Metal-ion Oxidations in Solution. Part 16.[1] The Oxidation of α-Hydroxycarboxylic Acids by Cerium(IV) in Perchloric Acid Media

By **Zahid Amjad, Alexander McAuley,*†** and (in part) **Umaru D. Gomwalk,** Departments of Chemistry, University of Glasgow, Glasgow G12 8QQ, and University of Victoria, Victoria, B.C. V8W 2Y2, Canada

The redox reactions between cerium(IV) ions and α-hydroxycarboxylic acids (HA) proceed *via* an inner-sphere mechanism. Investigations over the range 6.4—30 °C using stopped-flow methods have demonstrated the existence of intermediate complexes. The complex $[CeA]^{3+}$ is thermodynamically more stable than the protonated

$$[Ce(HA)]^{4+} \overset{K_3}{\rightleftharpoons} H^+ + [CeA]^{3+} \xrightarrow{k_2} Ce^{III} + A\cdot \qquad \text{(i)}$$

form $[Ce(HA)]^{4+}$ and is more reactive kinetically. Formation constants for the complexes have been obtained both from initial optical-density changes and kinetic data. For reactions (ii) the formation constants at 25 °C and

$$[Ce(OH)]^{3+} + HA \overset{K_2}{\rightleftharpoons} [CeA]^{3+} \qquad \text{(ii)}$$

thermodynamic parameters are: glycolic acid, $K_2 = 119 \pm 13$ dm³ mol⁻¹, $\Delta H_2 = -14.8 \pm 2.5$ kcal mol⁻¹, $\Delta S_2 = -40 \pm 5$ cal K⁻¹ mol⁻¹; lactic acid, $K_2 = 191 \pm 14$, $\Delta H_2 = -12.8 \pm 0.75$, $\Delta S_2 = 33 \pm 4$; 2-hydroxy-2-methylpropanoic acid, $K_2 = 372 \pm 46$, $\Delta H_2 = -18.5 \pm 3.3$, $\Delta S_2 = -50 \pm 6$; phenylglycolic acid, $K_2 = 645 \pm 120$ (17.5 °C), $\Delta H_2 = -14.7 \pm 1.5$, $\Delta S_2 = -37 \pm 5$. Rate constants, k_2, for the intramolecular redox reactions at 25 °C for the four substrates are 0.37, 2.25, 2.57, and 92 s⁻¹ respectively, the corresponding $\Delta H^\ddagger$ values being 28.8 ± 1.2, 25.0 ± 0.8, 28.5 ± 0.4, and 23.4 ± 1.3 kcal mol⁻¹. No medium effects have been observed on substitution of lithium for sodium as the counter ion of the background electrolyte. Attempts to characterise the radical A· using flow-e.s.r. techniques have been unsuccessful. The rate data are compared with those in sulphuric acid media and possible similarities in the reaction paths are discussed.

THE oxidation of α-hydroxycarboxylic acids by cerium(IV) has been studied under a variety of conditions. In sulphate media [2-5] the reactions are sufficiently slow for investigation by conventional methods. The predominant metal-ion species in these solutions are sulphatocerium(IV) complexes and there has been some controversy as to the precise nature of the oxidant, the complex ions $[Ce(SO_4)]^{2+}$ and $Ce[SO_4]_2$ being more favoured. In perchloric acid solutions,[6-11] however, the situation is more readily resolved in that at low concentrations of Ce^{IV} only Ce^{4+}(aq) and $[Ce(OH)]^{3+}$(aq) [12] are present and the oxidation rates are faster. In a recent paper [6] we described a method of preparation of solutions of the oxidant where the possibility of formation of a cerium(IV) dimer species is prevented and which the solutions are sufficiently stable to allow the study of reactions of this type to be undertaken. Also under these conditions, since the weakly co-ordinating perchlorate ion is not expected to participate in complexing with the metal centre, it is possible to establish inner-sphere mechanisms with the formation of transient intermediate complexes. Such species have been invoked in the reactions with primary [9,11] and secondary alcohols [8] and other substrates.[3] In the oxidation of malic acid [6] we reported the characterisation of such a species from both spectroscopic and kinetic data.

In the present paper, the effects of substituents R^1 and R^2 on the ligand $HO\cdot CR^1R^2\cdot CO_2H$, both on the thermodynamic parameters associated with the formation of the complexes and on the kinetics of their subsequent decomposition, are described.

EXPERIMENTAL

Stock solutions of Ce^{IV} were prepared either electrolytically or from ammonium cerium(IV) nitrate.[6,12] In each case this reagent, which was used within 10—12 h of preparation, was stored at 0 °C in order to prevent any slow oxidation of the solvent. Glycolic and 2-hydroxy-2-methylpropanoic acids were twice recrystallised from methanol and analysis indicated purity of >99.7%. Lactic (AnalaR) and phenylglycolic acids (Koch–Light, puriss) were used without further purification. The ionic strength was maintained constant at 1.50 mol dm⁻³ using $HClO_4$(AnalaR)–$Na[ClO_4]$(Fluka) mixtures. In some experiments designed to investigate possible medium effects, lithium perchlorate was used as the background electrolyte. This was prepared by reaction of lithium carbonate with perchloric acid and twice recrystallised from water. The $[Li^+]$ of a diluted sample was determined using an ion-exchange procedure. Stock solutions of Ce^{III} and $[NO_3]^-$ were made from cerium(III) nitrate (B.D.H.) and sodium nitrate (AnalaR) respectively. All the solutions were prepared with distilled water obtained from an all-glass still.

