

STUDIES IN OXIDATION

Part X. Mechanism of the Oxidation of Aromatic Aldehydes with Chromium (VI) Oxide

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AMONG a variety of oxidations by chromic acid, aromatic aldehydes have been reported to follow a mechanism put forward by Wiberg and Mill.¹ Using benzaldehyde as the substrate, the mechanism involved as an essential part the pre-formation, by a reversible reaction, of the conjugate acid of the aldehyde, which reacts with the HCrO_4^- ion, assumed to be the active oxidizing species, to form an ester intermediate. This ester then reacts with a base, in a slow rate-determining step to form the carboxylic acid, and a tetravalent chromium compound, losing the hydrogen at the secondary carbon as a proton. Using the deuterated aldehyde, Wiberg² also showed that the rate-determining step involved the removal of the C-H hydrogen in the part carrying the aldehyde group.

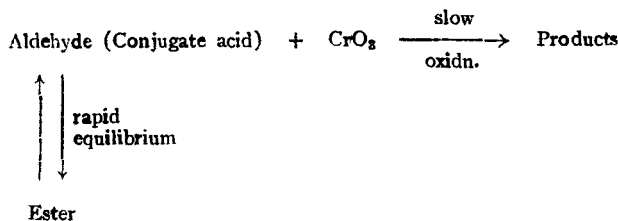
While the rupture of the C-H bond appears to be on a fairly certain ground, it appeared worthwhile examining the problem further. Our observations with a number of aldehydes have been communicated in earlier parts. We present here the essential results for elucidating the mechanism of the oxidation process. A tentative mechanism is also suggested. We may refer here to the publications of Roček^{3,4} and of Anantakrishnan and Venkatasubramanian,⁵ which represent a different point of view from the generally accepted mechanism put forward by Westheimer⁶ for chromic acid oxidation of secondary alcohols.

RESULTS AND DISCUSSION

The Formation of a Chromate Ester

The evidence in favour of the formation of an ester as a step in the chromic acid oxidation reactions is based on its isolation in benzene solution as a transient compound.^{6,7} In most of the bimolecular esterification reactions, the activation energy invariably has a value between 14 and 17 k.cals., while in the present investigations the values are much lower, about 10 k.cals.

If pre-formation of an ester were involved in the mechanism, a higher activation energy for the over-all oxidation may be expected. However, the ester may be formed as an inert species in equilibrium with the conjugate acid of the aldehyde and chromic acid as a side reaction:



Roček⁸ during a study of the oxidation of aliphatic primary alcohols by chromic acid, has shown that the equilibria for the ester formation between chromic acid and alcohols are insensitive to structural changes. The observed large effects of the substituents from these laboratories also are only to be attributed to their influence on the C—H bond cleavage and ester formation can at best be a side reaction not relevant to any mechanism for the reaction.

The Rupture of the C—H Bond in the C—H Group

As indicated earlier Wiberg (*loc. cit.*) determined the value of the discrimination factor, $k_{\text{H}}/k_{\text{D}}$, making use of the deuterated aldehyde as the substrate. The value of 6.6 clearly demonstrated that the rate-determining step involved the rupture of the C—H bond; but this does not distinguish straightaway between a proton transfer and a hydride anion transfer as the same value can be observed in either case.

The relative increase in the rate of oxidation in the presence of pyridine is regarded as supporting the proton-abstraction theory. Our results are presented in Table I. A reinvestigation of catalysis by pyridine in the oxidation of isopropyl alcohol⁹ has, however, revealed that even the small catalysis noticed can at best be only a salt effect than anything else. The chief difficulty with the Wiberg mechanism of proton abstraction was the requirement of a base in the last step. While a base, like pyridine, catalyzes the oxidation rate, the most likely base, water, inhibits the reaction. As the oxidation in the several solvents takes place under conditions of constant pH, this effect of increasing quantities of water appears anomalous.

TABLE I

Aldehyde	Temp. : 80° C. Solvent: 90% HOAc (v/v)		$k_2 \times 10^3$
	Concentration of pyridine		
Benzaldehyde	..	Nil	6.880
		0.007355 M	7.544
		0.015420 M	11.320
		0.023710 M	16.470
<i>Meta</i> -Nitro-benzaldehyde	..	Nil	17.060
		0.024390 M	22.120

Retarding Influence of Added Oxidisable Ions

Oxidations can involve either a one-electron transfer or a two-electron one. The two-electron process is invariably associated with considerable distortion of the co-ordination sphere of the oxidant. In the present investigations, the oxidant can be the neutral chromic acid molecule, the HCrO_4^- ion or some solvated cationic form, while the end product is the trivalent hydrated chromium ion. We have thus a change from a tetrahedral to an octahedral environment for the chromium atom. A change involving a two-electron transfer is thus possible for one step. Westheimer's technique of determining the induction factor by the use of competing reducing agents which are oxidized by one-electron transfer¹⁰ is a useful criterion. The rate reduction observed (Table II) are consistent with a two-electron transfer in the rate-determining step.

