634. *Kinetic Investigation of the Oxidation of Some α-Hydroxy-carboxylic Acids by Chromic Acid.*

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The kinetics of the initial stages of the oxidation of lactic, malic, and mandelic acid by chromic acid in perchloric acid have been studied. The oxidation is affected by $HCrO_4^-$ ions. The initial reaction resembles the oxidation of a secondary alcohol to a ketone. All the kinetic features of the oxidation of isopropyl alcohol by chromic acid are observed in these oxidations. The results support the Kwart–Francis scheme for oxidation of secondary alcohols by chromic acid.

WESTHEIMER[1] has pointed out that information regarding oxidation of hydroxy-acids by chromic acid is insufficient to elucidate the mechanism of oxidation. The present investigation was conducted to find out the mechanism of the oxidation.

EXPERIMENTAL

Materials.—60% Perchloric acid (E. Merck) was used without purification; sodium perchlorate solutions were prepared by neutralising the acid with " AnalaR," sodium hydroxide. Chromic acid solutions were prepared from " AnalaR " potassium dichromate. Pyridine and glacial acetic acid used were Baker's " Analysed Reagents." " AnalaR " lactic acid was used without purification. Malic acid (Riedel) and mandelic acid (Malinckrodt Chemical Works, U.S.A.) were purified by crystallisation. " Analar " manganous sulphate was employed. All other reagents were " chemically pure."

Kinetic Measurements.—The kinetic experiments were carried out at constant temperature (±0·02°). The ionic strength was kept constant by use of sodium perchlorate. Perchloric acid was used as a source of hydrogen ions. Since the concentration of dichromate was much smaller than those of the hydroxy-acid and hydrogen ions, the ionic strength and the hydrogen ion concentration did not change appreciably during the course of the experiment. Unless otherwise stated, the solvent used was 10% acetic acid. The reactants were brought to thermostat temperature and then rapidly mixed in a bottle previously brought to thermostat temperature. The dichromate solution was added last. Zero time was taken as that when half of the dichromate solution was in the flask. Aliquot parts were withdrawn at known interval of time and the gross concentration of chromium(VI) was estimated by iodometric methods, precautions being taken to minimise oxidation of the iodide by air.[2]

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[1] Westheimer, *Chem. Rev.*, 1949, **45**, 419.

[2] Wiberg and Mill, *J. Amer. Chem. Soc.*, 1958, **80**, 3022.

Effect of Light.—Oxidation of hydroxy-acids by chromic acid is known to be be photochemical.[3] Experiments showed that the reaction in dark as well as in diffuse daylight proceeded at the same rate. Consequently all reactions were carried out in diffuse daylight.

Test for Organic Free Radicals.—Levesley and Waters [4] used induced reduction of mercuric chloride to characterise the organic free radical in the oxidation of α-hydroxy-acids by manganic pyrophosphate. The same test was applied to characterise the organic free radical, if any, produced in the oxidation of α-hydroxy-acids by chromic acid.

RESULTS

Induced Reduction of Mercuric Chloride.—Oxidation of lactic, malic, and mandelic acid by chromic acid failed to induce the reduction of mercuric chloride. This shows that no free organic radical of the type HO·CHR· intervenes in these oxidations.

Rate Laws.—The rate at which the gross concentration of chromium(VI) disappears follows a first-order rate law. Further, when the initial concentration of chromium(VI) is much below $4\cdot0 \times 10^{-3}$M, the value of the pseudo-first-order rate constant is independent of the initial concentration of chromium(VI). This needs an explanation, in view of the fact that the pseudo-first-order rate constant is known to increase with decrease in the gross concentration of chromium(VI).[2] The equilibrium constant, $K = [HCrO_4^-]^2/[Cr_2O_7^{2-}] = 2(HCrO_4^-]^2/\{[Cr(VI)] - [HCrO_4^-]\}$, has a probable value of 0·023 at 25° and at an ionic strength of 0·400.[5] It can be shown that when $[Cr(VI)] < K/8$, *i.e.*, $3\cdot0 \times 10^{-3}$M,the concentration of $HCrO_4^-$ ions is the same as the gross concentration of chromium(VI). Experimentally this condition is achieved when $[Cr(VI)] \leqslant 4\cdot0 \times 10^{-3}$M. In view of the uncertainty in the value of K, the agreement between the theoretical and the experimental value is satisfactory. This result indicates that the oxidation is effected by $HCrO_4^-$ ions and that the rate is proportional to the first power of the concentration of $HCrO_4^-$.

