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Kinetics of Oxidation of *p*-Methylmandelic Acid by Cerium(IV) in Aqueous Sulphate Media

G. ARCOLEO, G. CALVARUSO, F. P. CAVASINO* and C. SBRIZIOLO
Istituto di Chimica Fisica, Università, 90123 Palermo, Italy

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The kinetics of the oxidation of p-*methylmandelic acid (MMA) by ceric sulphate has been studied in aqueous sulphuric acid solutions and in* H_2SO_4–$HClO_4$ *and* H_2SO_4–$LiHSO_4$ *mixtures. In these mixtures the observed rate law is:* $-d[Ce(IV)]/dt = k[MMA][Ce(IV)]$, *where* $k = k_1 + k_2/(1 + a)^2[HSO_4^-]^2 = k_1 + k_2/(1 + 1/a)^2[SO_4^{2-}]^2$ *(*a *is constant). The temperature dependence of the oxidation rate and the effect of ionic strength have been also investigated. It is pointed out that the kinetic data obtained for the solutions containing sulphuric acid alone are to be considered with caution because of the linear dependence existing between the stoichiometric molar concentration of* H_2SO_4 *and both the* HSO_4^-, SO_4^{2-} *and* H^+ *concentrations and the ionic strength over the acid range 0.050–3.97* M.

Introduction

The kinetics of oxidation of α-hydroxy-acids by cerium(IV) have been studied mainly in sulphate media, where the reactions are too slow to be followed by conventional techniques. As far as we know, the α-hydroxy-acids so far examined are: tartaric [1], citric [2], malic [3, 4], lactic [3, 5, 6], glycollic [7, 8], α-hydroxybutyric [9], α-hydroxyisobutyric [10], benzilic [6, 11, 12], atrolactic [10], mandelic [3, 9, 13], *p*-chloro- [14] and *p*-bromomandelic [15] acids. The mechanism postulated for the oxidation involves in the first step the formation of an intermediate complex which subsequently decomposes in the rate-determining electron-transfer step yielding a free radical and the cerium(III) species. The final reaction products are obtained by the subsequent fast oxidation of the organic radical.

In the present work we have studied the kinetics of cerium(IV) oxidation of *p*-methylmandelic acid in sulphate media at various ionic strengths and sulphuric acid concentrations. The temperature dependence of the oxidation rate has been also investigated. This study has been undertaken with the main purpose of examining the effects of the ionic strength and the sulphuric acid concentration upon the reaction rate. It will be subsequently extended to other substituted mandelic acids in order to obtain information about the influence of the substituent group under similar experimental conditions.

Experimental

Materials and Solutions

p-Methylmandelic acid was prepared and purified by the method described for the preparation of *p*-bromomandelic acid using Fluka *p*-methylacetophenone as starting product [16]. The melting point of the acid employed in the kinetic measurements agreed with that reported [17]. The purity of the acid was also checked by acid–base titration. Fluka *p*-tolualdehyde was purified by vacuum distillation. The other substances used [H_2SO_4, $HClO_4$, $Ce(SO_4)_2 \cdot 4H_2O$, Li_2SO_4] were of the highest purity available (C. Erba or Merck products). Deionized water was further purified before use by distillation from an alkaline permanganate solution.

Stock solutions of sulphuric and perchloric acids were standardised by titration against sodium hydroxide. Weighed amounts of lithium sulphate were dissolved in solutions containing equivalent quantities of sulphuric acid to obtain solutions of lithium bisulphate. Cerium(IV) solutions were prepared by dissolving ceric sulphate in sulphuric acid of known molarity and standardised against ferrous ammonium sulphate using N-phenylanthranilic acid as indicator. Solutions of *p*-methylmandelic acid were obtained by dissolving weighed quantities of this compound in solutions containing the desired electrolytes at the required concentrations and were then properly diluted with the same electrolyte solutions.

