

STUDIES IN OXIDATION

Part XI. Salt Effects on the Oxidation of Aromatic Aldehydes with Chromium (VI) Oxide

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It has been shown in the earlier part of this series¹ that the chromic acid oxidation of aromatic aldehydes in binary solvent mixtures of acetic acid and water proceeds possibly by a 'S_N2' mechanism. However, although the oxidation of the aldehyde molecule involves a two-electron reaction, the reduction of hexavalent chromium to the trivalent state is a three-electron change and should, therefore, involve a chromium species of valence four or five. Evidence has been put forward from kinetic studies carried out in these laboratories² that both the above species of chromium are formed during the reduction, although tetravalent chromium is a more significant intermediate.

Watanabe and Westheimer³ successfully employed the induced oxidation of the manganous ion as a diagnostic tool in determining which chromium species is formed in the first step of the oxidation of isopropyl alcohol in aqueous perchloric acid media. The present paper deals with the effect of added salts and oxidisable ions on the oxidation in acetic acid-water mixtures in the case of aromatic aldehydes.

EXPERIMENTAL

B.D.H. Manganous acetate Extrapure and E. Merck Cerous sulphate were used without further purification. All the other compounds were of reagent grade and were used after repeated crystallizations. The titrimetric procedure was the same as detailed in Part VII of this series.⁴

RESULTS AND DISCUSSION

Experiments with added oxidation product, *viz.*, the corresponding carboxylic acid, showed rates which were greater than those obtained in the absence of these products, while the addition of chromium acetate, the other product, produced a perceptible retardation in the rate of oxidation.

Increase in the rate of oxidation of formaldehyde by chromic acid by added formic acid has been observed earlier by Chatterji and Samir Kumar Mukherjee.⁵ Venkatasubramanian⁶ has reported retardation in the oxidation rate of secondary alcohols as a result of the prior addition of the inorganic product, chromium acetate.

It is difficult to explain *a priori* the acceleration due to the addition of the organic acid. It is pertinent here to recall the observations of Chatterji and Samir Kumar Mukherjee: "This may be partly due to its contribution of a small amount of hydrogen ions, which accelerate the reaction."

To establish the actual cause for the retardation—whether it is due to the ionic product of the reaction or due to a change in the ionic strength—the experiments were repeated with the addition of separate and equivalent quantities of aluminium acetate (giving a trivalent cation in solution) and calcium acetate (giving a divalent cation in solution). It was observed that aluminium retarded the reaction rate while calcium acetate increased it. Similar effects of added salts have been noticed earlier in the chromic acid oxidation of formaldehyde. It should, however, be said that the perceptible retardation, though small in magnitude in the case of added chromium acetate, is mainly due to specific presence of Cr^{3+} , the reduction product of hexavalent chromium, and consequent mass law effect. Such specific retardation by Cr^{3+} has been reported earlier in the chromic acid oxidation of ethylene glycol⁷ and substituted toluenes.⁸

The effect of added salts on the oxidation rates are given in Table I.

The next point to be settled was the determination of the oxidation state of the chromium species formed in the first stage of the oxidation; for, the oxidation of the aldehyde molecule would involve only a two-electron change, while the reduction of Cr (vi) to Cr (iii) is a three-electron change.

The effect of the initial addition of manganous acetate on the rate of oxidation of benzaldehyde and of *meta* nitrobenzaldehyde was first studied. It is seen that a marked reduction in rate occurs on the addition of Mn^{2+} ions and the rate is reduced to one-third of the value obtained in the absence of this ion.

An attempt was made to determine the stoichiometry of this induced oxidation. It was found that the oxidized manganese species did not precipitate from the acetic acid solutions. (Under the experimental conditions employed by Westheimer⁹ the oxidized manganese was precipitated as MnO_2 .) It seemed possible that the manganese was present as a complex acetate or

TABLE I

Temperature : 80 ° C

Solvent : 90% (v/v) HOAc

Compound oxidized	Substance added and its concentration	$k_2 \times 10^3$
Benzaldehyde	.. Nil	6.880
	0.048610 M Benzoic acid	11.20
	0.004394 M Chromium acetate	4.287
	0.006604 M Chromium acetate	4.123
	0.003199 M Calcium acetate	8.726
<i>m</i> -Nitrobenzaldehyde	.. Nil	17.06
	0.02527 M <i>m</i> -Nitrobenzoic acid	19.70
	0.03668 M <i>m</i> -Nitrobenzoic acid	19.61
	0.04956 M <i>m</i> -Nitrobenzoic acid	19.47
	0.004836 M Chromium acetate	10.98
	0.006984 M Chromium acetate	10.92
	0.002862 M Aluminium acetate	11.40
	0.006518 M Aluminium acetate	11.22
	0.003122 M Calcium acetate	21.90