Kinetics.—Kinetic studies were carried out under conditions of excess of ligand on a stopped-flow instrument described previously.[13] Comparison of solutions in which Ce^{IV} was mixed rapidly with acid perchlorate solution with those where ligand was present indicated formation of a

---

† *Present address:* The University of Victoria.

[1] Part 15, K. J. Ellis, A. G. Lappin, and A. McAuley, *J.C.S. Dalton*, 1975, 1930.

[2] B. Krishna and K. C. Tewari, *J. Chem. Soc.*, 1961, 3097.

[3] T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1964, 3193.

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

[5] T. J. Kemp, ' Comprehensive Chemical Kinetics,' vol. 7, eds. C. H. Bamford and C. F. H. Tipper, Elsevier, 1972, p. 274.

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

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

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

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

[10] P. S. Shankhla and R. N. Mehrotra, *Indian J. Chem.*, 1972, **10**, 1081.

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

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

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

complex within the time of mixing. Optical-density changes associated with the formation and redox decomposition of these species were analysed using a Nova 2000 computer. For slower reactions ($t_{\frac{1}{2}} > 20$ s), however, a hand-driven two-jet glass-mixer flow system was employed.[14] A Unicam SP 800 spectrophotometer with chart-recorder attachment was used to monitor changes in optical density. In this apparatus, in which a 1.00-cm flow-through cell was used, the ' dead time ' was 0.35 ± 0.05 s. The reservoirs, drive syringes, and mixing chamber were housed in a Plexi-glass thermostatted water-bath situated directly above the cell compartment of the spectrophotometer. First-order kinetic plots were linear to at least 80—90% completion of reaction and rate constants were reproducible to ±2%. No changes in rate were detected over the wavelength range 340—400 nm.

Stoicheiometry.—In the presence of excess of ligand (*i.e.* the conditions for the kinetic experiments), the oxidation of glycolic, lactic, 2-hydroxy-2-methylpropanoic, and phenylglycolic acids yielded as products formaldehyde, acetaldehyde, acetone, and benzaldehyde respectively, according to equation (1). Quantitative determinations of the

$$R^1R^2C(OH)\cdot CO_2H + 2Ce^{IV} \longrightarrow R^1R^2C{:}O + 2Ce^{III} + 2H^+ + CO_2 \quad (1)$$

carbonyl products indicated reaction of 0.5 ± 0.02 mol of Ce^{IV} per mol of organic substrate. In this regard, the stoicheiometry differs from that of malic acid[6] where 10 equivalents of oxidant are required for complete reaction. A possible explanation of the difference lies in the formation in the malic acid system [after a reaction analogous to (1)] of oxalacetic acid which is then rapidly further oxidised by Ce^{IV} to yield formic acid as the final product.

RESULTS AND DISCUSSION

(a) *Formation of Intermediate Complexes.*—From initial optical-density changes (ΔD), it was apparent that the addition of an organic acid caused a shift of about 40 nm in the absorption maximum of Ce^{IV} to $\lambda_{max.}$ *ca.* 350—360 nm. Using variations in ΔD with wavelength, it was possible to construct the spectra of the intermediates in this region and these data are presented in Figure 1, which includes the spectrum of malic acid not previously published. There are a few data available with which to make comparisons, but Rangaswamy and Santappa[9] identified a deepening of the yellow colour of Ce^{IV} on addition of alcohols as being suggestive of complex formation. The spectroscopic changes presented in their paper extend only to a wavelength of 380 nm, but extrapolation would yield a maximum at a wavelength near to that obtained in this investigation. Ardon[11] also established the intermediacy of a 1 : 1 complex in the oxidation of ethanol in perchlorate media but his data refer to only one wavelength (400 nm). We have included in Figure 1, however, the spectrum of the cerium(IV)–ethanol complex for comparison with the present data.

Under the experimental conditions employed ($[H^+] > 0.3$ mol dm^{-3}), the α-hydroxycarboxylic acids (HA) are present predominantly as the un-ionised forms[15] (pK_a *ca.* 3—4) and the optical-density increases may then be related to the reactions of the uncharged ligands with

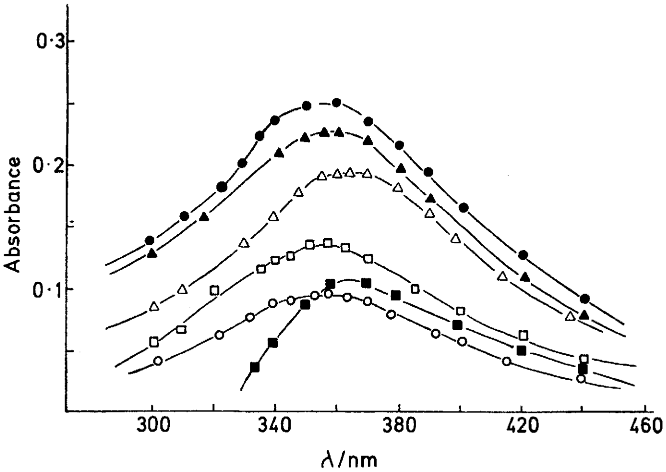

FIGURE 1 Spectra of the intermediates: (●) cerium(IV)–2-hydroxy-2-methylpropanoic acid, 10.6 °C, [HA] = 1.01 × 10^{-2}, $[H^+]$ = 0.605 mol dm^{-3}; (▲) cerium(IV)–malic acid, 10.2 °C, [HA] = 9.9 × 10^{-3}, $[H^+]$ = 0.73 mol dm^{-3}; (△) cerium(IV)–phenylglycolic acid, 10.5 °C, [HA] = 5.5 × 10^{-3}, $[H^+]$ = 1.08 mol dm^{-3}; (□) cerium(IV)–lactic acid, 10.6 °C, [HA] = 1.03 × 10^{-2}, $[H^+]$ = 0.862 mol dm^{-3}; (○) cerium(IV)–glycolic acid, 12.6 °C, [HA] = 1.08 × 10^{-2}, $[H^+]$ = 0.60 mol dm^{-3}; (■) cerium(IV)–ethanol, *ca.* 25 °C, [EtOH] = 0.2, $[H^+]$ = 1.0 mol dm^{-3}

