593. *Kinetics and Mechanism of Oxidation of Mandelic, DL-Malic, and Lactic Acid by Ceric Sulphate.*

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The mechanism proposed by Waters for the oxidation of α-hydroxy-acids by manganic pyrophosphate accounts for the kinetics of oxidation of mandelic, DL-malic, and lactic acid by ceric sulphate. The reactants pass through a cyclic transition state involving the hydroxy-acid and cerium(IV). It is suggested that the reactive species of cerium is $Ce(SO_4)_2$ and that the HSO_4^- ion plays the rôle of an active inhibitor by forming $H_2Ce(SO_4)_4^{2-}$ on reacting with the sulphate.

The kinetics and mechanism of oxidation of organic acids by ceric sulphate have not been adequately studied, though Benrath and Ruland[1] showed that oxidation of tartaric, malonic, citric, and oxalic acid by ceric sulphate is not of simple kinetic order. We have studied the oxidation of mandelic, DL-malic, and lactic acid by ceric sulphate in presence of varying amounts of sulphuric acid. Existing data on cerium(IV) complexes occurring in this medium permit elucidation of the mechanism of these oxidations.

Experimental

The materials employed were of the highest purity available ("AnalaR" or E. Merck's Guaranteed Reagent).

A solution[2] of ceric sulphate in 1 : 1 v/v sulphuric acid was diluted and standardized by titration against ferrous ammonium sulphate, *N*-phenylanthranilic acid being used as indicator. The solutions of organic acids were standardized by titration against sodium hydroxide. The progress of the reaction was followed as for the reaction between ceric ion and thallous ion.[3]

To determine the amount of ceric ion consumed, reaction mixtures in which the molar concentration of cerium was 10—15 times that of the acid were left in a thermostat-bath at 25° for several days,[4] after which the amount of ceric salt was determined by titration against ferrous ammonium sulphate. The average of five determinations in each case showed that 1 mole of mandelic, DL-malic, and lactic acid requires 2·0, 8·50, and 5·75 equivalents, respectively, of ceric ion. These values were used in calculating the normality of the acid used in the reaction mixture.

Order of the Reaction.—The reaction is of simple kinetic order if the molar concentration of ceric sulphate is not greater than that of the hydroxy-acid. A plot of log $[(a - x)/(b - x)]$ against time is a straight line (Fig. 1), which implies that the total order of the reaction is two. Here a and b are the initial concentrations of the reactants in terms of the titres of ceric sulphate required by 10 ml. of the reaction mixture. The second-order constant k_2 obtained from the graph represents the specific rate constant in terms of titre values of ceric sulphate and thus depends on the strength (S) of the titrating solution and the volume (V) of the reaction mixture titrated. To compare one experiment with another the value of k_2 is converted into a standard form k_s by multiplying k_2 by V/S. Some results are presented in Table 1. They show that k_s

Table 1. "*Standard*" k_s (*in* l. g.-equiv.$^{-1}$ min.$^{-1}$) *for oxidation of organic acids.*

Lactic acid			Mandelic acid			Malic acid		
$[H_2SO_4]$ 0·6N; 25°			$[H_2SO_4]$ 2·0N; 20°			$[H_2SO_4]$ 0·75N; 25°		
$[Ce(SO_4)_2]$ (10^{-2}N)	[Lactic] (10^{-3}N)	10^2k_s	$[Ce(SO_4)_2]$ (10^{-2}N)	[Mandelic] (10^{-2}N)	10^2k_s	$[Ce(SO_4)_2]$ (10^{-2}N)	[Malic] (10^{-3}N)	10^2k_s
1	28·75	34·4	1	1	339	1	10·625	134
1	57·75	34·1	1	2	346	1	21·250	132·5
1	115	34·8	2	1	318	1	42·50	121·5
0·5	57·5	39·6	0·5	1	359	0·5	21·250	151
2	57·5	33·45						

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[1] Benrath and Ruland, *Z. anorg. Chem.*, 1920, **114**, 267.