Further information is required before postulating any mechanism. For this we have to examine (i) the thermodynamic constants of the reaction in different solvents and (ii) the influence of addition of products of the reaction. Unlike the oxidation of secondary alcohols we find here an almost constant value for ΔH in all the solvent mixtures (*cf.* Part VII of the present series), while the entropy of activation which is quite appreciable is changing. This clearly shows that a mechanism for the oxidation of the aldehydes might not be the same as for the oxidation of secondary alcohols.

In non-aqueous media, estimate of ionic strength involves a number of variable factors but an approximate idea can be had by using comparable concentrations with identical anions. The addition of divalent ions causes

an acceleration and tervalent aluminium a retardation but the maximum retardation is observed with trivalent chromium. The addition of the product of oxidation is also small and if anything is one of positive catalysis. These can be noticed from our results in Table II.

TABLE II

Temp. : 80° C. Solvent: 90% (v/v) HOAc		
Compound	Substance added and its concentration	$k_2 \times 10^3$
Benzaldehyde ..	Nil	6.880
	0.003073 M Mn (ii) acetate	2.081
	0.002644 M Ce (iii) sulphate	3.461
	0.048610 M Benzoic acid	11.520
	0.006604 M Chromium acetate	4.123
	0.003199 M Calcium acetate	8.726
	<i>Meta</i> -nitrobenzaldehyde ..	Nil
0.003049 M Mn (ii) acetate		5.339
0.002596 M Ce (iii) sulphate		8.668
0.049560 M <i>m</i> -nitrobenzoic acid		19.47
0.006984 M Chromium acetate		10.92
0.006518 M Aluminium acetate		11.22
0.003122 M Calcium acetate		21.90

We may conclude from these that the role of Cr (iii) is a mass law effect on a reversible stage of the reaction while the positive catalysis by product may be a stabilisation of some intermediate valence state of chromium by forming a complex.

We are now in a position to examine clearly the possible mechanism of the process.

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 the rupture of the C—H bond of the carbonyl group.
- (ii) The rate-determining step involves a two-electron transfer.
- (iii) Electron-withdrawing groups generally accelerate the rate of oxidation and electron-releasing groups generally retard this.
- (iv) Decrease of water content increases the reaction rate.
- (v) Tervalent chromium has a retarding influence.

Assuming an approximate validity of the mixture law, it was observed (Part IX of the present series) that there is a linear relationship between the logarithm of the rate constant and the reciprocal of the dielectric constant. This might suggest an ion-dipole reaction, a view confirmed by applying the Amis' equation to the limiting case of the head-on approach of an ion to a dipolar molecule, *viz.*,

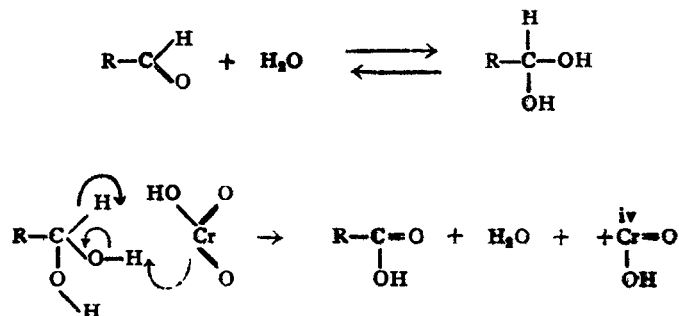
$$\ln k'_{D=D} = \ln k'_{D=\infty} + \frac{Ze\mu}{DkTr^3}$$

The slope of the line obtained by plotting $\log_{10} k$ against $1/D$ would correspond to $Z/2 \cdot 303 kTr^3$ and should give reasonable values of the parameter 'r'.¹¹ The values of 'r' obtained in the present investigations are of the right order of magnitude (Part IX of the present series) for a molecular radius (giving 'r' values of below 6 A.U. in all cases).

We have noticed earlier that the loss of the hydrogen of the C—H bond as a proton is unlikely in the reaction.