the ions $Ce^{4+}(aq)$ and $[Ce(OH)]^{3+}(aq)$. From the reaction scheme in equations (2)—(5) the observed

$$Ce^{4+} + HA \overset{K_1}{\rightleftharpoons} [Ce(HA)]^{4+} \quad (2)$$

$$[Ce(OH)]^{3+} + HA \overset{K_2}{\rightleftharpoons} [CeA]^{3+} \quad (3)$$

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

$$[Ce(HA)]^{4+} \overset{K_3}{\rightleftharpoons} [CeA]^{3+} + H^+ \quad (5)$$

absorption coefficient, ε_c, of a solution containing Ce^{IV} and organic substrate may be written as in (6) (charges

$$\varepsilon_c = \frac{\varepsilon_{Ce} + (\varepsilon_{CeOH}K_h/[H^+]) + \varepsilon_{CeHA}K_1[HA] + (\varepsilon_{CeA}K_2K_h[HA]/[H^+])}{1 + (K_h/[H^+]) + K_1[HA] + (K_2K_h[HA]/[H^+])} \quad (6)$$

are omitted for clarity). Equation (6) may be rearranged to the form (7)

$$\alpha[HA]^{-1} = \varepsilon_c(K_1[H^+] + K_2K_h) - (\varepsilon_{CeHA}K_1[H^+] + \varepsilon_{CeA}K_2K_h) \quad (7)$$

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

Kinetic measurements were made at 357 nm where $\varepsilon_{Ce} \sim \varepsilon_{CeOH}$ and, from a knowledge of K_h,[6,12] α was evaluated at different ligand and hydrogen-ion concentrations. Plots of $\alpha[HA]^{-1}$ against ε_c at fixed $[H^+]$ were linear with positive gradients (G) and negative intercepts

---

[14] J. P. McCann, Ph.D. Thesis, University of Glasgow, 1975.

[15] ' Handbook of Chemistry and Physics,' ed. C. D. Hodgman, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.

TABLE 1

Parameters relating to the intermediate complexes formed in the course of the redox reactions

Substrate	θ_c/°C	K_1/dm³ mol⁻¹		K_2K_h		K_2 [a,c] dm³ mol⁻¹	$10^{-3}\varepsilon_{CeHA}$ dm³ mol⁻¹ cm⁻¹		$10^{-3}\varepsilon_{CeA}$ dm³ mol⁻¹ cm⁻¹	
		a	*b*	*a*	*b*					
Glycolic acid	11.4	28.4 ± 1.8	33 ± 5	43.9 ± 1.4	40 ± 6	363 ± 12	2.12	2.48 ± 0.18	2.05	1.86 ± 0.13
	17.6	19.7 ± 2.0	25 ± 6	30.8 ± 2	30 ± 5	199 ± 12	2.51		1.69	
	25.2	19.8 ± 4.1	22 ± 5	28.7 ± 2.7	25 ± 6	119 ± 13	2.47		1.93	
	30.1	26.4 ± 3.2	23 ± 4	14.4 ± 2.7	18 ± 4	58 ± 11	2.81		1.77	
	$\Delta H_2 = -14.8 \pm 2.5$ kcal mol⁻¹, $\Delta S_2 = -40 \pm 8$ cal K⁻¹ mol⁻¹									
Lactic acid	10.0	33 ± 7.4	31 ± 5	67.5 ± 7.7	70 ± 10	563 ± 62	2.15	2.49 ± 0.17	1.52	1.48 ± 0.14
	20.0	17.2 ± 2.7	25 ± 6	41.8 ± 2.8	55 ± 7	246 ± 19	2.57		1.41	
	25.0	15.2 ± 2.9	15 ± 4	38.1 ± 2.8	40 ± 6	191 ± 14	2.75		1.72	
	30	18.5 ± 4.9	21 ± 7	27.8 ± 5.3	23 ± 9	111 ± 21	2.49		1.29	
	$\Delta H_2 = -12.8 \pm 1.3$ kcal mol⁻¹, $\Delta S_2 = -32.5 \pm 7$ cal K⁻¹ mol⁻¹									
2-Hydroxy-2-methyl-propanoic acid	11.3	43 ± 17	52 ± 15	212 ± 17	205 ± 28	1 752 ± 140	1.52	1.83 ± 0.18	1.92	1.71 ± 0.18
	16.1	84.8 ± 17	90 ± 20	167 ± 18	170 ± 120	1 152 ± 120	1.91		1.44	
	20.7	77 ± 14	77 ± 21	114 ± 14	145 ± 20	691 ± 80	1.77		1.85	
	25.0	55 ± 10	40 ± 12	74.5 ± 11	110 ± 18	373 ± 46	2.11		1.62	
	$\Delta H_2 = -18.5 \pm 4.2$ kcal mol⁻¹, $\Delta S_2 = -50 \pm 11$ cal K⁻¹ mol⁻¹									
Phenylglycolic acid [d]	6.4	66 ± 21		200 ± 21		2 000 ± 210				
	12.5	40 ± 13		151 ± 12		1 190 ± 100				
	17.5	75 ± 23		100 ± 14		645 ± 120				
	$\Delta H_2 = -14.7 \pm 3.9$ kcal mol⁻¹, $\Delta S_2 = -37.2 \pm 9$ cal K⁻¹ mol⁻¹									

[a] Derived using kinetic data [equation (11)]. [b] Determined spectrophotometrically [equation (7)]. [c] The temperature variation of K_h ($\Delta H = 5.2 \pm 0.7$ kcal mol⁻¹) [6,12] was used; 1 cal = 4.184 J. [d] Initial optical-density changes were too large to allow satisfactory resolution according to equation (7).