Stoichiometry

The stoichiometry of the reaction was determined by mixing together sulphuric acid solutions of cerium(IV) and organic acid in different ratios of concentration, the cerium(IV) concentration being always in excess. The reaction mixtures were allowed to stand for several days at 25 °C, after which the

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*Author to whom correspondence should be addressed.

excess of ceric ion was estimated by titration as described above. Five determinations showed that two (± 0.05) mol of cerium(IV) reacted per mol of organic acid according to Eqn. (1). A similar overall reaction

$$2\mathrm{Ce(IV)} + p\text{-}\mathrm{CH_3C_6H_4CH(OH)CO_2H} \rightarrow 2\mathrm{Ce(III)} + p\text{-}\mathrm{CH_3C_6H_4CHO} + 2\mathrm{H^+} + \mathrm{CO_2} \qquad (1)$$

was found for the oxidation of mandelic acid [3, 9] and its *p*-chloro [14] and *p*-bromo [15] derivatives, the reaction products being the corresponding substituted benzaldehydes. Both the reaction stoichiometry and the product of oxidation of *p*-methylmandelic acid were checked spectrophotometrically as follows. Sulphuric acid (0.800 *M*) solution containing cerium(IV) and *p*-methylmandelic acid in the molar ratio 2:1 was left at 25 °C until the oxidation was completed. After appropriate dilution with 0.800 *M* sulphuric acid, the ultraviolet absorption spectrum of the resulting solution was compared with that of *p*-tolualdehyde dissolved in 0.800 *M* sulphuric acid. The similarity of the two spectra confirmed the nature of the reaction product, whereas the estimate of the *p*-tolualdehyde formed in the oxidation process allowed us to determine the stoichiometry. Duplicate experiments using different molar concentrations of the reacting substances gave the same stoichiometry as above. Under the experimental conditions used, the absorption of the cerium (III) species can be neglected compared to that of *p*-tolualdehyde ($\log \epsilon = 4.20$ at the wavelength of maximal absorption $\lambda_{max} = 262$ nm; in 44.0% H_2SO_4 Yates and Stewart [18] found $\log \epsilon = 4.14$ at $\lambda_{max} = 264$ nm).

Kinetic Measurements

Most of the kinetic measurements were performed under conditions of excess of the organic substrate by following spectrophotometrically the rate of disappearance of cerium(IV) at 350–380 nm where Beer's law was found to be obeyed satisfactorily. Low concentrations of cerium(IV) [$(2\text{–}6) \times 10^{-4}$ *M*] were used because of the high extinction coefficients of cerium(IV) species in the solution. The measurements were made with a Beckman DU or a Beckman DK-2A spectrophotometer equipped with time drive attachment which permits the recording of the adsorbance as function of time at a fixed wavelength. Both spectrophotometers were equipped with thermostated compartments for 1 cm cells, the temperature of which was kept constant to ± 0.1 °C.

A few kinetic runs were carried out at 25 °C by titration using comparable concentrations of ceric ion [$(4\text{–}7) \times 10^{-3}$ *M*)] and organic substrate [$(3\text{–}6) \times 10^{-3}$ *M*] in the presence of 1.50 *M* or 1.00 *M* sulphuric acid. The kinetics were followed by removing portions of the thermostated reaction mixture at suitable intervals and quenching the reaction in a known excess of ferrous ammonium sulphate solution. The excess of ferrous ion was titrated against a standard ceric sulphate solution.

TABLE I. Kinetic Data Obtained in Solutions Containing Sulphuric Acid Alone (t = 25.0 °C).

$[H_2SO_4]$ (*M*)	$10^2[\mathrm{MMA}]^a$ (*M*)	10^3k_0 (sec^{-1})	10^2k^b ($M^{-1}\ \mathrm{sec}^{-1}$)
0.500	0.500	5.6	112
	0.750	8.3	
	1.00	11.3	
	1.25	13.9	
	1.50	17.2	
0.600	0.500	4.1	81
	0.750	6.0	
	1.00	8.3	
	1.50	11.6	
0.790	0.500	2.32	45
	0.750	3.3	
	1.00	4.6	
	1.50	6.6	
1.00	0.750	1.85	25.4
	1.50	3.9	
1.50	0.500	0.52	10.2
	0.750	0.76	
	1.00	0.99	
	1.25	1.30	
	1.50	1.55	
2.00	0.750	0.37	4.9
	1.50	0.73	
	0.750	1.25^c	16.7^c
	0.750	3.7^d	49^d
2.50	0.500	0.118	2.44
	0.750	0.183	
	1.00	0.247	
	1.25	0.313	
	1.50	0.37	
	2.41	0.57	
3.00	2.56	0.35	1.37
4.00	1.42	0.112	0.79

