BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2643—2645 (1970)

The Mechanism of the Oxidation of Acetaldehyde by Chromic Acid

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(Received March 16, 1970)

Aliphatic ketones are oxidized by chromic acid *via* their enol form.[1] There is a possibility that oxidation of aldehydes may also involve the enol intermediate. Chromic acid oxidation of aromatic aldehydes[2-4] and formaldehyde[5] has been studied in detail, but these aldehydes cannot enolize. Some preliminary studies have been carried out on the oxidation of acetaldehyde by Roček[6] and by Chat terji and Antony.[7] In the present investigation the role of enolization in the oxidation process has been studied.

Results

Product Study. Oxidation of acetaldehyde by aqueous chromic acid yielded acetic acid. The completely reduced reaction mixture gives a blue-brown colour with lanthanum nitrate and a drop of iodine solution in the presence of ammonia.[8]

Rate Laws. The rate of disappearance of Cr(VI) followed first order law, but the values of rate constants decreased with increase in the concentration of chromium(VI). The results show that the reaction is strictly of first order with respect to acid chromate ion, $HCrO_4^-$ (Table 1). The concentrations of $HCrO_4^-$ were calculated assuming a value 2.3×10^{-2} for association constant for dichromate formation ($K=[HCrO_4^-]^2/[Cr_2O_7^{2-}]$) at 25°C.[9]

The reaction is also of first order with respect to acetaldehyde (Table 2).

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

Effect of Solvent Composition. Increase in proportion of acetic acid in the solvent mixture

Table 1. Oxidant concentration dependence of the reaction rate

$[CH_3CHO]$: 4×10^{-2}M, $[H^+]$: 0.5M, Temp. 25°C

$10^3[Ce(VI)]$ mol/l	$10^4[HCrO_4^-]$ mol/l	$10^2\,k_1$ min^{-1}	$\frac{10^2k_1[Cr(VI)]}{[HCrO_4^-]}$
1.00	9.24	6.91	7.47
2.50	21.2	6.30	7.42
4.00	31.7	6.00	7.57
5.00	38.0	5.50	7.23
10.00	64.9	4.80	7.40

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Table 2. Substrate concentration dependence of the reaction

[Cr(VI)]: 1×10^{-3}M, [H$^+$]: 0.5M, Temp. 25°C

10^2[CH_3CHO] (mol/l)	1.00	2.00	3.00	4.00	5.00
10^2k_1 (min^{-1})	1.73	3.50	5.20	6.91	8.70
k_1/[CH_3CHO]	1.73	1.75	1.73	1.73	1.76

Table 3. Acidity dependence of the reaction velocity

[CH_3CHO]: 1×10^{-2}M, [Cr(VI)]: 1×10^{-3}M

Temp. −25°C, Ionic strength (μ) = 2M

[H$^+$] (mol/l)	0.25	0.50	0.75	1.00	1.25	1.50
10^2k_1 (min^{-1})	0.691	2.53	6.15	10.1	16.1	23.0
k_1/[H$^+$]^2	11.0	11.2	10.9	10.1	10.3	10.2

increases the rate of oxidation (Table 4), probably because of the lowering of dielectric constant of the medium,$^{10)}$ which favours reactions involving protonation. In acetic acid chromic acid exists as acetochromic acid, $CH_3COOCrO_3H$, which is assumed to be a stronger acid and a very powerful oxidizing agent$^{4,11)}$ and hence the rate increases.

Table 4. Solvent composition dependence of the reaction rate

[CH_3CHO]: 1×10^{-2}M, [Cr(VI)]: 1×10^{-3}M

[H$^+$]: 0.5M, Temp. 25°C

Precentage acetic acid	20	40	50	60	70	80
10^2 k_1 min^{-1}	1.73	2.30	3.45	5.07	10.4	18.4

Effect of Manganese(II). Addition of manganese(II) did not affect the rate of oxidation. This prevents any conclusion as to whether chromium(IV) or chromium(V) is formed in the rate-determining step. A similar effect was noted in the oxidation of cyclohexanone$^{1)}$ and has been attributed to the rapid oxidation of the organic substrate by Mn(III), formed by the reaction.

$$\text{Cr(IV)} + \text{Mn(II)} \longrightarrow \text{Cr(III)} + \text{Mn(III)} \qquad (1)$$

Effect of Temperature. Data on the effect of temperature on the reaction rate are summarized in Table 5. A plot of $\log k_1$ against reciprocal of temperature gave a straight line. The specific rate constant, k, is defined by

$$k = \frac{k_1\ (\text{min}^{-1})}{60\cdot[CH_3CHO][H^+]^2}$$

The activation parameters were evaluated in the usual manner.

Table 5. Effect of temperature on the reaction rate

[CH_3CHO]: 1×10^{-2}M, [Cr(VI)]: 1×10^{-3}M

[H$^+$]: 1.0M

Temp. °K	10^2 k_1 min^{-1}	$k\times10^2$ $l^3\cdot$mol$^{-3}\cdot$sec^{-1}	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.
293	5.53	9.21	9.03	−33.2
298	7.14	11.90	$\Delta F^{\neq}$	
303	9.21	15.35	298°	
308	11.7	19.50	18.9 kcal/mol	

Rates of Enolization. The rates of enolization were measured by bromination method.