(*I*). Typical data are shown in Figure 2 and using a treatment similar to that proposed previously [6] values of K_1, K_2, ε_{CeHA}, and ε_{CeA} were determined. These data are presented in Table 1. The small range of molar absorption coefficients is consistent with a common bonding mode to the metal centre. The temperature dependence of these constants also supports the data analysis. The values of ε_{CeHA} of $(2.4 \pm 0.15) \times 10^3$ and ε_{CeA} of $(2.05 \pm 0.20) \times 10^3$ dm³ mol⁻¹ cm⁻¹ for the malic acid complexes are comparable with those derived in the present study. These molar absorbances are approximately four times larger than the corresponding aqua-metal-ion species. Consideration of the thermodynamic parameters for the complexes will be held over until after discussion of the kinetic data.

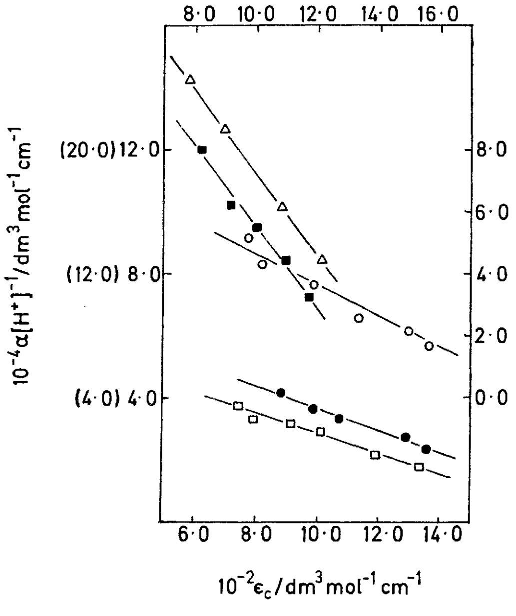

FIGURE 2 Plots of $\alpha[HA]^{-1}$ against ε_c [equation (7)] at various hydrogen-ion concentrations: (●) glycolic acid, [H⁺] = 0.75 mol dm⁻³, 30.1 °C and (□) [H⁺] = 0.35 mol dm⁻³, 30.1 °C; (○) lactic acid, [H⁺] = 0.50 mol dm⁻³, 25.0 °C (right-hand ordinates); (■) 2-hydroxy-2-methylpropanoic acid, [H⁺] = 1.00 mol dm⁻³, 20.7 °C and (△) [H⁺] = 1.25 mol dm⁻³, 20.7 °C [left-hand ordinates (in parentheses) and upper abscissae]

(b) *Kinetics and Mechanism*.*—The rates of these oxidation reactions were much higher in perchloric acid solutions than in sulphate media. Pseudo-first-order kinetic plots showed excellent linearity, and on plotting the observed rate constants ($k_{obs.}$) as a function of the ligand concentration substantial curvature was observed tending to a rate-limiting value. This behaviour is consistent with the complex formation monitored at the start of the reaction. Representative data for each organic acid at 25 °C are given in Table 2. Since in some of the kinetic runs the nitrate complex of Ce^{IV} was used, several experiments were made to establish any effects of $[NO_3]^-$ on the rate. As shown in Table 3, the presence of up to a 100-fold excess of nitrate ion showed no appreciable change in rate. Similar runs with Ce^{III} again showed no effects on $k_{obs.}$. This confirms that species other than Ce^{4+} or $[Ce(OH)]^{3+}$ and their substrate complexes are either not present in appreciable amounts or are kinetically inert.

Using the complex-formation scheme [equations (2)—(5)] the observed redox reactions are consistent with the

$$[Ce(HA)]^{4+} \xrightarrow{k_1} Ce^{III} + HA\cdot \qquad (8)$$

$$[CeA]^{3+} \xrightarrow{k_2} Ce^{III} + A\cdot \qquad (9)$$

---

* Basic kinetic data may be found in Supplementary Publication No. SUP 21898 (13 pp., 1 microfiche). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

TABLE 2

Observed rate constants at varying ligand (HA) and hydrogen-ion concentrations; $I = 1.50$ mol dm^{-3}, $\lambda = 357$ nm, $[\mathrm{Ce^{IV}}]_T = 2.50 \times 10^{-4}$ mol dm^{-3}. Intercepts (I') and gradients (G') were derived from least-square plots according to equation (11)