[a] *p*-Methylmandelic acid. [b] Mean values. [c] At 35.0 °C. [d] At 45.0 °C.

Results and Discussion

The rates at which cerium(IV) disappears in the presence of excess of organic substrate always follow a first-order law and the cerium(IV) concentration has no effect on the observed pseudo-first order rate constants k_0 reported in Tables I–III, V. These rate constants were evaluated mainly by Guggenheim's method and were reproducible within ± 3%. The order with respect to organic substrate is also unity, as shown by the satisfactory constancy of the second-order rate constants k obtained by dividing the

TABLE II. Kinetic Data[a] Obtained in H_2SO_4–$HClO_4$ Mixtures at 25.0 °C.

$[H_2SO_4]$ (*M*)	10^2[MMA][b] (*M*)	$[H_2SO_4] + [HClO_4]$[c]							
		0.790*M*		1.00*M*		2.00*M*		3.00*M*	
		10^3k_0	10^2k^d	10^3k_0	10^2k^d	10^3k_0	10^2k^d	10^3k_0	10^2k
0.500	0.750	7.3	97	6.6	88	4.4	59		
	1.50	14.6		13.3		8.9			
	2.37							8.3	35
0.600	0.750	5.3	70	4.7	63	2.98	41		
	1.50	10.5		9.5		6.3			
	2.35							5.6	23.8
0.660	0.750	4.6	60						
	1.50	8.9							
0.790	0.750		45^e	2.90	38	1.88	24.6		
	1.50			5.6		3.6			
	2.42							3.4	14.0
1.00	0.750				25.4^e	1.13	15.4		
	1.50					2.36			
	2.50							2.24	9.0
1.50	0.750					0.54	7.4		
	1.50					1.14			
	2.33							0.91	3.9
2.00							4.9^e		
3.00									1.37^e

[a] k_0 in sec^{-1} and k in M^{-1} sec^{-1}. [b] *p*-Methylmandelic acid. [c] If the dissociation of HSO_4^- is neglected, $[H_2SO_4] + [HClO_4] = \mu$ (see text). [d] Mean values. [e] Mean value obtained from the data of Table I.

TABLE III. Kinetic Data Obtained in H_2SO_4–$HClO_4$ Mixtures at 35.0 and 45.0 °C ($[H_2SO_4] + [HClO_4] = 2.00\,M$[a]).

t °C	$[H_2SO_4]$ (*M*)	10^2[MMA][b] (*M*)	10^3k_0 (sec^{-1})	10k (M^{-1} sec^{-1})
35.0	0.500	0.390	7.6	19.5
	0.600	0.440	6.0	13.6
	0.790	0.740	6.0	8.1
	1.00	0.700	3.6	5.1
	1.50	0.730	1.80	2.47
	2.00	0.750	1.25	1.67
45.0	0.500	0.390	22.1	57
	0.600	0.440	17.2	39
	0.790	0.740	17.9	24.2
	1.00	0.700	10.8	15.4
	1.50	0.730	5.7	7.8
	2.00	0.750	3.7	4.9

[a] If the dissociation of HSO_4^- is neglected, $[H_2SO_4] + [HClO_4] = \mu$ (see text). [b] *p*-Methylmandelic acid.

pseudo-first order rate constants k_0 by the hydroxy-acid concentrations (Tables I–III, V). The kinetic measurements performed using comparable concentrations of ceric ion and organic substrate in 1.50 *M* and 1.00 *M* sulphuric acid at 25 °C confirmed that the reaction is first-order with respect to each reactant. A linear trend was in fact obtained by plotting log $[(a - x)/(b - x/2)]$ against time, where a and b are the initial molar concentrations of cerium(IV) and *p*-methylmandelic acid, respectively, and x the amount of cerium(IV) that has reacted after a given time. The estimated second-order rate constants are in good agreement with those reported in Table I.