The rate of oxidation is also proportional to the concentration of the hydroxy-acid and of hydrogen ions (cf. Tables 1 and 2).

TABLE 1.

Variation of rate with concentration of hydroxy-acid in 10% acetic acid at 25°.

Lactic acid

$[H^+] = 0\cdot412$M. $[Cr(VI)] = 4\cdot0 \times 10^{-3}$M. $\mu = 0\cdot418$.

[Lactic acid] (10^{-2}M)	1·56	3·12	4·68	6·24	7·02	7·80
k_1 (10^{-2} min.$^{-1}$)	1·42	2·82	4·49	5·60	6·46	7·50
$10k_1$/[Lactic acid]	9·10	9·04	9·60	9·0	9·20	9·61

Malic acid

$[H^+] = 0\cdot400$M. $[Cr(VI)] = 4\cdot0 \times 10^{-3}$M. $\mu = 0\cdot406$.

[Malic acid] (10^{-2}M)	1·44	2·83	4·32	5·76	6·48	7·20
k_1 (10^{-2} min.$^{-1}$)	1·52	2·76	4·60	6·10	6·68	7·40
$10k_1$/[Malic acid]	10·5	9·6	10·7	10·6	10·3	10·3

Mandelic acid

$[H^+] = 0\cdot400$M. $[Cr(VI)] = 4\cdot0 \times 10^{-3}$M. $\mu = 0\cdot406$.

[Mandelic acid] (10^{-2}M)	1·00	2·00	5·00	7·00	9·00	10·0
k_1 (10^{-2} min.$^{-1}$)	2·53	4·61	12·0	16·6	19·1	20·7
$10k_1$/[Mandelic acid]	25·3	23·0	24·0	23·7	21·2	20·7

Rates in Presence of Mn^{2+}.—The rate of oxidation is diminished to one-half of that in the absence of manganous ions, when the concentration of Mn^{2+} is $2\cdot5 \times 10^{-2}$M or more. This result is expected if the manganous ions catalyse the disproportion of the intermediate valency states of chromium, and indicates that chromium(IV) is probably involved as an intermediate.[1, 2, 6] The results on the effect of manganous ions on the rates of oxidation are given in Table 3.

Effect of the Solvent Composition.—Results on the effect of solvent composition on the rates of oxidation have been presented in Table 4. Fig. 1 shows that logarithm of the rate constant increases linearly with increase in the proportion of acetic acid in the mixture. This suggests

[3] Bhattacharya and Dhar, *Z. anorg. Chem.*, 1928, **169**, 381.

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

[5] Westheimer and Novick, *J. Chem. Phys.*, 1943, **11**, 506.

[6] Watanabe and Westheimer, *J. Chem. Phys.*, 1949, **17**, 61.

an ion–dipole interaction, if it is assumed that the reciprocal of the dielectric constant of the acetic acid–water mixture is proportional to the percentage of acetic acid in the solvent mixture.[7] Cohen and Westheimer[8] explained the increased rate of oxidation of isopropyl alcohol by chromic acid in 86·5% acetic acid on the basis of increased protonation of $HCrO_4^-$ before reaction in a solvent of low dielectric constant. Cohen and Westheimer's explanation[8] is valid also for the oxidation of hydroxy-acids.

TABLE 2.

Variation of rate with concentration of hydrogen ions in 10% acetic acid at 25°.

Lactic acid

[Lactic acid] = 7·80 × 10^{-2}M. [Cr(VI)] = 4·0 × 10^{-3}M. μ = 0·406.

[H^+] (10^{-2}M)	8·0	16·0	24·0	32·0	40·0
k_1 (10^{-2} min.$^{-1}$)	1·38	2·99	4·38	5·99	7·37
$10k_1$/[H^+]	1·72	1·87	1·83	1·87	1·84

Malic acid

[Malic acid] = 4·0 × 10^{-2}M. [Cr(VI)] = 4·0 × 10^{-3}M. μ = 0·406.