Substrate	θ_c/°C	[H+]/mol dm^{-3}	10^2[HA]/mol dm^{-3}	$k_{obs.}$/s^{-1}	$10^4G'$	I'	[H+]/mol dm^{-3}	10^2[HA]/mol dm^{-3}	$k_{obs.}$/s^{-1}	$10^4G'$	I'
Glycolic acid	25.2	0.35	0.581	1.34	329 ±8	1.84 ±0.08	0.70	0.746	1.15	496 ±11	1.99 ±0.09
			0.913	1.82				1.245	1.70		
			1.245	2.15				1.659	2.03		
			1.66	2.67				2.323	2.43		
			2.323	3.12				3.319	2.79		
			3.319	3.53							
		0.85	0.664	0.86	596 ±23	2.33 ±0.22					
			0.830	1.09							
			0.996	1.21							
			1.328	1.48							
			1.991	1.86							
			3.319	2.37							
Lactic acid	25.0	0.25	0.789	16.2	26.6 ±1.2	0.26 ±0.02	0.50	0.50	9.35	40.5 ±0.07	0.264 ±0.01
			1.018	19.9				0.75	12.30		
			1.527	24.0				1.00	14.7		
			2.545	26.4				2.50	23.9		
			5.091	31.5				3.50	26.0		
								5.00	28.3		
		0.75	0.50	7.13	56.4 ±0.7	0.28 ±0.01	1.25	0.50	4.98	84.6 ±0.05	0.318 ±0.005
			1.00	11.6				1.00	8.53		
			2.50	19.9				1.50	11.4		
			3.50	23.3				2.50	15.0		
			5.00	25.3				3.50	18.1		
								5.00	20.5		
		1.50	0.764	6.11	97.3 ±1.9	0.366 ±0.014					
			1.018	7.45							
			1.527	10.2							
			3.054	14.8							
			5.091	18.2							
			7.632	19.3							
2-Hydroxy-2-methylpropanoic acid	25.0	0.60	0.25	19.2	9.61 ±0.25	0.131 ±0.005	0.90	0.25	15.1	12.6 ±0.2	0.154 ±0.005
			0.375	26.1				0.375	20.8		
			0.50	31.8				0.50	24.6		
			0.625	35.1				0.625	27.8		
			0.875	40.7				0.875	33.0		
			1.25	47.3				1.25	39.6		
		1.20	0.256	12.4	16.6 ±0.3	0.156 ±0.007	1.50	0.258	9.95	20.9 ±0.3	0.196 ±0.006
			0.375	16.9				0.377	13.2		
			0.50	20.3				0.532	16.6		
			0.625	23.3				0.629	19.1		
			0.875	28.5				0.755	21.3		
			1.250	35.8				1.258	26.9		
Phenylglycolic acid	17.5	0.75	0.25	145	1.22 ±0.056	0.0197 ±0.0015	1.00	0.25	109	1.69 ±0.05	0.0232 ±0.0012
			0.375	196				0.375	146		
			0.50	225				0.50	178		
			0.625	252				0.625	203		
								1.250	262		
		1.25	0.25	95.5	2.04 ±0.04	0.0259 ±0.0025					
			0.50	144							
			0.625	171							
			1.250	243							

rate determining steps (8) and (9) with subsequent rapid reaction of the radical intermediate with a second mol of Ce$^{\mathrm{IV}}$. The rate of disappearance of Ce$^{\mathrm{IV}}$ is given by the rate law (10). The observed first-order rate constant

$$\frac{-\mathrm{d}[\mathrm{Ce^{IV}}]}{\mathrm{d}t} = 2k_1[\mathrm{Ce(HA)^{4+}}] + 2k_2[\mathrm{CeA^{3+}}]$$

$$= \frac{(2k_1K_1[\mathrm{H^+}] + 2k_2K_2K_h)[\mathrm{Ce^{IV}}]_T[\mathrm{HA}]}{[\mathrm{H^+}] + K_h + (K_1[\mathrm{H^+}] + K_2K_h)[\mathrm{HA}]} \quad (10)$$

may thus be expressed in the form (11). Plots of $k_{obs.}^{-1}$

$$\frac{1}{k_{obs.}} = \frac{([\mathrm{H^+}] + K_h)}{(2k_1K_1[\mathrm{H^+}] + 2k_2K_2K_h)[\mathrm{HA}]} + \frac{(K_1[\mathrm{H^+}] + K_2K_h)}{2k_1K_1[\mathrm{H^+}] + 2k_2K_2K_h} \quad (11)$$

against $[\mathrm{HA}]^{-1}$ should thus be linear and treatment of the kinetic data in this manner showed excellent linearity (*cf.* Figure 3). From the gradients (G') and intercepts (I') of such plots [equation (11)] an expression similar to that obtained for the spectrophotometric measurements was derived and the equilibrium data obtained from both sources are compared in Table 1. The agreement is considered good and the predominance of equilibrium (3) in the complex-formation reactions is confirmed.

The rate constants k_1 and k_2 for the intramolecular redox reactions may be evaluated from the gradients (G') of the plots of $k_{obs.}^{-1}$ against $[\mathrm{HA}]^{-1}$ [equation (11)]. Rearrangement of this term yields the expression (12),