As can be seen from Table I, the second-order rate constant k decreases markedly as the sulphuric acid concentration increases. A straight line is obtained by plotting k against the reciprocal of the square of the stoichiometric sulphuric acid concentration (see Figure 1). However, the quantity $k[H_2SO_4]^2$ does not remain constant and decreases with increasing sulphuric acid concentration. A negative intercept is estimated by the least-square analysis of the k against $1/[H_2SO_4]^2$ plot. Similar decreases in the rates of organic substrate oxidations by cerium(IV) in sulphate media were also observed [1–3, 5–15] in previous investigations and were generally ascribed to the competition between bisulphate ion and organic substrate as ligands for the cerium(IV).

For solutions containing sulphuric acid alone, the concentration of the anions HSO_4^- and SO_4^{2-} present in solution can be properly estimated from that of sulphuric acid by means of Eqn. (2), where Q_2 represents the second dissociation constant of H_2SO_4:

$$[H_2SO_4] = [HSO_4^-](1 + Q_2/[H^+]) = \\ = [SO_4^{2-}](1 + [H^+]/Q_2) \qquad (2)$$

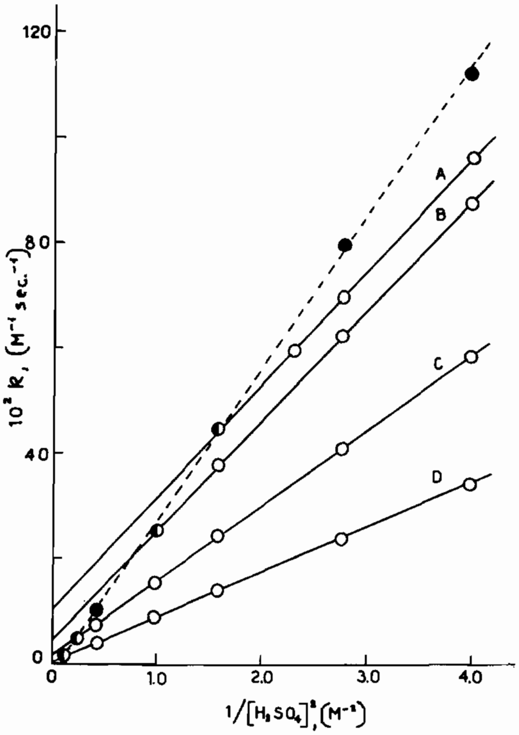

Fig. 1. Plots of k against $1/[H_2SO_4]^2$ at 25.0 °C for sulphuric acid solutions (● and ◐) and for H_2SO_4–$HClO_4$ mixtures (○): A, $[H_2SO_4] + [HClO_4] = 0.790\,M$; B, $[H_2SO_4] + [HClO_4] = 1.00\,M$; C, $[H_2SO_4] + [HClO_4] = 2.00\,M$; D, $[H_2SO_4] + [HClO_4] = 3.00\,M$; ◐ common points. The points at $[H_2SO_4] = 2.50$ and $4.00\,M$ have been omitted.

It can be seen from published data [19] that in the acid concentration range 0.050–3.97*M* both Q_2 and $[H^+]$ increase approximately to the same extent with increasing sulphuric acid concentration and, consequently, both bisulphate and sulphate ion concentrations appear to be linear functions of $[H_2SO_4]$, the quantity $(1 + Q_2/[H^+])$ being equal to 1.42 ± 0.03. A linear dependence also exists between $[H_2SO_4]$ and Q_2, $[H^+]$ and ionic strength ($\mu = 3[H_2SO_4] - 2[HSO_4^-]$). Since the ratio $[SO_4^{2-}]/[HSO_4^-]$ is equal to 0.42 ($= Q_2/[H^+]$), it is wrong to neglect the presence of the SO_4^{2-} ion in solution and to identify the stoichiometric H_2SO_4 concentration with that of the HSO_4^- species, as made in the majority of the previous kinetic studies. The observed linear dependence of k on $1/[H_2SO_4]^2$ indicates therefore that the rate constant k is also linearly dependent on the reciprocal of $[HSO_4^-]^2$, $[SO_4^{2-}]^2$, $[H^+]^2$ and μ^2. No indication on the rate equation can be, of course, obtained from these kinetic data alone. It is to be noted that a large variation of ionic strength occurs on passing from 0.500 *M* ($\mu = 0.80\,M$) to 4.00 *M* ($\mu = 6.4M$) sulphuric acid solutions.