other similar species—presumably Mn (iv) is tightly complexed by the acetate ion. It should, therefore, be noted that any experimental procedure to determine the excess of hexavalent chromium will determine both the Cr (vi) concentration and the concentration of the manganese species of oxidation state higher than two. Several attempts were made, in vain, to evolve an analytical procedure which would distinguish between Cr (vi) and the higher states of manganese. On account of this, any mechanism with reference to this induced oxidation can at best be only highly tentative. Dhar¹⁰ while studying the chromic acid oxidation of formic acid and more recently Wiberg and Mill¹¹ in their investigations of the chromic acid oxidation of substituted benzaldehydes were also faced with a similar situation.

Experiments with the cerous ions were, however, more successful. In the presence of cerous sulphate, the oxidation of benzaldehyde and of *meta* nitrobenzaldehyde gave rates which were nearly half the rates of oxidation in the absence of this ion—a result quite in agreement with earlier findings. Since the only known valence states of cerium are three and four, the valence of cerium should be increased by one during the reaction. Hence Ce³⁺ probably reacts with a compound containing Cr (iv) which should therefore be the initial reduction product of hexavalent chromium.

The influence of added oxidisable cations, Mn⁺⁺ and Ce⁺⁺, on the rate of chromic acid oxidation of the aromatic aldehydes is given in Table II.

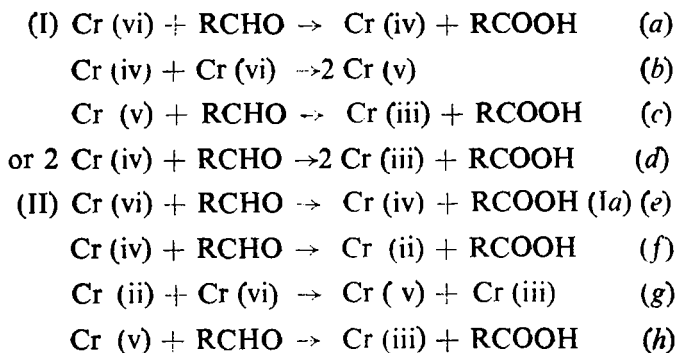
TABLE II

Temperature : 80 °C.

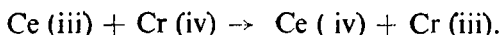
Solvent : 90% (v/v) HOAc

Compound oxidized	Substance added and its concentration	$k_2 \times 10^3$
Benzaldehyde	0·003073 M Manganous acetate	2·081
	0·002644 M Cerous sulphate	3·461
	Nil	6·880
<i>m</i> -Nitrobenzaldehyde ..	0·003049 M Manganous acetate	5·339
	0·002596 M Cerous sulphate	8·668
	Nil	17·060

A study of the several possible schemes for the oxidation shows that the following could explain the observed reduction in rate:



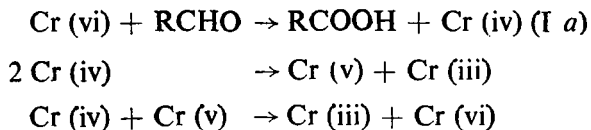
and in the presence of tervalent cerium,



Either of the above two schemes would account for the observed retardation by Ce (iii). Since Cr (vi) is consumed not only in I (a), but also in I (b) or II (g), if Cr (iv) is reduced by Ce (iii), before it has a chance to undergo the rest of the reactions, the rate of consumption of Cr (vi) is then necessarily halved.

The reaction proceeding *via* Cr (iv) which is then oxidized by Cr (vi) to give two molecules of Cr (v). I (a), (b) and (c) have a precedent in the work of Watanabe and Westheimer (*loc. cit.*) and of Venkatasubramanian (*loc. cit.*) who have established that the two-electron change, I (a) or II (e), is the first step in the oxidation of isopropyl alcohol by chromic acid.

One attractive explanation for the threefold reduction in rate in the presence of Mn^{++} ions is that of Wagner,¹² *viz.*, that Mn^{++} possibly catalyzes the disproportionation of Cr (iv) and Cr (v) to Cr (iii) and to chromate.



the last two steps being catalyzed by Mn^{++}

This would account for the observation that in the presence of the manganese ion, the rate of disappearance of chromic acid is only one-third as great as it is in the absence of that ion.

SUMMARY

The effect of added salts and oxidizable cations on the chromic acid oxidation of aromatic aldehydes in acetic acid-water mixtures is discussed and a tentative scheme for the intermediate stages of reduction of the chromium species is presented.

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