The rate of bromination of acetaldehyde is of first order with respect to acetaldehyde and hydrogen ions but of zero-order for bromine. Table 6 records the rate constants of bromination (k_2) at different temperatures and activation parameters.

Table 6. Effect of temperature on the bromination rate

Temp. °K	10^4 k_2 $l\cdot$mol$^{-1}\cdot$sec^{-1}	$\Delta H^{\neq}$ kcal/mol	$\Delta F^{\neq}$ 298° kcal/mol
293	1.08	15.3	
298	1.63	$\Delta S^{\neq}$	22.8
303	2.50	−25.3 e.u.	
308	3.83		

Discussion

A comparison of Tables 5 and 6 shows that oxidation is much faster than enolization. Moreover, the activation energy is much lower in the chromic acid oxidation than in enolization. On these grounds we are forced to conclude that enolization cannot be an essential step in the oxidation reaction.

The results obtained here are consistent with the following rate equation, which is very similar to that previously derived for the oxidation of isopropyl alcohol.$^{9)}$

$$-d[\text{Cr(VI)}]/dt = k[CH_3CHO][HCrO_4^-][H^+]^2$$

It has been proposed that aliphatic aldehydes are oxidized *via* their hydrates.$^{5,6)}$ The kinetic solvent isotope effect demonstrated by acetaldehyde$^{12)}$ is of the same order as that by formaldehyde$^{5)}$ and hence either the acetaldehyde hydrate or its simple derivative is the most likely intermediate. Because the aldehyde hydrates so closely resemble alcohols both is structure as well as in practically all aspects of oxidation, it is reasonable

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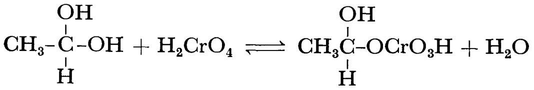
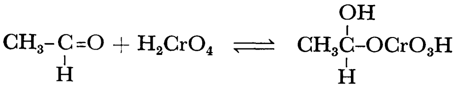
to expect a similarity in the mode of their oxidation as well.

Very recently Wiberg and Schäfer have established that oxidation of alcohols proceeds *via* chromate esters.[13] Analogously the oxidation of acetaldehyde can best be interpreted by assuming the reversible formation of a similar intermediate, which will then decompose in the rate-determining step. As long as the chromic acid ester is in rapid equilibrium with acetaldehyde and its hydrate, it is immaterial whether it is formed by the esterification to the hydrate or by a carbonyl addition reaction to the free aldehyde.



$$CH_3\text{-}\underset{H}{\overset{OH}{C}}\text{-}OH + H_2CrO_4 \rightleftharpoons CH_3\underset{H}{\overset{OH}{C}}\text{-}OCrO_3H + H_2O \qquad (2)$$

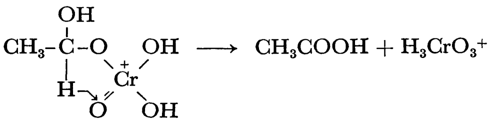


$$CH_3\text{-}\underset{H}{C}{=}O + H_2CrO_4 \rightleftharpoons CH_3\underset{H}{\overset{OH}{C}}\text{-}OCrO_3H \qquad (3)$$

However, the second-order dependence on [H+] and magnitude of kinetic solvent isotope effect[12] ($k_{D_2O}/k_{H_2O}=6.29$), show that the rate-determining step must involve a protonated reaction complex. Thus formation of ester is followed by protonation of the chromic acid moiety of the ester.

$$CH_3\text{-}CH(OH)O\text{-}CrO_3H + H^+ \rightleftharpoons CH_3CH(OH)\text{-}\overset{+}{O}CrO_3H_2 \qquad (4)$$

The activation parameters suggest that C–H bond is ruptured in the rate-determining step[14,15] and this reasoning is made clear by the fact that both formaldehyde[5] and acetaldehyde[16] show a primary isotope effect. It is, however, far less clear whether hydrogen leaves as a proton, an atom or an anion. Westheimer[4] prefered the abstraction of proton in cyclic process by one of the chromate oxygen atoms. Roček,[6,17] however argued in favour of a hydride transfer. There are no data which permit one to distinguish conclusively between these two mechanisms. Recently, however, it has been shown that several two-electron oxidants oxidize alcohols by a hydride transfer mechanism[18,19] and it is likely that oxidation of acetaldehyde by chromic acid involves a hydride transfer as follows.



(5)

Experimental

Materials. Perchloric acid (60%, E. Merck) was used as a source of hydrogen ions; sodium perchlorate (Riedel) was used to adjust the ionic strength. Acetaldehyde (B.D.H.) was purified by the usual method. Acetic acid (99.5%, B.D.H.) was distilled over chromic acid before use. All other chemicals used were of "AR" grade.

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

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