In order to investigate the effect of the HSO_4^- (or SO_4^{2-}) concentration at (nearly) constant hydrogen-ion concentration and ionic strength, kinetic experiments were carried out in the presence of mixtures of H_2SO_4 and $HClO_4$ [7, 20] at constant total molar electrolyte concentration (*i.e.*, at 25 °C, $[H_2SO_4] + [HClO_4] = 0.790\,M$, $1.00\,M$, $2.00\,M$, $3.00\,M$; at 35° and 45 °C, $[H_2SO_4] + [HClO_4] = 2.00\,M$; see Tables II and III).

The plots of Figure 1 show that a linear relationship still exists between k and $1/[H_2SO_4]^2$, but a positive intercept is now obtained for all the mixtures considered. Unlike what was seen above in the case of sulphuric acid solutions, the HSO_4^- and SO_4^{2-} concentrations in the H_2SO_4–$HClO_4$ mixtures cannot be accurately evaluated because the dissociation constant Q_2 is not known under the experimental conditions used in the present work. If the dissociation of HSO_4^- were assumed to be negligible (*i.e.*, $[SO_4^{2-}] \ll [HSO_4^-]$), we should have $[HSO_4^-] = [H_2SO_4]$ and $[H_2SO_4] + [HClO_4] = [H^+] = \mu$ and, consequently, the diagrams of Figure 1 would correspond to linear plots of k against $1/[HSO_4^-]^2$ at constant ionic strength (or $[H^+]$). However the actual values of the hydrogen-ion concentration and ionic strength are indeed somewhat different from the values of $[H_2SO_4] + [HClO_4]$ as shown by Eqns. (3) and (4), and those of $[HSO_4^-]$

$$[H^+] = [H_2SO_4] + [HClO_4] + ([H_2SO_4] - [HSO_4^-]) \tag{3}$$

$$\mu = [H_2SO_4] + [HClO_4] + 2([H_2SO_4] - [HSO_4^-]) \tag{4}$$

also different from the $[H_2SO_4]$ values.

If we consider the Q_2 value ($= 0.30\,M$) obtained at 25 °C and $\mu = 1.0\,M$ for perchloric acid solution ($[HClO_4] = 1.0\,M$) containing small amounts of Na_2SO_4 [21], it is calculated that the quantity $(1 + Q_2/[H^+])$ ($= 1.30$) is very close to that seen above for various sulphuric acid solutions. It can be hence desumed that for the H_2SO_4–$HClO_4$ mixtures at one molar total concentration, the quantity $(1 + Q_2/[H^+])$ is constant. This result can be reasonably extended by analogy to the other mixtures examined. Thus, the plots of Figure 1 show, in accordance with Eqn. (2), the existence of a linear dependence of k on $1/[HSO_4^-]^2$ or $1/[SO_4^{2-}]^2$ at various (nearly constant) ionic strengths or hydrogen-ion concentrations.