[2] Krishna and Sinha, *Z. phys. Chem.* (*Frankfurt*), 1959, **212**, 149.

[3] Krishna and Sinha, *Z. phys. Chem.* (*Frankfurt*), 1959, **212**, 155.

[4] Shorter and Hinshelwood, *J.*, 1950, 3277.

is sensibly constant in each case, and that the total order of the reaction is two (unity with respect to each reactant).

Inhibitory Action of Sulphuric Acid and Sulphates.—An important feature of the reaction is that the rate is inversely proportional to the square of concentration of sulphuric acid present

FIG. 1.

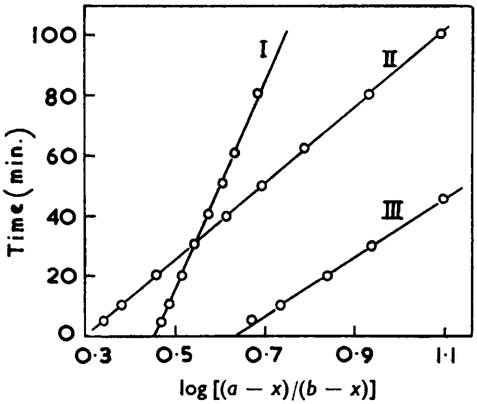


FIG. 2.

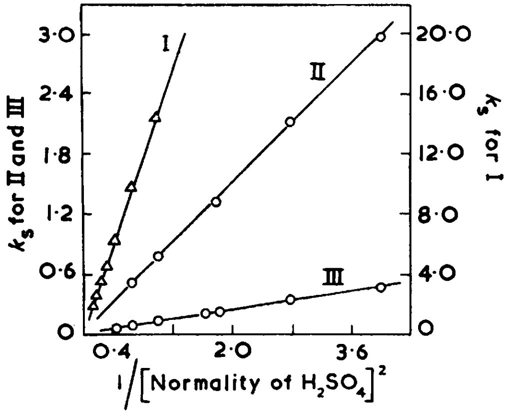


FIG. 1. *Reactions of hydroxy-acids with ceric sulphate.*

	Lactic (I)	Mandelic (II)	Malic (III)
$[Ce(SO_4]_2]$ (10^{-3}N)	10	5	5
[Acid] (10^{-2}N)	2·875	1	2·125
$[H_2SO_4]$ (N)	0·6	2·0	0·75
Temp.	25°	20°	25°

FIG. 2. *Dependence on sulphuric acid concentration.*

	Mandelic (I)	Malic (II)	Lactic (III)
$[Ce(SO_4)_2]$ (10^{-2}N)	1	1	1
[Acid] (10^{-2}N)	1	2·125	5·75
Temp.	20°	25°	25°

TABLE 2. *Dependence of " standard "* k_s (*in* l. g.-equiv.$^{-1}$ min.$^{-1}$) *on sulphuric acid concentration in oxidation of organic acids.*

Lactic acid: 5·75 × 10^{-2}N $Ce(SO_4)_2$: 10^{-2}N; 25°		Mandelic acid: 10^{-2}N $Ce(SO_4)_2$: 10^{-2}N; 20°		Malic acid: 21·25 × 10^{-2}N $Ce(SO_4)_2$: 10^{-2}N; 25°	
$[H_2SO_4]$ (N)	10^2k_s	$[H_2SO_4]$ (N)	10^2k_s	$[H_2SO_4]$ (N)	10^2k_s
0·50	46·2	1·00	1442	0·5	270
0·60	34·1	1·25	983	0·6	212·5
0·75	23·05	1·50	622	0·75	132·5
0·78	20·6	1·75	445	1·00	77·6
1·00	14·3	2·00	339	1·25	52·3
1·25	8·85	2·25	266·5		
1·50	6·4	2·50	203·5		

TABLE 3. *Effect of added salts on* k_s (*in* l. g.-equiv.$^{-1}$ min.$^{-1}$) for oxidation of organic acids.

