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Mechanism of Chromic Acid Oxidation of Aldehydes

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In a previous communication[1] we showed that the oxidation of acetaldehyde by Cr(VI) involves an attack on the keto-form of the aldehyde and suggested that the reaction proceeds through the transfer of a hydride ion. The present study of the oxidation of chloroacetaldehydes and formaldehyde by chromic acid was undertaken to substantiate the mechanism proposed earlier.

Results

Product Analysis. Oxidation of monochloro-, dichloro-, trichloro-acetaldehydes and formaldehyde by aqueous chromic acid yielded the corresponding carboxylic acid as characterized by the spot tests.[2]

It was observed that for every mole of Cr(VI) consumed, nearly 1.5 mol of the carboxylic acid was formed. The overall reaction may be written as follows.

$$3RCHO + 2CrO_4^{2-} + 10H^+ \longrightarrow 3RCOOH + 5H_2O + 2Cr^{3+} \qquad (1)$$

Rate Laws. When the concentrations of the aldehyde and hydrogen ion are in excess, the rate of disappearance of Cr(VI) follows first order rate laws, but the values of rate constants decrease with increase in the concentration of Cr(VI). The results show that the reaction is strictly of first order with respect to acid chromate ion $HCrO_4^-$. Since the results in all aldehydes are similar, only results of reaction with monochloroacetaldehyde (MCA) are reproduced (Table 1). The concentrations of $HCrO_4^-$ were calculated assuming a value of 2.3×10^{-2} for association constant for dichromate formation ($K=[HCrO_4^-]^2/[Cr_2O_7^{2-}]$) at 30°C.[3]

Table 1. Dependence of reaction rate on the concentration of chromic acid
[MCA] 5.0×10^{-2}M, [H$^+$] 1.0M, temp. 30°C

10^3[Cr(VI)] mol·l^{-1}	$10^4[HCrO_4^-]$ mol·l^{-1}	10^5k_1 sec^{-1}	$\frac{10^5k_1[\text{Cr(VI)}]}{[HCrO_4^-]}$
1.0	9.24	6.5	7.0
2.5	21.2	5.9	7.0
4.0	31.7	5.6	7.1
5.0	38.0	5.3	7.0
10.0	64.9	4.5	6.9

Table 2. Dependence of the reaction rate on the concentration of aldehyde
[Cr(VI)] 1×10^{-3}M, [H$^+$] 1.0M, temp. 30°C

10^2[MCA]mol·l^{-1}	1.0	2.0	3.0	4.0	5.0
10^4k_1(sec^{-1})	1.3	2.6	4.0	5.4	6.5
10^2k_1/[MCA]	1.30	1.30	1.33	1.35	1.30

The reactions are also of first order with respect to aldehyde (Table 2).

Under the conditions of constant ionic strength the rate is proportional to the square of hydrogen ion concentration (Table 3). There is also a marked positive ionic salt effect.

Table 3. Acidity dependence of the reaction rate
[MCA] 2×10^{-2}M, [Cr(VI)] 1×10^{-3}M, temp. 30°C
Ionic strength (μ)=2.0M

[H$^+$] mol·l^{-1}	0.50	0.75	1.00	1.25	1.50	2.0
10^4k_1 (sec^{-1})	1.2	2.8	5.0	8.1	11.5	20.0
$10^4k_1/[H^+]^2$	6.0	5.0	5.0	5.2	5.1	5.0

Effect of Solvent Composition. Increase in the proportion of acetic acid in the solvent mixture increases the rate of oxidation (Table 4), probably because of the lowering of dielectric constant of the medium,[4] which favours reactions involving protonation. Moreover, in acetic acid, chromic acid exists as acetochromic acid which is assumed to be a stronger acid and a much more powerful oxidizing agent.[5] This also contributes to the increase in the reaction rate.

Effect of Temperature. Data on the effect of temperature on the oxidation rate are summerized in Table 5. A plot of log *k* against the inverse of temperature gives a straight line. The Arrhenius equation is, therefore, valid for these reactions. The specific rate constant *k* is obtained from the relation $k=k_1/[\text{Aldehyde}][H^+]^2$.

The activation parameters were also evaluated (Table 6).

Discussion

It has been proposed that aliphatic aldehydes are oxidized *via* their hydrates.[6,7] The aldehydes we studied exist mostly as hydrates in solution, and hence either the aldehyde hydrate or its simple derivative is the most likely intermediate. Since the aldehyde hydrates so closely resemble the alcohols in structure

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TABLE 4. SOLVENT COMPOSITION DEPENDENCE OF REACTION RATE $10^3k(l^3\mathrm{mol}^{-3}\mathrm{sec}^{-1})$

Compound	Acetic acid, %					
	20	40	50	60	70	80
HCHO[a]	47	105	150	230	360	510
$ClCH_2CHO$[a]	13	26.5	38.5	50	80	110
Cl_2CHCHO[b]	1.4	2.7	3.8	4.7	6.3	10
CCl_3CHO[b]	0.23	0.37	0.50	0.66	0.93	1.10

Temp.: a) 30°C, b) 35°C.