[H^+] (10^{-2}M)	8·0	16·0	24·0	32·0	40·0
k_1 (10^{-3} min.$^{-1}$)	8·90	17·1	26·0	34·6	42·0
$10k_1$/[H^+]	1·11	1·06	1·08	1·08	1·05

Mandelic acid

[Mandelic acid] = 9·75 × 10^{-2}M. [Cr(VI)] = 4·0 × 10^{-3}M. μ = 0·406.

[H^+] (10^{-2}M)	8·0	16·0	24·0	32·0	40·0
k_1 (10^{-2} min.$^{-1}$)	4·37	8·53	13·0	17·0	20·9
$10k_1$/[H^+]	5·46	5·33	5·42	5·31	5·23

TABLE 3.

Effect of manganous ions on the reaction rate in 10% acetic acid at 25°.

(*a*) [Lactic acid] = 3·90 × 10^{-2}M. [Cr(VI)] = 4·0 × 10^{-3}M. [H^+] = 0·412M. μ = 0·618.
(*b*) [Malic acid] = 4·00 × 10^{-2}M. [Cr(VI)] = 4·0 × 10^{-3}M. [H^+] = 0·320M. μ = 0·606.
(*c*) [Mandelic acid] = 6·0 × 10^{-2}M. [Cr(VI)] = 4·0 × 10^{-3}M. [H^+] = 0·400M. μ = 0·606.

Mn^{2+} (10^{-2}M)	—	0·5	1·0	1·5	2·0	2·5	5·0
k_1 (10^{-2} min.$^{-1}$), *a*	3·68	2·60	2·30	2·14	1·96	1·84	1·84
b	3·46	2·19	1·96	1·91	1·77	1·73	1·73
c	14·0	9·10	7·62	7·26	6·92	6·92	6·92

TABLE 4.

Effect of solvent composition on the reaction rate at 25°.

Acetic acid (%)	10	20	30	40	50
H_0	0·39	0·43	0·49	0·51	0·47
k_2 (10^{-2} l.^{2} mole^{-2} sec.$^{-1}$):					
lactic acid	3·10	4·18	4·66	5·30	6·04
malic acid	4·57	4·93	5·74	6·54	7·77
mandelic acid	9·35	10·2	11·8	14·2	16·6

Effect of Pyridine on Reaction Rates.—The results about the effect of pyridine on the rates of oxidation are presented in Table 5. The dissociation constant of pyridinium ion[9] is of the order of 5 × 10^{-6} at 25°. Pyridine thus effectively removes hydrogen ions, and the effective hydrogen ion concentration in the presence of pyridine would correspond to ([H^+] − [Py]). If pyridine catalyses the oxidation, the value of K_1/([H^+] − [Py]) is expected to increase with increase in the concentration of pyridine; this value would decrease, if pyridine retards the reaction and would be constant if pyridine has no effect on the rate of oxidation. In the case of lactic acid the rate of oxidation is unaffected by pyridine; in the case of malic acid and mandelic acid pyridine has a small retarding effect. The results confirm the findings of Roček and

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[7] Anantakrishnan and Venkatasubramanian, *Proc. Indian Acad. Sci.*, 1960, **51**, 310; Venkatasubramanian, *ibid.*, 1961, **53**, 80; Frost and Pearson, " Kinetics and Mechanism," J. Wiley, New York, 1953, pp. 137, 197.

[8] Cohen and Westheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4387.

[9] Holloway, Cohen, and Westheimer, *J. Amer. Chem. Soc.*, 1951, **73**, 65.

TABLE 5.

Effect of addition of pyridine on the reaction rates at 25°.

[Cr(VI)] = 4·0 × 10^{-3}M. μ = 0·406.

(a) [Lactic acid] = 7·80 × 10^{-2}M. [H$^+$] = 0·200M.
(b) [Malic acid] = 3·00 × 10^{-2}M. [H$^+$] = 0·400M.
(c) [Mandelic acid] = 5·00 × 10^{-2}M. [H$^+$] = 0·400M.

