·50	$0{\cdot}61_0$		
	0·75	0·25	$0{\cdot}27_5$	5·51 ± 0·06	1·44 ± 0·01
		0·375	$0{\cdot}34_6$		
		0·50	$0{\cdot}38_9$		
		0·75	$0{\cdot}45_8$		
		1·50	$0{\cdot}55_3$		
		2·50	0·61		
		3·75	$0{\cdot}63_7$		
	1·00	0·25	$0{\cdot}23_8$	$6{\cdot}65 \pm 0{\cdot}12_8$	1·51 ± 0·26
		0·375	$0{\cdot}30_7$		
		0·50	0·36		
		0·75	$0{\cdot}40_7$		
		1·50	0·51		
		2·50	0·56		
		3·75	$0{\cdot}59_7$		
	1·45	0·25	0·19	$8{\cdot}87 \pm 0{\cdot}22_8$	1·68 ± 0·05
		$0{\cdot}37_5$	$0{\cdot}25_4$		
		0·50	$0{\cdot}28_7$		
		0·75	0·34		
		1·50	$0{\cdot}44_3$		
		3·75	0·53		

[a] The nitrate salt of Ce^{IV} was used. [b] The perchlorate salt of Ce^{IV} was used.

tained, and equilibrium constants derived from the kinetic plots are compared with those from initial optical-density changes in Table 4. The agreement of the data is considered satisfactory and again indicates the existence of two complexes, one of which is much more stable than the other.

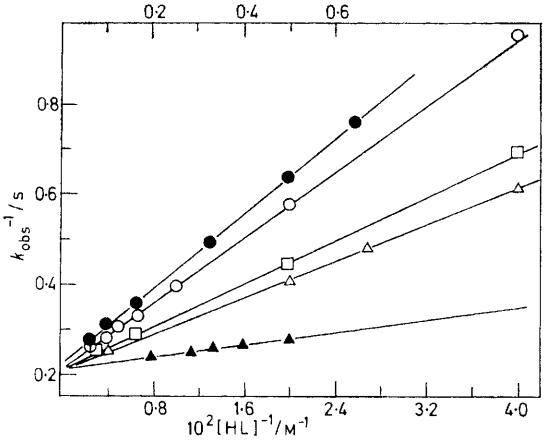


FIGURE 3 Rate data at 25 °C: plots of k_{obs} (s^{-1}) against [HL]$^{-1}$ at [Ce^{IV}] = $2{\cdot}50 \times 10^{-4}$, I = 1·50, and [H$^+$] = 1·45 (●), 1·25 (○), 0·80 (□), 0·60 (△), and 1·00M (▲) (upper abscissae)

Rate parameters were derived using gradients, G', from plots [equation (13)] of k_{obs}^{-1} against [HL]$^{-1}$, since using the variation with ligand concentration these gradients (Table 2) could be measured to within ±2%. Rearrangement of this term in equation (13) gives (14),

$$([H^+] + K_h)/G' = 10k_\alpha K_1[H^+] + 10k_\beta K_2 K_h \quad (14)$$

so that a plot of ([H$^+$] + K_h)/G' against [H$^+$] should be linear. The data for such plots are given in Table 3, where it may be seen that no significant variation with [H$^+$] was observed over the concentration range 0·25—1·45M, indicating that only one complex undergoes intramolecular decomposition (k_β), namely the species [CeL]$^{3+}$. Either the rate constant k_α is markedly smaller than k_β, a feature which is considered unlikely since protonation would not be expected to alter radically the redox potential of the cerium(IV) complex, or the complex is present in too low a concentration for observation under the present experimental conditions. This alternative is certainly supported by the fact that the equilibrium constant for formation of the protonated complex [equation (4)] is at or near the limits of detection by the methods used in this study. Also if negligible concentrations of this complex are present in solution, the assumptions made earlier for the derivation of K_h are justified. This study then yields a measurement of K_h by kinetic methods and further substantiates our finding of a value for the hydrolysis constant which is considerably lower than that quoted previously. The rate constant k_β was then calculated [equation (10)] using the value of K_2K_h derived kinetically. Activation parameters and rate constants are given in Table 4. The activation energy for electron transfer involving the complex $[CeL]^{3+}$ may be compared with that of 27·3 kcal mol^{-1} for the comparable reaction with i-propyl alcohol.[3,*]

TABLE 3

Derivation of rate constants for the redox reaction based on equation (14)

θ_c/°C	$[H^+]$/M	$\frac{([H^+] + K_h)/s^{-1}}{G'}$
25·0	0·60	790 ± 6
	0·80	805 ± 15
	1·00	833 ± 50
	1·25	798 ± 8
	1·45	800 ± 10
20·0	0·50	504 ± 9
	0·75	495 ± 10
	1·00	475 ± 15
	1·25	504 ± 4
	1·50	489 ± 13
16·0	0·30	302 ± 10
	0·90	305 ± 5
	1·25	310 ± 1
	1·50	304 ± 6
10·6	0·25	180 ± 15
	0·50	152 ± 4
	0·75	158 ± 2
	1·00	169 ± 4
	1·45	177 ± 4

