

# KINETICS OF OXIDATION OF ALCOHOLS BY CHROMIC ACID—THE MECHANISM OF THE REACTION

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## INTRODUCTION

OXIDATIONS of a variety of organic compounds by chromic acid have been extensively studied and the generally accepted mechanism is the one put forward by Westheimer.<sup>9</sup> Using isopropyl alcohol as the substrate, the main features of the mechanism involved as an essential part, the rapid formation of an ester—an alkyl chromate, followed by interaction with a base, water playing this role, in the slow rate-determining step. Using deuterated compounds, Westheimer also showed that the rate-determining step involved the removal of the C—H hydrogen in the part carrying the alcohol group. Further, it was considered that in the last step, the chromium was reduced to the tetravalent state while the hydrogen was removed as a proton.

While the rupture of the C—H bond appears to be on fairly certain ground, it appeared worth while to investigate the problem further. In two preliminary communications<sup>(a-b)</sup> we had indicated the complex nature of the reaction and the difficulties in the Westheimer mechanism and in a further detailed study, one of us had presented the results with a group of aliphatic secondary alcohols.<sup>8a</sup> In the present communication we are presenting the essential results for elucidating the mechanism of the reaction and a tentative mechanism is also proposed. We have to refer in this connection also to the publications of Roček<sup>6</sup> which represent a different point of view from that of Westheimer.

## THE FORMATION OF A CHROMATE ESTER

The evidence in favour of the formation of an ester as a step in the reaction is based on its isolation in benzene solution as a transient compound.<sup>9a-b</sup> Generally it is found that esterification involves an activation energy of the order of 13 K. calories or more while the apparent activation energy is very much lower in the present case. Further, esterification

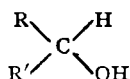
of secondary butyl alcohol involves a higher activation energy than isopropyl alcohol<sup>4 a</sup> while we find a lower activation energy for the oxidation of the secondary butyl compound.<sup>8 a</sup> Similarly the rates of hydrolysis of the sec. butyl esters are consistently slower than those of the corresponding isopropyl esters.<sup>7</sup> On both grounds we are forced to the conclusion that the formation of a chromate ester cannot be an essential step in the oxidation reaction and any mechanism proposed has to deal only with the two reactants independently.

#### THE RUPTURE OF THE C—H BOND IN THE C—H (OH) GROUP

As indicated earlier, Westheimer has demonstrated that the rate-determining step involved a rupture of the C—H bond with the removal of the hydrogen atom as a proton. While we can accept the first part, we find it difficult on the evidence available to accept the second part. Roček (*loc. cit.*) in his mechanism has left the question open. The study of a series of compounds with a systematic variation in the structure as well as a graded system of solvent mixtures was expected to provide some of the information required. For our purpose, it is adequate to consider only the Arrhenius activation energies and the rate constants at any one temperature. These are presented in Tables I and II.

TABLE I

*Activation energies in the oxidation of secondary alcohols*



*by chromic acid in 50% acetic acid and the Arrhenius Pre-exponential factor*

R	R'	E <sub>a</sub> (kilocalories)	Log <sub>10</sub> PZ	k <sub>2</sub> × 10 <sup>4</sup> at 50° C.
Me	Me	14.31	5.57	0.7800
Me	Et	13.54	5.29	1.3620
Me	n-Pr	13.45	5.37	1.8810
Me	Ph	14.18	6.28	4.8420
Ph	Ph	13.50	6.22	11.750

It will be noticed that with increasing electron release by a substituent group, activation energy for the reaction progressively gets reduced and the

TABLE II

*Rate constants ( $10^4 k_2$ ) in acetic acid-water mixture at 40° C.*

Alcohol	Volume % acetic acid in medium					
	30	40	50	60	70	80
Isopropyl	.. 0.098	0.198	0.390	0.835	1.90	..
Sec-butyl	.. 0.172	0.345	0.715	1.445	3.47	..
Alpha-phenyl ethyl	.. ..	..	2.42	4.61	10.1	23.2
Benzhydrol	.. ..	..	6.03	8.64	18.2	50.1
Fluorenol-9	.. ..	..	9.42	18.0	38.3	76.7

trend of rate constants follows the trend of resonance stabilisation of a carbonium ion. The influence of the environment by change to conditions of lower water content which favours a stabilisation of any carbonium ion intermediate is also in the right direction. This necessarily implies that in the rate-determining step the hydrogen transfer is essentially a hydride ion transfer. Lewis and Symons<sup>3</sup> in analysing various aspects of rupture of a C—H bond arrive at a conclusion that electron repelling groups by their inductive effect facilitate such transfers and the reaction between triphenylmethyl cation and isopropyl alcohol studied by Bartlett and McCollum<sup>2</sup> bears out such group influence.