[Pyridine] (10^{-2}M)	k_1 (10^{-2} min.$^{-1}$) (a)	(b)	(c)	$10k_1$/([H$^+$] − [Pyridine]) (a)	(b)	(c)
0·00	3·68	3·11	12·0	1·84	0·78	3·00
2·48	3·22	2·80	10·8	1·84	0·75	2·90
4·96	2·72	2·52	9·70	1·83	0·72	2·77
7·44	2·30	2·22	8·52	1·83	0·68	2·60
9·92	1·84	1·96	7·40	1·83	0·65	2·46
12·4	1·38	1·61	6·20	1·83	0·58	2·24

Krupicka[10] who showed that pyridine does not catalyse the oxidation of isopropyl alcohol (cf. Chang and Westheimer[11]).

Effect of Ionic Strength on Reaction Rates.—Increase of ionic strength is known to decrease the rate of oxidation of benzaldehyde by chromic acid and this has been attributed to the effect of ionic strength on the acid chromate–dichromate equilibrium.[2] Increase in ionic strength would shift the equilibrium to the dichromate ion and this would decrease the reaction

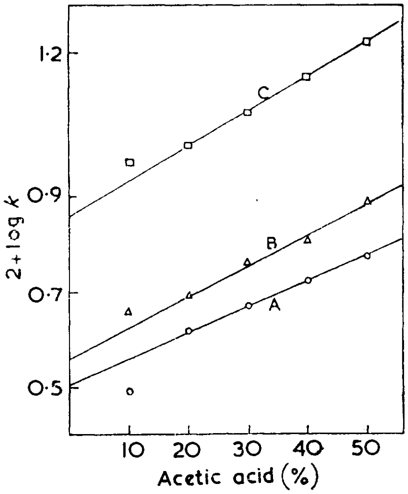

FIG. 1. Effect of solvent composition on rate of oxidation of (A) lactic, (B) malic, and (C) mandelic acid by chromic acid.

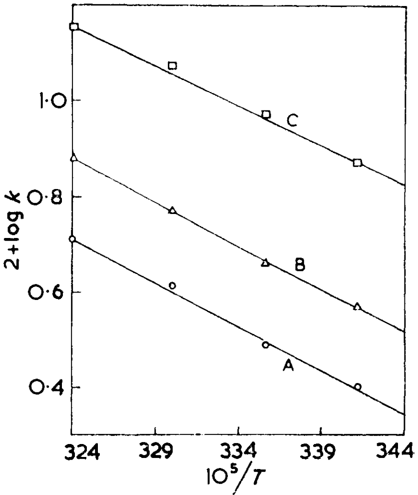

FIG. 2. Effect of temperature on rate of oxidation. (A), (B), (C) as Fig. 1.

TABLE 6.

Effect of temperature on the reaction rate.

Acid	k (10^{-2} l.^{2} mole^{-2} sec.$^{-1}$) 20°	25°	30°	35°	ΔH (kcal. mole^{-1})	pZ (10^4 l.^{2} mole^{-2} sec.$^{-1}$)	ΔS (e.u.)
Lactic	2·50	3·10	4·10	5·10	8·44	5·18	−37·3
Malic	3·71	4·57	5·90	7·60	8·36	6·66	−37·3
Mandelic	7·38	9·35	11·8	14·3	7·30	2·21	−39·5
Pr^{i}OH *					12·86	18·2	−34·6

* From Venkatasubramanian, *Proc. Indian Acad. Sci.*, 1960, **50**, 156.

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[10] Roček and Krupicka, *Coll. Czech. Chem. Comm.*, 1958, **23**, 2068.

[11] Chang and Westheimer, *J. Phys. Chem.*, 1959, **63**, 438.

rate. In the present study changes in ionic strength did not affect the reaction rates. In the experimental conditions used, sexivalent chromium exists wholly as $HCrO_4^-$ and, therefore, changes in ionic strength will have little effect on the equilibrium or the reaction rate.