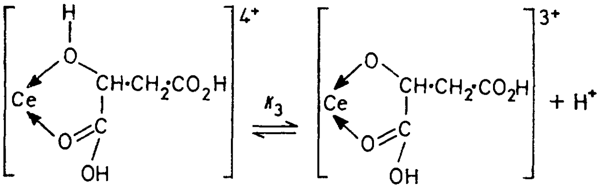
TABLE 4

Kinetic and thermodynamic parameters[a]

θ_c/°C	k_β [b]/s^{-1}	K_h [c]/mol l^{-1}	K_2K_h		K_1/l mol 1		$10^{-3}K_2$/l mol^{-1}	K_3/mol l^{-1}
			d	*e*	*d*	*e*		
10·6	0·085 ± 0·010	$0{\cdot}12_6$	195 ± 20	175 ± 25	30 ± 10	50 ± 30	1·55	5 ± 3
16·0	0·149 ± 0·001	0·14	205 ± 10	220 ± 15	10 ± 4	35 ± 15	1·46	15 ± 5
20·0	$0{\cdot}25_9$ ± 0·007	$0{\cdot}16_7$	190 ± 10	200 ± 20	20 ± 10	25 ± 10	1·14	8 ± 3
25·0	0·52 ± 0·06	0·20	155 ± 15	145 ± 25	10 ± 4	16 ± 10	0·78	11 ± 4

[a] Spectrophotometric data were derived from equation (9). The average values of ε_{CeHL} and ε_{CeL} over the temperature range studied were (2·4 ± 0·15) × 10^3 and (2·05 ± 0·20) × 10^3 l mol^{-1} cm^{-1} respectively. See text for comparison with uncomplexed ions. [b] $\Delta H^‡ = 20{\cdot}6 \pm 1{\cdot}5$ kcal mol^{-1}, $\Delta S^‡ = 9{\cdot}5 \pm 5$ cal K^{-1} mol^{-1}. [c] Including data from ref. 13 (see text); $\Delta H = +5{\cdot}2 \pm 0{\cdot}7$ kcal mol^{-1}, $\Delta S = 14{\cdot}3 \pm 4$ cal K^{-1} mol^{-1}. [d] Determined kinetically. [e] Determined spectrophotometrically.

It is to be noted that $K_2K_h = K_3K_1$ and that, whilst we have adopted an approach which yields confirmation of K_h and K_2 values, an alternative path for complex formation is *via* dissociation of the protonated complex $[Ce(HL)]^{4+}$ as in (15). A value of $K_3 \simeq$ 5—15 mol l^{-1} may be calculated from the present data, the inaccuracy resulting from uncertainties in K_1. This mechanism was preferred in the case of the reaction with i-propyl alcohol,[3] where $K_3 \approx 1$. There are certain attractions in this approach in that it is difficult to envisage from electrostatic considerations why the tripositive $[Ce(OH)]^{3+}$ ion should complex more strongly than the Ce^{4+}(aq) ion, and it may be that, although thermodynamically the overall reaction (5) is favoured ($-\Delta G = 3{\cdot}94$ kcal mol^{-1}), in fact K_2 represents a composite equilibrium constant in which one of the formation steps is kinetically slow. If this were the case, then reaction (15) would represent the route by which the reactive species in the redox system is formed. It is of interest to note that in the corresponding reaction with malonic acid[21,22] the overall $[H^+]$ dependence of the reaction rate differs radically from the present study (k_{obs} in fact increases with $[H^+]$) and a possible explanation lies in a much smaller value of K_3 ($\ll 1$). Malonic acid has no α-hydroxyl proton which will dissociate on complexing with the metal ion. Increasing $[H^+]$ in the present system merely forces equilibrium (15) to the left and so reduces the concentration of reactive complex.



(15)

The reaction stoicheiometry may be understood if the ligand is oxidised in a one-electron step to yield cerium(III) and a radical which further reacts rapidly with cerium(IV) in a series of steps to give formic acid. The nature of the radicals produced in reactions of α-hydroxy-acids, $R{\cdot}CH(OH){\cdot}CO_2H$, has been the subject of some discussion,[7] stabilisation of a radical of the type $R{\cdot}\dot{C}H(OH)$ being considered important. Oxidation of this species would, however, in the present study be expected to produce $R{\cdot}CO_2H$, malonic acid. The oxidation of this substrate, however, is slower than for malic acid,[21,22] and it may be that, where $R = CH_2{\cdot}CO_2H$, further decarboxylation of the radical occurs with accompanying increase in the number of moles of oxidant required.

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[*] 1 cal = 4·184 J.

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

[22] Z. Amjad and A. McAuley, unpublished work.