Lactic acid: 5·75 × 10^{-2}N $Ce(SO_4)_2$: 10^{-2}N H_2SO_4: 0·6N; 25°			Mandelic acid: 10^{-2}N $Ce(SO_4)_2$: 10^{-2}N H_2SO_4: 2·0N; 20°			Malic acid: 21·25 × 10^{-2}N $Ce(SO_4)_2$: 10^{-2}N H_2SO_4: 0·75N; 25°		
[Salt] (M)		10^2k_s	[Salt] (M)		10^2k_s	[Salt] (M)		10^2k_s
K_2SO_4	0·02	30·1	$(NH_4)_2SO_4$	0·02	285	$(NH_4)_2SO_4$ ...	0·05	99·7
	0·04	25·5		0·04	270		0·10	79
	0·06	21·3		0·05	260		0·13	68·0
	0·08	18·2		0·08	230·5	$KHSO_4$	0·05	94·6
	0·10	15·9	$KHSO_4$	0·02	314		0·10	73·7
$KHSO_4$	0·04	32·9		0·04	296		0·15	52·5
	0·08	31·3		0·08	247			
				0·10	230			

(Fig. 2, Table 2). However, addition of an acid other than sulphuric acid (nitric or hydrochloric) produces only an insignificant retardation. Thus the main inhibitory ion is probably HSO_4^-.

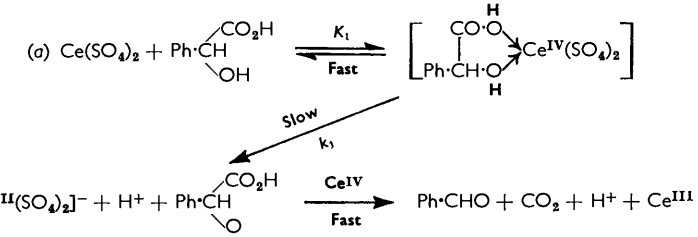
Potassium hydrogen sulphate, potassium sulphate, and ammonium sulphate produce significant retardations (see Table 3), though not according to any mathematical regularity.

The retardation produced by SO_4^{2-} ions might well be due to the formation of HSO_4^- ions by union with hydrogen ions from the sulphuric acid; the results for hydrogen sulphate or sulphate ions have only qualitative significance.

Salt Effect.—Addition of potassium chloride or nitrate also produces retardation, though not to the same extent as does sulphate or hydrogen sulphate ion. On the other hand, addition of sodium nitrate produces no retardation. We are thus not dealing here with the usual kinetic effect: the nature of the present salt effect is not clear.

DISCUSSION

The reaction mechanism suggested here is based on Waters's theory[5] for the oxidation of α-hydroxy-acids by manganic pyrophosphate. Ceric sulphate and the organic hydroxy-acids (mandelic, DL-malic, or lactic acid) react rapidly to form an activated complex which then decomposes slowly to form a free radical, hydrogen ion, and cerous complex. The free radical takes up further cerium(IV) and by fast steps forms the rest of the reaction products. This is best illustrated in case of mandelic acid, where the mechanism is clear:



The presence of benzaldehyde and carbon dioxide was confirmed by the usual tests. The antocatalytic activity of HSO_4^- ion is explained by assuming that the reactive ceric salt species, $Ce(SO)_4)_2$, is removed by the following reactions:

$$(b)\ Ce(SO_4)_2 + HSO_4^- \overset{K_2}{\rightleftharpoons} HCe(SO_4)_3^-$$

$$(c)\ HCe(SO_4)_3^- + HSO_4^- \overset{K_3}{\rightleftharpoons} H_2Ce(SO_4)_4^{2-}$$

Taking into account the reaction schemes (*a*), (*b*), and (*c*) we then obtain:

$$-\frac{d[Ce^{IV}]}{dt} = \frac{k_1}{K_2K_3} \times \frac{[H_2Ce(SO_4)_4^{2-}][\text{Mandelic acid}]}{[HSO_4^-]^2} \qquad (1)$$