A mechanism involving the abstraction of the secondary hydrogen as an anion from a cyclic transition state, similar to that suggested by Roček

and Krupicka¹² and by Anantakrishnan and Venkatasubramanian⁵ for the secondary alcohols oxidation, suggests itself:

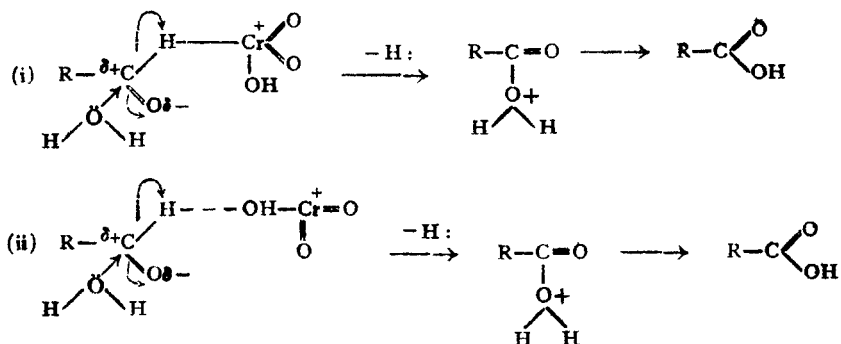


It is of course difficult to decide *a priori* whether the hydride ion is transferred primarily to the chromium or to one of the oxygen atoms of the oxidizing agent, but Roček⁸ put forth that it is more likely that the hydrogen goes to an oxygen atom than to the chromium atom.

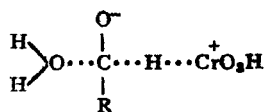
The aldehyde molecule has the carbonyl carbon hybridised trigonally. Conversion to a glycol will mean a change to tetrahedral orbitals. Further, this carbon also is the positive end of the dipole. The introduction of a nitro group in the benzene ring attached to this carbon atom should decrease the electron density on this carbon atom. The conversion of the tetrahedral intermediate into the acid molecule involves a reversal of the hybridisation again to a trigonal form. It is much simpler to envisage a mechanism which does not require any such change in hybridisation. The influence of substituents also is against such hybridisation changes. The shape of the electrophilic reagent, namely, the hexavalent chromium species, is also consistent with such a picture.

The catalysis by pyridine can be either through its functions as a base or as a complexing agent for one or more of the valence states of chromium. Hydride migrations are known to be catalyzed by bases.¹³⁻¹⁷ On the other hand, stabilisation of intermediate valence states can alter the stages in the mechanism. We have shown elsewhere that this is an important factor.

While a mechanism similar to that of Swain¹⁷ is possible, we prefer as an alternative one simulating the well-known S_N2 mechanisms.¹⁸ Two alternatives are possible even here, depending on whether the hydride ion is transferred primarily to the chromium or to one of the oxygen atoms of the oxidizing agent. The following scheme is suggested as a probable course:



As the attacking nucleophile, here water, or a suitable base, seeks a centre of positive charge, any group like the *para*-nitro group, which is conjugated with the carbonyl group and is thus able to increase the positive charge at the centre will increase the rate of oxidation. The rate-determining step involves a simultaneous removal of the secondary hydrogen as a hydride anion by the electrophilic reagent, HCrO_3^+ . Here is the driving force for the faster oxidation. The attack of the nucleophile on the positive centre and the removal of the secondary hydrogen with the bonding pair of electrons in the transition state can be represented thus:



This again brings out clearly the very close similarity to the activated complex of a typical $\text{S}_{\text{N}}2$ reaction.

This similarity between the chromic acid oxidation of aldehydes and the $\text{A}_{\text{Ac}}2$ mechanism of ester hydrolysis also accounts for the small magnitude of the polar effects. The rate under these conditions is controlled by two factors that respond differently to polarity. Such a reaction will be accelerated if the conversion of the substrate to the conjugate acid is made more complete (this will be facilitated by electron-repelling groups), but it will also be accelerated if the protonated substrate co-ordinates more readily with the displacing reagent (this will be facilitated by electron-attracting groups). These opposing tendencies naturally reduce the magnitude of the polar effects.

The above $\text{S}_{\text{N}}2$ mechanism first put forward by us¹⁸ for the chromic acid oxidation of aromatic aldehydes has recently been extended by Venkata-

subramanian¹⁹—formerly of these laboratories—for the chromic acid oxidation of secondary alcohols.

SUMMARY

Both structural and solvent influences on the rate of oxidation of a series of aromatic aldehydes by chromic acid show the following features: the formation of a chromate ester is not a prerequisite to oxidation; in the rate-determining step of the reaction the C—H hydrogen is removed as a hydride anion. That the rate-determining step involves a two-electron transfer has been proved by a study of the Induction Factor method. A tentative mechanism, based on an analogy to the well-known 'S_N2' process, has been proposed.

ACKNOWLEDGEMENTS

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