$$([\mathrm{H^+}] + K_h)/G' = 2k_1K_1[\mathrm{H^+}] + 2k_2K_2K_h \quad (12)$$

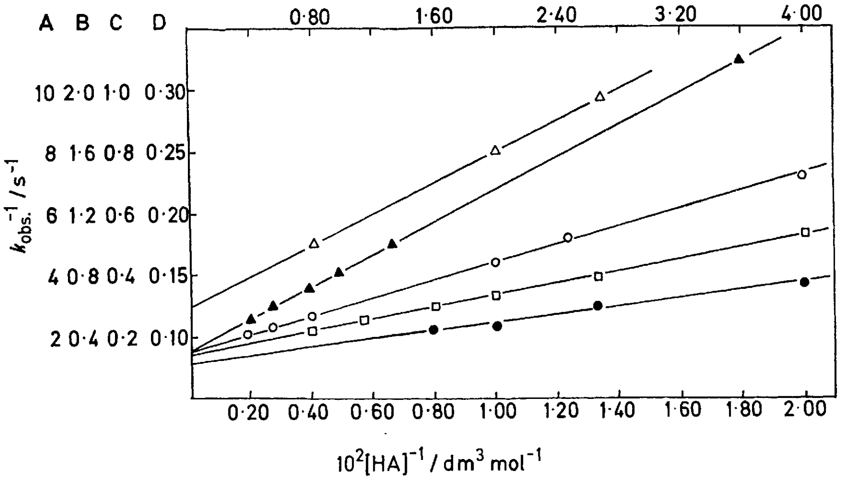

FIGURE 3 Plots of $k_{obs.}^{-1}$ against $[HA]^{-1}$ [equation (11)] at various temperatures: (▲) glycolic acid, $[H^+] = 1.25$ mol dm^{-3}, 30.1 °C (ordinate scale A, lower abscissae); (○) lactic acid, $[H^+] = 0.75$ mol dm^{-3}, 25.0 °C (ordinate scale B, lower abscissae); (□) 2-hydroxy-2-methylpropanoic acid, $[H^+] = 0.60$ mol dm^{-3}, 25.0 °C (ordinate scale C, upper abscissae); (△) phenylglycolic acid, $[H^+] = 1.35$ mol dm^{-3}, 6.4 °C and (●) $[H^+] = 0.25$ mol dm^{-3}, 6.4 °C (ordinate scale D, upper abscissae)

so that a plot of $([H^+] + K_h)/G'$ against $[H^+]$ should be linear. Treatment of the data in this manner showed no significant hydrogen-ion dependence (Table 4), indicating that the k_1 term is negligibly small and that the principal mode of electron transfer is *via* the complex $[CeA]^{3+}$. This feature is similar to that previously observed in the oxidation of malic acid where again the concentration of the protonated complex is considered too low to be kinetically significant. Rate constants k_2 obtained using equation (12) are presented in Table 5 together with the associated thermodynamic parameters for the redox process.

TABLE 3

Effect of Ce^{III} and nitrate ions on the reaction rates; $[Ce^{IV}] = 2.50 \times 10^{-4}$ mol dm^{-3}, $\lambda = 357$ nm, $I = 1.50$ mol dm^{-3}

$10^3[Ce^{III}]$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}	$10^3[NO_3^-]$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}
[Glycolic acid] = 6.07×10^{-3}, $[H^+] = 0.430$ mol dm^{-3}, 11.3 °C			
0.0	0.225	0.0	0.225
0.249	0.225	0.251	0.226
0.746	0.227	0.752	0.224
2.240	0.227	2.254	0.223
4.98	0.222	5.01	0.222
[Lactic acid] = 9.90×10^{-3}, $[H^+] = 0.605$ mol dm^{-3}, 7.8 °C			
0.0	0.135	0.0	0.135
0.25	0.138	0.25	0.136
0.75	0.136	0.75	0.134
2.25	0.134	1.875	0.137
5.00	0.134	2.50	0.135
[2-Hydroxy-2-methylpropanoic acid] = 9.63×10^{-3}, $[H^+] = 0.605$ mol dm^{-3}, 7.8 °C			
0.0	0.459	0.0	0.459
0.25	0.455	0.75	0.460
2.25	0.454	1.875	0.453
5.00	0.458	5.00	0.461
[Phenylglycolic acid] = 2.50×10^{-3}, $[H^+] = 1.00$ mol dm^{-3} 6.4 °C			
0.0	3.58	0.0	3.58
0.250	3.56	0.250	3.55
0.750	3.55	0.750	3.57
2.25	3.55	5.00	3.58

Confirmation of only one redox process derives from an investigation of the rates at high ligand concentrations. Under these conditions, it may be seen from equation (10) that the observed rate becomes independent of [HA] with a rate-limiting constant, $k_{lim.}$. If only k_2 contributes to the redox reaction, expression (13) should hold. Data obtained for the phenylglycolic

$$\frac{1}{k_{lim.}} = \frac{K_1[H^+]}{2k_2K_2K_h} + \frac{1}{k_2} \tag{13}$$

acid reaction at 6.4 °C are presented in Table 6 and a linear plot of $k_{lim.}^{-1}$ against $[H^+]$ yielded a value of 6.25 s^{-1} for k_2 which may be compared with 6.35 ± 0.06 s^{-1} from measurements at lower ligand concentrations. Also the quotient $K_1/K_2K_h = 0.48$ dm^3 mol^{-1} derived under limiting conditions is in reasonable agreement with the value 0.34 dm^3 mol^{-1} obtained earlier.

Medium effects[16,17] have also been seen to be an important factor in redox and substitution reactions where uncertainties in hydrogen-ion effects may be related to differences in the activity coefficients of the counter ions (usually Na^+ and Li^+) which are used in the variation of $[H^+]$ at constant ionic strength. These effects are usually not so marked for intramolecular redox reactions and the absence of a significant difference in rates was observed in these systems. In Table 7 are presented the data for phenylglycolic acid, where the counter ions are varied over a five-fold concentration range without change in $k_{obs.}$. Similar behaviour was observed with the other α-hydroxycarboxylic acids.

The rate constants k_2 decrease in the order phenylglycolic > 2-hydroxy-2-methylpropanoic > lactic > glycolic acid which is consistent with the increased ease of formation of the organic radicals produced.[18] This order is also observed in sulphate media and a comparison of the data (Table 8) shows that for the series the rate constants are *ca.* 10^3 times slower in sulphuric

---

[16] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.

[17] C. Lavalee and T. W. Newton, *Inorg. Chem.*, 1972, **11**, 2616.

[18] T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1964, 1189.

