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KINETICS OF OXIDATION OF α-HYDROXY ACIDS BY CHROMIUM(VI) AND CERIUM(IV).

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Kinetics of oxidation of α-hydroxy acids by Cr(vi) and Ce(iv) have been studied by a number of investigators in aqueous as well as in acetic acid - water systems. The present investigation deals with the oxidation of α-hydroxy acids and some of their esters (at 0.025 M $HClO_4$) in varying proportions of acetone - water mixtures. Solvent oxidation was routinely checked for each set of oxidants used and the rate constants were corrected for these blanks. The reactions are first order with substrate and first order with oxidant with both oxidants. Increasing proportions of acetone increase the rate as found in other oxidations. But certain abnormal features have been noticed in these oxidations with Ce(iv). The rate of oxidation of esters is higher with Ce(iv) than with Cr(vi), quite in consonance with their redox potentials of 1.0v and 1.5v respectively. But with α-hydroxy acids lactic and mandelic acids the reactions are slower with Ce(iv) and there is also a reversal of activity as lactic acid is oxidised faster than mandelic acid. This finding is novel as in aqueous systems by Ce(iv) the order is quite normal, mandelic acid > lactic acid. The rate constants are given below.

Table I

Second order rate constants ($k \times 10^5$ l. $moles^{-1}$ min^{-1})
Solvent - 70% v/v acetone + 30% v/v water, Acidity 0.025 M $HClO_4$

Compound(0.05 M)	Oxidant - Cr(vi) (0.0017 M)			Oxidant - Ce(iv)(0.004 M)		
Temp.	30°C	35°C	40°C	30°C	35°C	40°C
Mandelic acid	522.9	892.8	1325.0	5.95	15.64	37.98
Isoamyl mandelate	24.28	45.0	61.22	79.39	150.6	333.0
Ethyl mandelate	15.4	36.21	52.67	45.15	84.74	196.6
Benzyl mandelate	12.15	18.97	26.02	30.59	42.46	68.25
Lactic acid	120.6	185.7	248.3	7.74	16.14	50.31

It has been established that there is a substantial kinetic isotope effect[1] (k_H/k_D = 8.6, C - H bond cleavage) in oxidations of α-hydroxy acids by Cr(vi) whereas with α-hydroxy acids by Ce(iv) there is negligible isotopic effect (k_H/k_D = 1.1). Hence the mechanisms of oxidations are entirely different not only

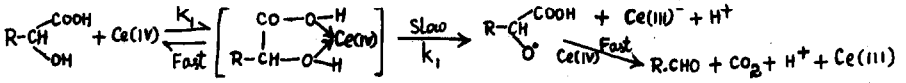
as to the two or one electron transfer but also regarding the point of rate determining fission.

Table II

Second order rate constants ($k \times 10^5$ l. moles^{-1} min^{-1}) Temp. 35°C
Acidity 0.025 M $HClO_4$

Acetone - water (v/v)	Lactic acid		Mandelic acid	
	Cr(vi)	Ce(iv)	Cr(vi)	Ce(iv)
50 - 50	117.0		400.5	
60 - 40	140.6		588.5	
70 - 30	185.7	16.14	892.8	15.64
75 - 25		49.90		42.07
80 - 20		115.40		78.05

It appears that Ce(iv) oxidations involve a O - H bond cleavage as follows.[2]



This fact indicates that in these acetone - water mixtures the α-hydroxy acids are intermolecularly hydrogen bonded with the organic component of the solvent mixture causing a over all reduction in rate. This possibility does not affect the oxidations with Cr(vi) as the cleavage of C - H bond is rate determining. This abnormality is due to the solvent system and to the different mechanism operating with Ce(iv) as against Cr(vi).

The heats and entropies of activation, and frequency factors for the Cr(vi) oxidation of lactic acid are 16.55, -14.29 and 9.66, whereas for Ce(iv) oxidation, they are 51.89, + 50.67 and 19.48, which brings out clearly the difference in the two mechanistic pathways.

To sum up (1) α-hydroxy acids are retarded in Ce(iv) due to a specific solvent effect, (2) Cr(vi) involves two electron transfer and C - H cleavage with loss of proton through the ester mechanism postulated by Hwart and Francis[3], (3) Ce(iv) oxidation is by a one electron transfer and the rate determining step is a O - H fission as seen by the abnormalities in acetone - water mixtures.

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