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EVIDENCE OF ESTERIFICATION DURING THE OXIDATION OF SOME AROMATIC ALDEHYDES BY CHROMIUM (VI) IN ACID MEDIUM AND THE MECHANISM OF THE OXIDATION PROCESS

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Abstract - The oxidation kinetics of some aromatic aldehydes by chromium (VI) have been studied in perchloric acid medium. Kinetic and spectrophotometric results indicate the formation of a 1:1 intermediate ester between the reactive chromium (VI) species and protonated benzaldehyde. The rate is directly proportional to the square of hydrogen ion concentrations. The rate of oxidation decreases with the presence of electron donating groups and increases with electron withdrawing groups on the aromatic ring. The activation parameters associated with the rate determining step and the thermodynamic values associated with the equilibrium step have been computed. An attempt has been made to compare the results obtained with those for the oxidations of some aliphatic aldehydes which do not have enolizable hydrogen.

The stoichiometry, kinetics and mechanism of the oxidation of various organic compounds such as alcohols[1-7], aliphatic and aromatic aldehydes[8-14], hydroxy acids[15,16], and oxalic acid[17] by chromic acid and by other intermediate valence states of chromium[12,18,19] have been studied. The mechanism of the oxidation of aldehydes by chromic acid which has been suggested is not firmly established[20]. There is neither kinetic nor spectrophotometric evidence for intermediate complex formation between benzaldehyde and chromium (VI). The present investigation on the oxidations of some aromatic aldehydes by chromium (VI) was carried out in perchloric acid medium in view of the interesting results obtained with some oxidizing agents[21].

EXPERIMENTAL

Reagents Potassium dichromate (GR, E.Merck), perchloric acid (BDH) and sodium perchlorate (Riedel, W.Germany) were used. Glacial acetic acid (BDH).

AnalaR) was heated under reflux for 6 h with excess of potassium dichromate and distilled just before use. The solid aldehydes were recrystallized from suitable solvents. The liquid samples were purified by distillation under reduced pressure just before use. Acetaldehyde (Aldrich), bromal (Fluka) and chloral (BDH) were used without further purification. Fluoral was prepared[22] by the oxidation of 2,2,2-trifluoro ethanol (Sigma). Benzaldehyde-d_1 was prepared[23] by the reduction of benzil (Merck) with lithium alumnium deuteride (Fluka, AG) to give the diol followed by the oxidation of diol by lead tetra-acetate. The product exhibited ν_{max} (film), 2100 and 2050 cm^{-1} ; $\delta(CCl_4)$ 7.2-7.9 (complex multiplet, aromatic H) and no signal for the aldehyde H.

Kinetic measurements A large excess of each substrate was used for all kinetic measurements. Both titrimetric and spectrophotometric methods were employed in the oxidations of aromatic aldehydes. The aliphatic aldehydes were studied spectrophotometrically. The titrimetric method was followed by removing aliquots after suitable intervals of time and quenching the reaction mixture by adding it to an excess of potassium iodide solution under a blanket of carbon dioxide. Liberated iodine was titrated against a standard thiosulphate maintaining the appropriate acidity. The pseudo-first-order rate constants (k_{obs}) were calculated from the slopes of log T (T=titre) against time plots. The rate of decrease of chromium (VI) was followed at 380 nm and not at the absorption maximum of chromium (VI) in order to minimize the error due to carbonyl compounds. A cell of pathlength of 1 cm or 0.1 cm was used depending upon the concentration of chromium (VI). The pseudo-first-order rate constants were obtained graphically from log A (A=absorbance) against time plots. The values of k_{obs} obtained titrimetrically in the oxidation of benzaldehyde are $(6.4 \pm 0.2) \times 10^{-3}$, $(5.04 \pm 0.1) \times 10^{-3}$ and $(4.26 \pm 0.12) \times 10^{-3}$ s^{-1} at [Chromium (VI)] of 6.66×10^{-4}, 33.33×10^{-4} and 50.0×10^{-4}M respectively whereas those obtained spectrophotometrically are $(6.2 \pm 0.15) \times 10^{-3}$, $(4.98 \pm 0.12) \times 10^{-3}$ and $(4.32 \pm 0.1) \times 10^{-3}$ s^{-1} at the respective chromium (VI) concentrations. The results agree very well. The rate constants were reproducible to within ± 3 % . Some typical pseudo-first-order plots are shown (Figure 1).

Product analysis An attempt was initially made to isolate the oxidation product under kinetic condition and despite several attempts benzoic acid could not be isolated in quantitative yield. Hence the reaction was carried out at much higher reactant concentrations. The yield and identity of the oxidation product were established in the following way.