According to these findings, the rate equation (5) is valid at a fixed ionic strength or $[H^+]$ and the second-order rate constant k is given by expression (6), where $a = Q_2/[H^+] =$ constant ([MMA] represents the total molar concentration of

$$-d[Ce(IV)]/dt = k[MMA][Ce(IV)] \tag{5}$$

$$k = k_1 + k_2/[H_2SO_4]^2 = k_1 + k_2/(1+a)^2[HSO_4^-]^2 = k_1 + k_2/(1 + 1/a)^2[SO_4^{2-}]^2 \tag{6}$$

TABLE IV Rate Constants k_1 and k_2 at Various Temperatures and Ionic Strengths ($[H_2SO_4] + [HClO_4]$)

t °C	$[H_2SO_4] + [HClO_4]^a$ (M)	10^2k_1 ($M^{-1}sec^{-1}$)	10^2k_2 ($M\,sec^{-1}$)
25 0	0 790	10 ± 4	22 ± 2
	1 00	5 ± 2	21 ± 1
	2 00	1 1 ± 0 3	14 4 ± 0 5
	3 00	0 23 ± 0 06	8 6 ± 0 3
35 0	2 00	4 0 ± 0 9	48 ± 2
45 0	2 00	16 ± 3	138 ± 5

[a] If the dissociation of HSO_4^- is neglected, $[H_2SO_4] + [HClO_4] = \mu$ (see text)

TABLE V Kinetic Data Obtained in H_2SO_4–$LiHSO_4$ Mixtures at 25 0 °C ($[H_2SO_4] + [LiHSO_4] = 2\ 00\,M^a$)

$[H_2SO_4]$ (M)	$10^2[MMA]^b$ (M)	10^3k_0 (sec^{-1})	10^2k^c ($M^{-1}sec^{-1}$)
0 500	0 750	0 299	4 1
	1 50	0 63	
0 600	0 750	0 322	4 2
	1 50	0 65	
0 790	0 750	0 310	4 1
	1 50	0 62	
1 00	0 750	0 320	4 2
	1 50	0 63	
1 50	1 50	0 66	4 4
2 00			4 9^d

[a] If the dissociation of HSO_4^- is neglected, $[H_2SO_4] + [LiHSO_4] = \mu = [HSO_4^-]$ (see text) [b] *p*-Methylmandelic acid [c] Mean values [d] Mean value obtained from the data of Table I

p-methylmandelic acid) The linear regression analysis of the plots of Figure 1 yields the values of k_1 and k_2 reported in Table IV The values of these rate constants obtained at 35 °C and 45 °C are also given in Table IV

Figure 1 (*cf* also Table II) shows that at a given sulphuric acid concentration the rate constant k decreases markedly with increasing ionic strength (or $[H^+]$) A similar decrease is also observed in both k_1 and k_2 (*cf* Table IV) In order to ascertain whether this decreasing rate has to be ascribed to the hydrogen-ion concentration or to an effect of the ionic strength, kinetic measurements were performed at 25 °C by using H_2SO_4–$LiHSO_4$ mixtures at constant total molarity 2 00 M (see Table V) These mixtures allow us to vary the hydrogen-ion concentration at constant HSO_4^- (or SO_4^{2-}) concentration and ionic strength Lithium ion is used to replace hydrogen ion because they exhibit a quite similar medium effect When the dissociation of HSO_4^- is neglected, we have $[HSO_4^-] = \mu = [H_2SO_4] + [LiHSO_4] = 2\ 00\,M$ and $[H^+] = [H_2SO_4]$ The actual values of $[HSO_4^-]$, $[SO_4^{2-}]$, $[H^+]$ and μ are instead given by Eqns (7)–(9)

$$[HSO_4^-](1 + Q_2/[H^+]) = [SO_4^{2-}](1 + [H^+]/Q_2) = \\ = [H_2SO_4] + [LiHSO_4] = 2\ 00 \qquad (7)$$

$$[H^+] = 2[H_2SO_4] + [LiHSO_4] - [HSO_4^-] = \\ = [H_2SO_4] + (2 - [HSO_4^-]) \qquad (8)$$