If various forms of ceric salt are held in rapid equilibrium (see below) the concentration of $H_2Ce(SO_4)_4^{2-}$ ion will be proportional to the total Ce^{IV} present in the reaction mixture. Hence eqn. (1) can be written in the form:

$$-d[Ce^{IV}]/dt = k_s'[Ce^{IV}][\text{Mandelic acid}]/[H_2SO_4]^2, \qquad (2)$$

where k_s' is another rate constant. For any given concentration of sulphuric acid eqn. (2) can be written in the form:

$$-d[Ce^{IV}]/dt = k_s[Ce^{IV}][\text{Organic acid}]$$

where k_s is the second-order constant determined experimentally.

The mechanism formulated explains the results observed for mandelic acid and ceric sulphate. With lactic acid the activated complex is of the same type. In the oxidation of lactic acid 5·75 equivalents of ceric sulphate are used and 0·3 mole of formic acid is

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[5] Levesley and Waters, *J.*, 1955, 217.

produced for each mole of lactic acid oxidised. The amount of formic acid produced was estimated by standard methods.[4,6] Carbon dioxide is also evolved. We thus assume that lactic acid is oxidised in two ways:

$$(d)\quad \mathrm{Me{\cdot}CH(OH){\cdot}CO_2H + 10Ce^{IV} + 3H_2O \longrightarrow H{\cdot}CO_2H + 2CO_2 + 10H^+ + 10Ce^{III}}$$

$$(e)\quad \mathrm{Me{\cdot}CH(OH){\cdot}CO_2H + 4Ce^{IV} + H_2O \longrightarrow AcOH + CO_2 + 4H^+ + 4Ce^{III}}$$

About 30% of the lactic acid undergoes reaction (*d*), and 70% reaction (*e*); this requires 5·8 equivalents of ceric sulphate and 0·3 mole of formic acid, very nearly as required. Both for lactic acid and for DL-malic acid it is difficult to visualize the actual course of the decomposition of the free radical, but since the kinetics of oxidation of both these acids is similar to that of mandelic acid one may assume that these oxidations proceed in a general way as follows:

$$\mathrm{Ce(SO_4)_2} + \alpha\text{-Hydroxy-acid} \overset{\text{Fast}}{\rightleftharpoons} [\text{Activated complex}] \xrightarrow{\text{Slow}}$$

$$\mathrm{H^+ + Ce(SO_4)_2} + \text{Organic free radical} \xrightarrow{\text{Fast}} \text{Products}$$

In aqueous solutions of ceric sulphate containing sulphuric acid, a variety of complex ions is known to exist.[7] Depending on concentrations of sulphate and hydrogen ions, the composition of these solutions is believed to be governed by equilibria such as the following:

$$\mathrm{Ce(SO_4)_2 \rightleftharpoons Ce(SO_4)^{2+} + SO_4^{2-}}$$

$$\mathrm{Ce(SO_4)_2 + SO_4^{2-} \rightleftharpoons Ce(SO_4)_3^{2-}}$$

$$\mathrm{Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^- \rightleftharpoons Ce(SO_4)_3^{2-} + H^+}$$

$$\mathrm{HCe(SO_4)_3^- + HSO_4^- \rightleftharpoons H_2Ce(SO_4)_4^{2-} \rightleftharpoons Ce(SO_4)_4^{4-} + 2H^+}$$

If the species $\mathrm{Ce(SO_4)_2}$ is the oxidant, the inhibiting effect of $\mathrm{HSO_4^-}$ ions then arises because these ions compete with the organic hydroxy-acids as ligands for cerium.

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[6] Vogel, "Text Book of Quantitative Inorganic Analysis," Longmans, Green & Co., London, 1953, p. 289.

[7] Moore and Anderson, *J. Amer. Chem. Soc.*, 1944, **66**, 1476; King and Pandou, *ibid.*, 1953, **75**, 3063; Hargreaves and Sutcliffe, *Trans. Faraday Soc.*, 1955, **51**, 1105; Hardwick and Robertson, *Canad. J. Chem.*, 1951, **29**, 828.