To a stirred mixture of benzaldehyde (freshly distilled ; 2.5 g) and a solution of perchloric acid (70% ; 50 ml) in water (100 ml), was added dropwise a solution of potassium dichromate (4.9 g) in water (50 ml) in course of half an hour. The stirring was continued for another half an hour, then the reaction mixture was left at room temperature (30°C) for 16 h. It was then extracted with chloroform (3 x 50 ml). The organic layer was washed with water (10 ml), extracted with saturated sodium bicarbonate solution (3 x 25 ml, preserved) and again washed with water, dried over anhydrous sodium sulphate. On removal of the solvent, only a trace amount of neutral fraction was obtained which furnished the 2,4-DNP (50 mg) of benzaldehyde, identified through melting point and mixed melting point determination.

The aforementioned sodium bicarbonate extract was acidified (congo red) with concentrated hydrochloric acid and extracted with chloroform (3 x 50 ml). The organic layer was washed with water (10 ml) and dried over anhydrous sodium sulphate. On removal of the solvent over steam bath, a solid residue (2.7 g ; 95 %) m.p. 118°, was obtained which remained undepressed on admixture with authentic benzoic acid.

The aliphatic aldehydes were quantitatively oxidized when these were mixed with large excess of dichromate ions in perchloric acid medium (1M) and stored for 24 hr at 30°C according to the equation,

$$3CX_3CHO + 2Cr(VI) \longrightarrow 3CX_3COOH + 2Cr(III)$$

Spectrophotometric evidence for the intermediate complex Westheimer et al[2,3] have investigated the kinetics of the oxidation of 2-propanol by acid chromate ions in the aqueous solution and have shown that the primary step in the reaction is the formation of an ester. Later on spectrophotometric evidence[24] for 1:1 complex of acid chromate ion with some aliphatic alcohols and acetaldehyde have been put forward. An attempt was made to determine the equilibrium constant (K_e) of the 1:1 complex between benzaldehyde and $HCrO_4^-$ spectrophotometrically. Benzaldehyde showed three main absorption bands in the uv region. They are at 300 nm (low intensity), 250-280 nm (medium intensity) and 210 nm (strong intensity band). Benzaldehyde is transparent at 380 nm. The following relation (1)[24] was used in determining the value of K_e of 1:1 complex and measurements were made of the difference in extinction ($\Delta\epsilon$) of two solutions, both containing acid chromate and perchloric acid, one of them furthermore benzaldehyde.

$$\frac{\Delta\epsilon}{C_a} = K_e \Delta\epsilon' l C_o - K_e \Delta\epsilon \qquad (1)$$

where K_e = equilibrium constant, l = optical path length in cm, C_a = concentration of the substrate, C_o = concentration of the acid chromate and the difference between the extinction coefficient of the complex and that of the acid chromate ion at 380 nm. The plot of $\Delta\epsilon/C_a$ against $\Delta\epsilon$ yields a straight line making an intercept on the y-axis (Figure 2). The value of K_e has been calculated to be 20 lit mol^{-1} at 31.5°C.

RESULTS

The reactions were investigated at varying concentrations of chromium (VI) and fixed concentrations of other reactants. Each experiment was performed at constant ionic strength (I) of 1.0 M maintained by the addition of sodium perchlorate. The pseudo-first-order rate constants are not independent of chromium (VI) concentrations. The values of $HCrO_4^-$ concentrations and k_{cor} have been calculated as mentioned in earlier communication[6]. The results presented in Table 1 indicate that the reactions are effected by $HCrO_4^-$.

The effect of variation of the benzaldehyde concentrations on the pseudo-first-order rate constant was studied at constant [Cr(VI)] and $[H^+]$. The plots of k_{obs} against [PhCHO] are not linear passing through the origin. The plots of $1/k_{obs}$ against 1/[PhCHO] are, however, linear (Figure 3) at different temperatures making intercepts on the y-axis indicating an intermediate complex formation between the reactants. The order with respect to substrate can be expressed as,

$$-\frac{d[Cr(VI)]}{dt} = \frac{k_d K_e [Cr(VI)][PhCHO]}{1 + K_e[PhCHO]} \qquad (2)$$

where k_d and K_e can be identified as the electron transfer constant for the decomposition process of the intermediate complex and equilibrium constant of the 1:1 complex respectively in perchloric acid medium. The rate of the reaction increases linearly with the increase in $[CX_3CHO]$ passing through the origin (Figure 4) in the oxidations of fluoral, chloral and bromal and there is no kinetic evidence for the formation of intermediate esters during the oxidations of these aliphatic aldehydes.