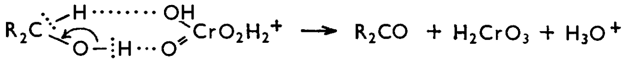
Effect of Temperature on Reaction Rates.—Table 6 and Fig. 2 give the reaction rates at different temperatures. The specific rates constants were calculated from the pseudo-first-order rate constants from the relation, $k = K_1/([\text{Hydroxy-acid}][H^+])$. The heat of activation, the frequency factor, and the entropy of activation were estimated from the results given in Table 6.

DISCUSSION

Oxidations of lactic, malic, and mandelic acid by chromic acid failed to induce reduction of mercuric chloride. This is in contrast with the acid permanganate oxidation of hydroxy-acids which induces reduction of mercuric chloride (cf. Drummond and Waters [12]). This suggests that the hydroxy-acids are not oxidised at the carboxyl group. The rate laws of oxidation of lactic, malic, and mandelic acid by chromic acid are similar to the rate laws for the similar oxidation of secondary alcohols, which also contain the group $>CH{\cdot}OH$. The values for the heat of activation and entropy of activation for oxidation of isopropyl alcohol by chromic acid are 12·86 kcal. mole^{-1} and —34 e.u., respectively.[13] The corresponding quantities for oxidation of benzaldehyde by chromic acid are 12·6 kcal. mole^{-1} and —28 e.u.[2] These quantities are of the same order as has been found for oxidation of lactic, malic, and mandelic acid by chromic acid. Oxidation of isopropyl alcohol and of benzaldehyde by chromic acid involves the rupture of the C–H bond on the α-carbon atom. It is, therefore, reasonable to suppose that the oxidation of these hydroxy-acids involve rupture of this bond.

Roček and Krupicka [14] consider that the slow step is removal of a hydride ion by a protonated chromic acid molecule (I):

(I)



The observed order of reactivity, mandelic acid > malic acid > lactic acid, runs contrary to the order of reactivity expected on the basis of Roček and Krupicka's mechanism.

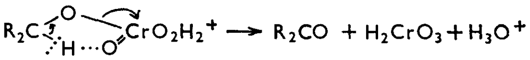
Westheimer [1] considers that oxidation of alcohols by chromic acid involves reversible formation of a chromate ester (II) which slowly decomposes by a process catalysed by bases:

(II)

The observed order of reactivity agrees with Westheimer's scheme. But this scheme is unsatisfactory inasmuch as it requires catalysis by bases like pyridine. Such catalysis has not been observed.

A minor variant of the Westheimer scheme in which the proton is removed intramolecularly (cf. III) instead of by an external base has been suggested by Kwart and Francis [15] to account for the relative rates of oxidation of a series of cyclic secondary alcohols:

(III)



Decomposition of the chromic ester does not require the presence of an external base. The removal of a proton in the cyclic transition state explains the observed order of

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[12] Drummond and Waters, *J.*, 1953, 3836.

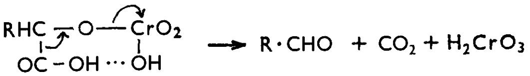
[13] Venkatasubramanian, *Proc. Indian Acad. Sci.*, 1960, **50**, 156.

[14] Roček and Krupicka, *Chem. and Ind.*, 1957, 1668; *Chem. Listy*, 1958, **52**, 1735.

[15] Kwart and Francis, *J. Amer. Chem. Soc.*, 1955, **77**, 4097.

reactivity. The Kwart–Francis scheme, therefore, appears satisfactory for the oxidation of lactic, malic, and mandelic acid by chromic acid.

Alternatively, it may be supposed that the oxidation leads directly to the formation of aldehyde and carbon dioxide by way of a chromic ester:



This process requires rupture of C–C bond and is similar to the mechanism for oxidation of pinacol by chromic acid suggested by Chang and Westheimer.[16] From Chang and Westheimer's results[16] it is estimated that such a process would require an energy of activation of about 18 kcal. mole^{-1} and a small entropy of activation. The values of the energy of activation and the entropy of activation for the oxidation of lactic, malic, and mandelic acid, however, make such a process improbable.

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[16] Chang and Westheimer, *J. Amer. Chem. Soc.*, 1960, **82**, 1401.