$$\mu = 3([H_2SO_4] + [LiHSO_4]) - 2[HSO_4^-] = \\ = 6 - 2[HSO_4^-] \qquad (9)$$

As far as we know, Q_2 values for H_2SO_4–$LiHSO_4$ (or H_2SO_4–Li_2SO_4) mixtures or for pure $LiHSO_4$ solutions are not available, whereas those for H_2SO_4–Na_2SO_4 solutions [22] and for pure $MeHSO_4$ solutions (Me = Na^+, K^+, NH_4^+) exist If we consider the Q_2 values for 2 00 M solution of pure $MeHSO_4$ [23], it can be calculated that the quantity $(1 + Q_2/[H_2])$ is equal to 1 72, 1 35 and 1 52 for $NaHSO_4$, $KHSO_4$ and NH_4HSO_4, respectively These values are very close to that estimated above for pure sulphuric acid solutions and it is very reasonable to think that the corresponding value for $LiHSO_4$ is not different Therefore, taking also into account the fact that the Q_2 values for H_2SO_4–Na_2SO_4 solutions (*i e*, H_2SO_4–$NaHSO_4$ mixtures) in the vicinity of one molal total solute concentration [22] are intermediate between that for pure H_2SO_4 solution and that for pure $NaHSO_4$ solution, it follows that $[HSO_4^-]$, $[SO_4^{2-}]$ and μ [Eqns (7) and (9)] remain indeed constant when H_2SO_4 is replaced by $LiHSO_4$ and that the hydrogen-ion concentration [Eqn (8)] is a linear function of $[H_2SO_4]$

From the kinetic results obtained at constant bisulphate (or sulphate) concentration (Table V) it can be seen that the rate constant k appears to be independent of the sulphuric acid concentration (*i e*, $[H^+]$) The small increase in k with increasing $[H^+]$ can be reasonably ascribed to a slight different medium effect of Li^+ and H^+ [24] As a consequence, we can finally conclude that, under the experimental conditions used, the oxidation of *p*-methylmandelic acid by cerium(IV) occurs in accordance with the rate law (5) and that an increase in ionic strength decreases both the second-order rate constant k and the rate constants k_1 and k_2, the decrease of k_1 being much more significant than that of k_2 (*cf* Table IV)

In the light of all the above considerations, we deem that the linear trend of the k against $1/[H_2SO_4]^2$ plot observed for the sulphuric acid solutions (Table I) is the fortuitous result of the combination of ionic strength effects on the rate constants k_1 and k_2 and of the peculiar feature of the acid solutions, that is, the linear dependence between $[H_2SO_4]$ and $[HSO_4^-]$, $[SO_4^{2-}]$, $[H^+]$ and μ

Therefore the kinetic data obtained for these solutions have always to be considered with caution.

According to Eqn. (6), two reaction paths contribute significantly to the oxidation reaction. The enthalpy and entropy of activation for the two reactions, estimated from the linear plots of $\log(k_1/T)$ and $\log(k_2/T)$ against $1/T$ for H_2SO_4–$HClO_4$ mixture at 2.00 *M* total concentration (*cf.* Table IV), are: $\Delta H_1^{\ddagger} = 25 \pm 4$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = 15 \pm 10$ cal mol^{-1} K^{-1}, $\Delta H_2^{\ddagger} = 20.7 \pm 0.7$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = 7 \pm 2$ cal mol^{-1} K^{-1}. The activation parameters are quite similar for both reaction paths. The entropies of activation are close to those obtained for other hydroxy-acid oxidation reactions which take place *via* the formation of an intermediate complex between cerium(IV) and organic substrate [9, 14, 25].

Although no kinetic or spectrophotometric evidence for complex formation has been found in this work, it seems likely that each reaction path involves initial formation of a complex, decomposition of which is the rate-determining step, as proposed for other analogous reactions [1–15].

Cerium(IV) in aqueous sulphuric acid solutions may exist in a number of complex forms, but there are controversial opinions about the nature of these complexes and hence about the stoichiometry of the equilibria involved [26]. From a kinetic point of view all these complexes do not seem to take part in the oxidation process. However, owing to the large number of possible and, in many cases, kinetically equivalent equilibria involved, it is impossible to identify the actual reacting species with any certainty and, consequently, various complex species such as $CeSO_4^{2+}$, $Ce(SO_4)_2$, $Ce(OH)_2^{2+}$, $Ce(HSO_4)_3^{+}$, $H_2Ce(SO_4)_4^{2-}$, have been assumed by different investigators as the reactive cerium(IV) species to account for the observed rate expressions.