TABLE 4

Derivation of rate constants for the redox reactions [equation (12)]

Substrate	θ_c/°C	[H⁺]/mol dm⁻³	([H⁺] + K_h)/G' / s⁻¹	θ_c/°C	[H⁺]/mol dm⁻³	([H⁺] + K_h)/G' / s⁻¹
Glycolic acid	11.4	0.30	3.47 ± 0.11	17.6	0.70	6.75 ± 0.26
		0.50	3.33 ± 0.11		1.00	6.53 ± 0.07
		0.70	3.48 ± 0.05		1.25	6.80 ± 0.20
		0.90	3.49 ± 0.02			
		1.25	3.26 ± 0.05	30.1	0.35	27.2 ± 0.6
					0.60	28.1 ± 0.4
	25.2	0.35	16.7 ± 0.40		0.75	27.1 ± 0.4
		0.70	18.1 ± 0.40		1.00	31.4 ± 0.5
		0.85	17.6 ± 0.68		1.25	31.8 ± 0.8
Lactic acid	10.0	0.40	30.0 ± 1.2	20.0	0.30	90.3 ± 2.1
		0.70	32.8 ± 0.4		0.60	93.9 ± 2.3
		1.20	32.3 ± 0.7			
		1.50	37.8 ± 1.1		1.50	96.4 ± 1.1
	25.0	0.25	169 ± 7.6	30.0	0.50	262 ± 2
		0.50	173 ± 3		0.75	281 ± 3
		0.75	168 ± 2.2		1.00	308 ± 8
		1.25	171 ± 1		1.50	296 ± 2
		1.50	175 ± 3.4			
2-Hydroxy-2-methylpropanoic acid	11.3	0.50	245 ± 9	16.1	0.50	425 ± 11
		0.75	240 ± 5		0.75	447 ± 16
		1.00	204 ± 3		1.00	406 ± 7
					1.25	426 ± 16
	20.7	0.35	594 ± 23	25.0	0.60	832 ± 21
		0.50	639 ± 15		0.75	840 ± 18
		0.75	581 ± 10		0.90	874 ± 14
		1.00	556 ± 11		1.20	841 ± 15
		1.25	587 ± 16		1.35	838 ± 15
		1.50	576 ± 11		1.50	812 ± 12
Phenylglycolic acid	6.4	0.25	2 430 ± 253	12.5	0.50	4 460 ± 190
		0.50	2 930 ± 129		0.75	4 260 ± 125
		0.75	2 620 ± 154		1.00	4 340 ± 100
		1.00	2 530 ± 82		1.25	4 160 ± 50
		1.35	2 290 ± 20			
		1.50	2 450 ± 120	17.5	0.75	7 210 ± 330
					1.00	6 690 ± 200
					1.25	6 830 ± 130

acid. There is, however, a marked consistency in the ratios of both the rate constants and the activation energies and this may be attributable to a common inner-sphere mechanism. Assuming the rate differences resulting from electronic effects are similar, the reduction in reaction rate in sulphuric acid could be due to the much lower equilibrium constant for the intermediate complex formed. This is borne out by the fact that in H_2SO_4 there is no deviation from linearity of plots of $k_{obs.}$ against [HA],[2,4,18] a condition which will obtain if the concentration of any intermediate is low [*cf.* equation (10)]. It appears that the co-ordination of $[SO_4]^{2-}$ is more thermodynamically favourable than that of the organic acid and a ternary complex may thus be formed. Although the activation energies are lower in sulphate media the reactions are slower. The ratios of the enthalpies of activation (Table 8) are, however, not very

TABLE 5

Rate constants and thermodynamic parameters for the redox reaction [equation (9)]

Glycolic acid

θ_c/°C	11.4	17.6	25.2	30.1
k_2/s⁻¹	0.0388 ±0.0036	0.109 ±0.04	0.374 ±0.06	1.01 ±0.16

$\Delta H^\ddagger = 28.8 \pm 1.2$ kcal mol⁻¹, $\Delta S^\ddagger = 36 \pm 7$ cal K⁻¹ mol⁻¹

Lactic acid

θ_c/°C	10.0	20.0	25.0	30.0
k_2/s⁻¹	0.246 ±0.066	1.18 ±0.04	2.25 ±0.038	5.20 ±0.098

$\Delta H^\ddagger = 25.0 \pm 0.8$ kcal mol⁻¹, $\Delta S^\ddagger = 27 \pm 5$ cal K⁻¹ mol⁻¹

2-Hydroxy-2-methylpropanoic acid

θ_c/°C	11.3	16.1	20.7	25.0
k_2/s⁻¹	0.516 ±0.10	1.24 ±0.06	2.57 ±0.06	5.60 ±0.08

$\Delta H^\ddagger = 28.5 \pm 0.4$ kcal mol⁻¹, $\Delta S^\ddagger \pm 41 \pm 6$ cal K⁻¹ mol⁻¹

Phenylglycolic acid

θ_c/°C	6.4	12.5	17.5
k_2/s⁻¹	6.35 ±0.06	14.2 ±0.4	34.1 ±0.1

$\Delta H^\ddagger = 23.4 \pm 1.3$ kcal mol⁻¹, $\Delta S^\ddagger = 29 \pm 5$ cal K⁻¹ mol⁻¹

TABLE 6

Determination of the redox rate for the complex of phenylglycolic acid under concentration-limiting conditions; 6.4 °C, $[Ce^{IV}] = 5.0 \times 10^{-4}$, $[HA] = 1.6 \times 10^{-2} - 2.45 \times 10^{-2}$, $I = 1.50$ mol dm⁻³ (Li[ClO₄])

[H⁺]/ mol dm⁻³	0.80	1.00	1.20	1.40	1.50
$k_{\text{lim.}}$/s⁻¹	8.90 ±0.30	8.33 ±0.20	7.80 ±0.20	7.60 ±0.20	7.20 ±0.15

TABLE 7

Effects of lithium (*a*) or sodium perchlorate (*b*) on the rate of the cerium(IV)–phenylglycolic acid reaction; $[Ce^{IV}] = 2.50 \times 10^{-4}$, [Phenylglycolic acid] $= 5.0 \times 10^{-3}$, $I = 1.50$ mol dm⁻³, 6.4 °C, 357 nm

[H⁺]/mol dm⁻³	0.25	0.50	0.75	1.00	1.25
k_N/s⁻¹ (*a*)	9.70	7.45	5.98	5.18	4.13
(*b*)	9.65	7.60	5.96	5.25	4.08

different from the ratio 1.12 : 1 of the Ce^{IV}–Ce^{III} electrode potentials in H_2SO_4 (1.44 V) and $HClO_4$ (1.61 V). Co-ordination *via* the oxygen atoms of the organic ligand may thus have little effect on the redox potential of the complexes.