TABLE 5. EFFECT OF TEMPERATURE ON OXIDATION RATE $10^3k(l^3\mathrm{mol}^{-3}\mathrm{sec}^{-1})$

Compound	Temp. (°C)			
	25	30	35	40
HCHO	34	47	64	87
$ClCH_2CHO$	9.5	13.0	17.3	23
Cl_2CHCHO	0.76	1.05	1.42	1.90
CCl_3CHO	0.12	0.17	0.23	0.32

TABLE 6. ACTIVATION PARAMETERS

Compound	ΔE^* kcal mol^{-1}	ΔS^* e.u.	ΔF^* 298°K kcal mol^{-1}
HCHO	11.6	−27	19.6
$ClCH_2CHO$	10.9	−32	20.4
Cl_2CHCHO	11.4	−35	21.8
CCl_3CHO	12.0	−37	23.8

as well as in practically all aspects of oxidation, it is reasonable to expect a similarity in the mode of their oxidation as well.

Recently, Wiberg and Schafer[8] established that oxidation of alcohols by chromic acid proceeds *via* the chromate esters. We have shown[1] that oxidation of aldehydes is also best represented by assuming the formation of a similar intermediate which then decomposes in the rate-determining step.

The activation parameters suggest that C–H bond is ruptured in the rate-determining step.[9,10] This was confirmed by the fact that formaldehyde shows a primary isotope effect.[6] It is, however, far less clear whether hydrogen leaves as a proton, an atom or an anion. Wiberg and Mill,[11] and Graham and Westheimer[12] preferred the abstraction of proton whereas Rocek[7] favoured the transfer of hydride ion from the substrate to the oxidant. When the rate constants of the aldehydes studied here are plotted against Taft's σ^* values,[13] a straight line is obtained with a value of ρ^* approximately −1.1 (Fig. 1).

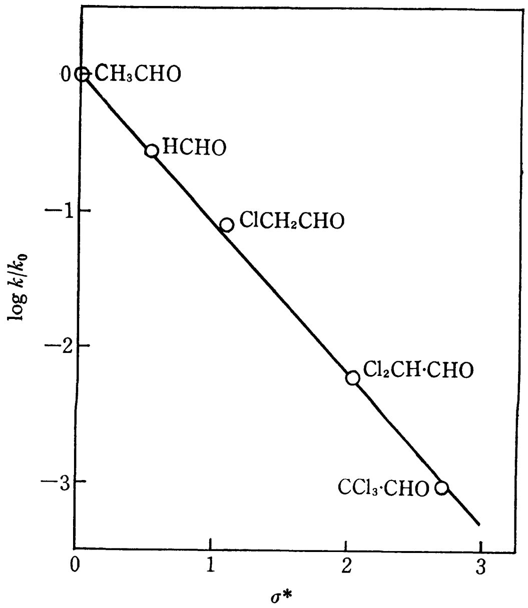
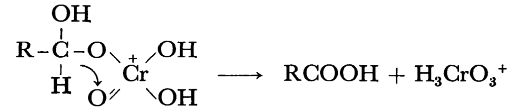


Fig. 1. Dependence of rate constants on Taft's σ^* values (Rate data of MeCHO are taken from Ref. 1).

This result indicates that oxidation is facilitated by a high electron density at the C–H bond and strongly suggests that the oxidation of aldehydes by chromic acid involves a hydride transfer as follows:



$$\mathrm{R{-}\underset{H}{\overset{OH}{C}}{-}O{-}\overset{+}{Cr}(=O)(OH)_2 \longrightarrow RCOOH + H_3CrO_3^{+}}$$

Experimental

Materials. Aldehydes were purified by the usual methods. Perchloric acid (60%, E. Merck) was used as a source of hydrogen ions. Acetic acid (B. D. H., AnalR) was distilled over chromic acid before use. All other chemicals used were chemically pure.

Product Analysis. For a quantitative estimation of carboxylic acid, the completely reduced reaction mixture was shaken with ether, and the amount of the acid present in the ether solution was determined colorimetrically by ferric hydroximate method.[14]

Kinetic Measurements. The reactions were carried out at constant temperature (±0.05°C). Unless otherwise stated the solvent was 20% acetic acid (v/v). The aldehydes were always kept in excess. Reactions were followed iodometrically.

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