A possible reaction mechanism is here proposed by considering that, under the conditions of acidity used, the concentration of HSO_4^- (or SO_4^{2-}) is much larger than that of cerium(IV) and by assuming that the predominant equilibria involved [1, 3, 8, 27] are those shown in (10) and (11) and that the reactive cerium(IV) species are $Ce(SO_4)_2$ and $H_2Ce(SO_4)_4^{2-}$.

$$Ce(SO_4)_2 + HSO_4^- \overset{K_1}{\rightleftharpoons} HCe(SO_4)_3^- \qquad (10)$$

$$HCe(SO_4)_3^- + HSO_4^- \overset{K_2}{\rightleftharpoons} H_2Ce(SO_4)_4^{2-} \qquad (11)$$

The mechanism of the oxidation process can be depicted as follows:

$$H_2Ce(SO_4)_4^{2-} + MMA \overset{K_1^C}{\rightleftharpoons} \text{Complex I}$$

$$Ce(SO_4)_2 + MMA \overset{K_2^C}{\rightleftharpoons} \text{Complex II}$$

$$\text{Complex I} \xrightarrow[\text{slow}]{k_1'} Ce(III) + H^+ + MMA^{\cdot}$$

$$\text{Complex II} \xrightarrow[\text{slow}]{k_2'} Ce'(III) + H^+ + MMA^{\cdot}$$

$$Ce(IV) + MMA^{\cdot} \xrightarrow{\text{fast}} Ce(III) + CO_2 + H^+ + TA$$

($MMA^{\cdot}$ and TA denote the free radical and *p*-tolualdehyde, respectively).

According to this reaction mechanism and considering $1 \gg K_1^C[MMA], K_2^C[MMA]$, the following rate expression can be derived:

$$-\frac{d[Ce(IV)]}{dt} = (2k_1'K_1^C[H_2Ce(SO_4)_4^{2-}] + $$
$$+ 2k_2'K_2^C[Ce(SO_4)_2])[MMA] =$$
$$= (2k_1'K_1^C + \frac{2k_2'K_2^C}{K_1K_2[HSO_4^-]^2})[H_2Ce(SO_4)_4^{2-}][MMA] \qquad (12)$$

If the concentration of $H_2Ce(SO_4)_4^{2-}$ is given in terms of the total molar concentration of cerium(IV) [Eqn. (13)] and the assumption is made that

$$[H_2Ce(SO_4)_4^{2-}] =$$
$$= \frac{[Ce(IV)]}{1 + 1/K_2[HSO_4^-] + 1/K_1K_2[HSO_4^-]^2} \qquad (13)$$

$K_1K_2[HSO_4^-]^2 \gg K_2[HSO_4^-]$, 1, Eqn. (12) can be written as:

$$-\frac{d[Ce(IV)]}{dt} =$$
$$\left(2k_1'K_1^C + \frac{2k_2'K_2^C}{K_1K_2[HSO_4^-]^2}\right)[MMA]\,[Ce(IV)] \qquad (14)$$

Bearing in mind that a linear dependence exists between $[H_2SO_4]$ and $[HSO_4^-]$, Eqn. (14) is identical to the experimentally observed rate law (5) with $k_1 = 2k_1'K_1^C$ and $k_2 = 2k_2'K_2^C(1 + a)^2/K_1K_2$.

The possible dependence of the second-order rate constant k on $1/[SO_4^{2-}]^2$ [Eqn. (6)] could also be explained by considering that, owing to the fact that the concentration of SO_4^{2-} is only a factor of *ca.* 2 smaller than that of HSO_4^-, the divalent anion may indeed compete with the univalent one as ligand in the cerium sulphate complex formation [reactions (10) and (11)]. In this case the derived rate expression (14) would involve $[SO_4^{2-}]^2$ instead of $[HSO_4^-]^2$ and k_2 would be equal to $2k_2'K_2^C(1 + 1/a)^2/K_1K_2$.

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