#### THE INFLUENCE OF PRODUCTS OF THE REACTION AND OF IONIC STRENGTH ON THE OXIDATION REACTION

In every instance, the addition of the ketone formed by the oxidation had no influence on the rate and the changes in ionic strength of the medium by suitable additions of different acetates had no appreciable effect. On the other hand, the addition of tervalent chromium had a definite retarding influence though the reduction appears to be small (Table III) (Roček, *loc. cit.*).

The only addition that appears to have any pronounced influence is thus the chromium ion and the change in rate constant appears to be proportional to the square-root of the chromium ion concentration.

In support of the postulated mechanism, Westheimer<sup>9 a</sup> has reported that the addition of a base like pyridine catalyses the oxidation. It will be

TABLE III

*Effect of change in ionic strength on the oxidation of isopropyl alcohol by chromic acid in sulphuric acid*  
(Roček and Krupička, loc. cit.)

Temp.: 25° C. Concentrations: HClO<sub>4</sub> 0·0046 M      Rate constants × 10<sup>6</sup>  
CrO<sub>3</sub> 0·0002 M  
Iso-propylalcohol 0·2600 M

Salt added	Concentrations		
	0·04 M	0·08 M	0·26 M
NaClO <sub>4</sub>	.. 1·6	1·5	1·3
Pyridinium perchlorate	.. 1·7	1·6	1·45
Trimethyl ammonium perchlorate	.. 1·6	1·4	..
None	.. 2·0	..	..

TABLE IV

*Influence of products of the reaction and added ions on the oxidation of dl-alpha-phenyl ethyl alcohol in 70% acetic acid at 45° C.*

Compound added	Concentration Moles	k <sub>2</sub> × 10 <sup>4</sup>	
None	.. ..	13·75	(18·49 at 50° C.)
Calcium Acetate	.. 0·00505	13·02	..
Aluminium Acetate	.. 0·00505	13·14	..
Chromium Acetate	.. 0·00300	12·10	..
	0·00505	11·75	..
	0·00666	11·30	..
	0·01135	10·80	..
Acetophenone	.. 0·03614	18·52	at 50° C.

noticed from the data of Roček (*loc. cit.*) that there is room for a difference of opinion. We are unable to confirm Westheimer's catalysis by pyridine. The influence if any is slight and then it is one of retardation, not acceleration.

TABLE V

*Influence of pyridine on the oxidation of alcohols by chromic acid in 70% acetic acid at 50° C.*

Alcohol	Concentration of pyridine added	$k_2 \times 10^5$
Isopropyl alcohol	.. Nil	40.37
	.. 0.00689 M	40.03
	.. 0.01767 M	38.86
	.. 0.03203 M	38.24
$\alpha$ -phenyl ethyl alcohol	.. Nil	184.9
	.. 0.01937 M	181.9

#### RETARDING INFLUENCE OF ADDED OXIDISABLE IONS

It is generally observed that the commonest oxidations involve only a one-electron transfer though instances are not wanting where the change involves a two-electron transfer. The two-electron process is invariably associated with considerable dislocations in the co-ordination sphere. In the present studies the starting material is chromic acid or the acid chromate ion while the end product is the trivalent chromium ion in a solvated condition. We have thus a change from tetrahedral disposition of atoms to an octahedral distribution of the solvent molecules or of water. A change involving two-electron transfer is thus a possibility. Westheimer's technique of determining the induction factor by the addition of manganous ions is a convenient test while trivalent cerium is also an equally useful tool. Under the conditions indicated by Westheimer, manganese should be precipitated as  $MnO_2$  but in our case it remains wholly in solution, any tetravalent manganese being kept as an acetate complex. The rate determinations are to some extent rendered less accurate on this account. This difficulty is however not present with the cerium compound. The addition of a manganous

compound reduces the rate to  $\frac{1}{3}$  of the value while that of cerium reduces it to  $\frac{1}{2}$ . (Table VI).

TABLE VI  
*Oxidation of isopropyl alcohol at 50° C. (0.02 M)*

Solvent composition % Acetic acid by volume	Second order rate constants $\times 10^5$		
	Absence of $Mn^{++}$ or $Ce^{+++}$	In presence of $Ce^{+++}$ 0.00293 M	In presence of $Mn^{++}$ 0.00293 M
70	40.37	21.02	13.80
50	7.80	4.05	2.67

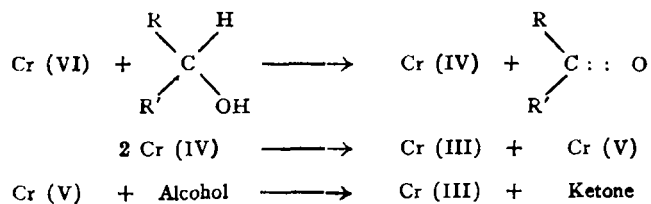
It is thus clear that the rate-determining step in the reaction involves a two-electron transfer.