The reaction stoicheiometry may be interpreted in terms of a one-electron oxidation to yield Ce^{III} and the organic radical, followed by a second rapid electron transfer. Attempts to characterise the radicals formed using flow-e.s.r. techniques under similar conditions to those used in the kinetic studies were unsuccessful. This may be the result of the radical formed reacting very rapidly with the second mol of oxidant. In a study of the corresponding reaction with L-cysteine, radical intermediates have been detected [19] with the electrons localised on the sulphur atom. In this case, however, the *d* orbitals of the sulphur probably play an important role in stabilising these species.

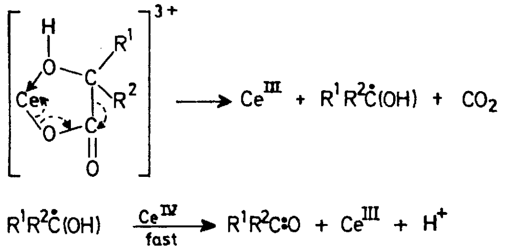

TABLE 8

Relative rate and activation parameters for cerium(IV) oxidations of α-hydroxycarboxylic acids in sulphate and perchlorate media

	Acid			
	Glycolic	Lactic	2-Hydroxy-2-methyl-propanoic	Phenyl-glycolic
$10^4k_{SO_4}$ [a]/ $dm^3\ mol^{-1}\ s^{-1}$	1.0	9.8	37	700
k_{ClO_4} [b]/s^{-1}	0.37	2.25	5.60	86
$10^{-3}\dfrac{k_{ClO_4}}{k_{SO_4}}$/mol dm^{-3}	3.7	2.3	1.51	1.22
$\Delta H_{SO_4}^{\ddagger}$	23.2 [c]	22.5 [d]		18.9 [c]
$\Delta H_{ClO_4}^{\ddagger}$ [b]	28.8	25.0	28.5	23.4
$\Delta H_{SO_4}^{\ddagger}$/ $\Delta H_{ClO_4}^{\ddagger}$	1.24	1.14		1.23

[a] Ref. 18. [b] Present work. Ref. 4. [d] K. P. Bhargava, R. Shanker, and J. N. Joshi, *J. Sci. Ind. Res., India*, 1962, **216**, 373; G. St. Nikolov, *Inorg. Chim. Acta*, 1971, **5**, 559.

The equilibrium constants (K_1) for the complexes (Table 1) may be compared with other carboxylic acids and alcohols. The values are considerably greater than those for formic [20] and acetic [21] acids ($K_1 < 1$) and for monohydric alcohols, *e.g.* isopropyl alcohol [22] or ethanol.[11] The increase may be attributed to chelation. Whilst the temperature variation and errors in K_1 preclude any meaningful determination of the thermodynamic parameters, it appears that in these systems K_1 passes through a minimum value indicative of a non-zero ΔC_p of formation. A possible exception is the 2-hydroxy-2-methylpropanoic acid where there is little temperature variation. It is of interest to note that a similar observation has been made in the ionisation constants of the corresponding α-mercaptocarboxylic acids,[23] the origin of the effect being attributed to solvation changes. Thermodynamic parameters have been derived (Table 1) for the reaction of $[Ce(OH)]^{3+}$ with HA. Enthalpy changes are quite negative suggesting some covalency in the Ce–O bonding.[24]

The existence of an equilibrium between the protonated and unprotonated complexes $[Ce(HA)]^{4+}$ and $[CeA]^{3+}$ (K_3 *ca.* 1.5—4 mol dm^{-3}) has been discussed previously.[8] The values of K_3 derived in this study are similar to those for cerium(IV)–isopropyl alcohol [8] and –malic acid [6] complexes. It is of interest that the position of this equilibrium may have a bearing on the nature of the hydrogen-ion dependences observed for cerium(IV) oxidations. In the present study and for other substrates, the rate of oxidation is increased on lowering the hydrogen-ion concentration. The reverse is true, however, for alcohols and some carboxylic acids. In these cases, however, values of K_3 are generally much lower, with a predominance of the protonated forms of the complex, an observation consistent with the somewhat different spectra of the intermediate complexes from those derived in the present study.

We thank the University of Glasgow for the award of a demonstratorship (to Z. A.), the British Council for a Visiting Fellowship (to U. D. G.), and the S.R.C. and the University of Victoria for support.

[6/1091 *Received, 7th June, 1976*]

---

[19] Z. Amjad, A. McAuley, and P. Premovic, unpublished work.

[20] C. F. Wells and M. Husain, *J. Chem. Soc.* (*A*), 1971, 381.

[21] I. M. Mathai and R. Vasudevan, *J. Chem. Soc.* (*B*), 1970, 1361.

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

[23] K. J. Ellis, A. G. Lappin, and A. McAuley, *J. Solution Chem.*, to be published.

[24] S. Ahrland, *Structure and Bonding*, 1966, **1**, 207.