#### THE MECHANISM OF THE OXIDATION REACTION

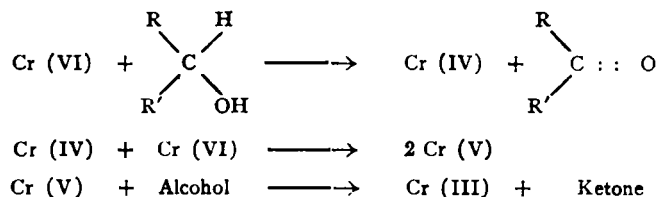
Any mechanism that can be postulated for the reaction has thus to take into account the following factors:—

- (i) The rate-determining step involves a hydride transfer.
- (ii) The rate-determining step involves a two-electron transfer.
- (iii) The reaction is facilitated by inductive electron release in the alcohol.
- (iv) Decrease of water content increases the reaction rate.
- (v) Tervalent chromium has a retarding influence.

Two alternative schemes can be proposed for the purpose as follows:—

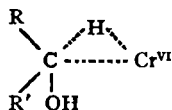


Scheme I



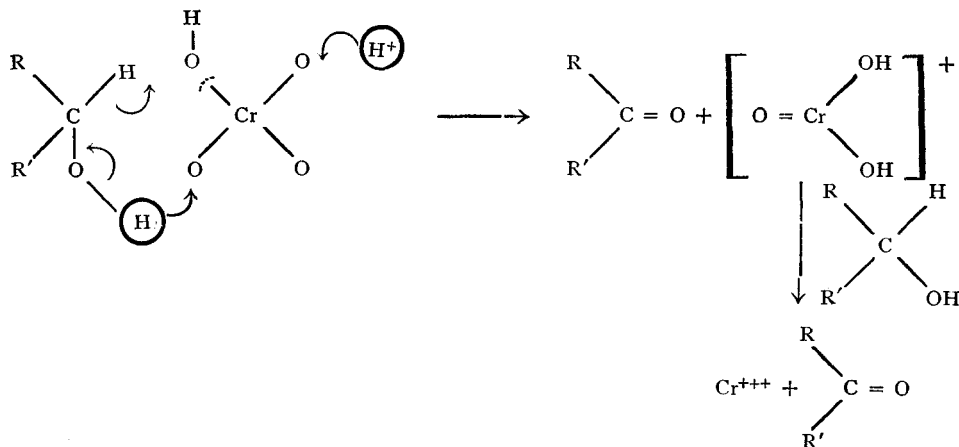
Scheme II

Dielectric constant values for the different solvent mixtures used in the study were not available but assuming an approximate validity of the mixture law, it was observed<sup>6b</sup> that there is a linear relationship between the logarithm of the rate constant and the reciprocal of the dielectric constant. The mechanism has then to be visualised as an ion-dipole reaction and the removal of the hydride ion has to be a stage after the formation of the transition state. We have ample evidence to support the participation of Cr (V) in oxidations. Mosher and his associates have shown that alcohol oxidations can be effected by this transient body.<sup>5</sup> An interesting feature of his study is the postulate of the cation  $\text{HCrO}_3^+$  as the reacting ion in chromic acid solutions and Roček also has postulated this species in the oxidation of hydrocarbons.<sup>6 b</sup> While one cannot rule out the possibility of the presence of this cation in glacial acetic acid and in solutions with a higher proportion of this component in the solvent mixtures, it is doubtful if any appreciable concentration of the cation can exist in the more aqueous systems. In our view, evidence is as yet inadequate to decide among the various alternative oxidising species but we can be fairly certain about the valence state of the oxidiser. The comparatively small effect of the changes in ionic strength suggests a transition state of the following type followed by a rapid abstraction of the hydroxyl hydrogen along with the transfer of the hydride ion in the next and final stage of the reaction. Of the two alternative modes



of removal of tetravalent chromium, we consider that mechanism I is the more probable. Disproportionation of a less stable form to a higher and lower state of oxidation has several analogies in the fifth, sixth and seventh groups in the periodic table and it is only in mechanism I where the formation of Cr (V) from Cr (IV) can be retarded by the presence of Cr (III). The retardation of the reaction by trivalent chromium that we find can thus be held to favour this view. Other techniques than simple rate studies are

obviously necessary for a positive identification of the transient reactive intermediate species. Apparently a cyclic process nearer the Roček mechanism is to be preferred to the Westheimer mechanism for these oxidations:—



Further work in progress in these laboratories may be expected to give a clearer picture.

#### SUMMARY

An analysis of the various factors affecting the oxidation of secondary alcohols by chromic acid in aqueous acetic acid systems shows the following features. The formation of an ester of chromic acid is not essential to oxidation. Both structural and solvent influences from the study of a series of secondary alcohols, aliphatic as well as aromatic, suggest that in the rate-determining step of the reaction the C—H hydrogen is removed as a hydride ion. The rate-determining step involves a two-electron transfer and the reacting species can be hexavalent and pentavalent chromium. A tentative mechanism of the reaction has been suggested incorporating these features.

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