The reaction was studied at different hydrogen ion concentrations varied by addition of perchloric acid. Since pseudo-first-order rate constant increases to the extent of 20 % in 2M sodium perchlorate concentrations (Table 2), the ionic strength (I) at lower acidities (< 2.0 M) was adjusted constant by the addition of sodium perchlorate ($I = 1.0$ M). The rate increases with the increase in perchloric acid concentrations. The plot of k_{obs} against $[H^+]^2$ is linear (Figure 5) in the oxidation of benzaldehyde. The pseudo-first-order rate constants for the oxidations of the aliphatic aldehydes were also determined at different acidities but at constant ionic strength. The results are plotted in Figure 6 which indicate that these aliphatic aldehydes are oxidized by different mechanistic path.

The rate of oxidation of benzaldehyde was studied at various concentrations of manganese (II) sulphate but at constant concentrations of other reactants. The pseudo-first-order rate constant decreased with the increase in manganous ion concentrations (Table 2). A limiting value is reached at higher manganous ion concentrations ($\geqslant 2.4 \times 10^{-3}$M) and the rate is reduced to one-third of that in the absence of manganous ion.

The values of k_d are 0.28×10^{-3}, 0.5×10^{-3}, 1.0×10^{-3} and 2.0×10^{-3} s^{-1} at 40, 50, 60 and 70°C respectively whereas those of K_e are 14.0, 10.0, 6.7 and 4.4 mol^{-1} at the respective temperatures. The enthalpy of activation ($\Delta H^{\neq}$) has been calculated from the plot of log (k_d/T) against $1/T$ (Figure 7) followed by the calculation of entropy of activation ($\Delta S^{\neq}$). The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been found to be 55.8 kJ mol^{-1} and -135.3 JK^{-1} mol^{-1} respectively. The enthalpy change (ΔH) associated with 1:1 intermediate complex was calculated from the plot of log K_e against $1/T$ (Figure 7) followed by entropy change (ΔS) which are -33.1 kJ mol^{-1} and -83.8 JK^{-1} mol^{-1} respectively. The second order rate constants for the oxidations of some aliphatic aldehydes were determined at different temperatures and log k_2/T are plotted against $1/T$ (Figure 8). The activation parameters are recorded in Table 3.

The oxidations of *meta* substituted compounds could not be studied under the condition at which *para* substituted aldehyde were oxidized. The oxidations of all these substituted aldehydes could be studied in 90 % (v/v) acetic acid and at $[HClO_4]$ and temperature of 1.0×10^{-1}M and 30°C respectively. The reactions were found to be second order with no evidence for intermediate ester formation. The results are recorded in Table 4. A plot of the logarithm of the relative rates against the Hammett σ-values is

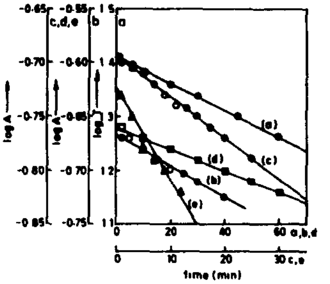


Figure 1 Typical pseudo-first-order plots of some reactions at $[HClO_4] = 1\,M$ and Temp = 40°C

a & b, $[PhCHO] = 3\,0 \times 10^{-2}\,M$, $[Cr(VI)] = 1\,66 \times 10^{-3}\,M$

c, $[Fluoral] = 8{\cdot}05 \times 10^{-4}\,M$, $[Cr(VI)] = 1\,66 \times 10^{-4}\,M$

d, $[Chloral] = 4\,0 \times 10^{-2}\,M$, $[Cr(VI)] = 1\,66 \times 10^{-4}\,M$

e, $[Bromal] = 3\,28 \times 10^{-3}\,M$ $[Cr(VI)] = 1\,66 \times 10^{-4}\,M$

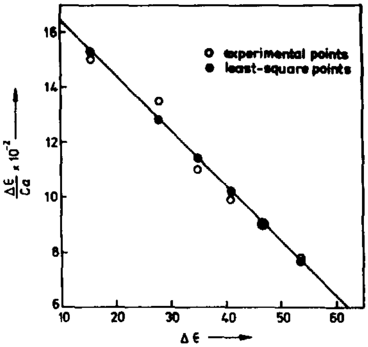


Figure 2 Plot of $\Delta\epsilon/Ca$ vs $\Delta\epsilon$ for acid chromate solutions containing benzaldehyde

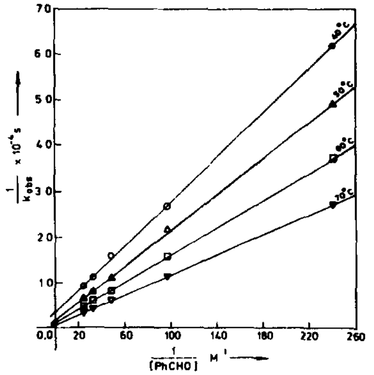


Figure 3 Plots of reciprocal of the first-order rate constants against reciprocal of substrate concentrations at different temperatures

$[Cr(VI)] = 1\,67 \times 10^{-3}\,M$, $[HClO_4] = 1\,M$

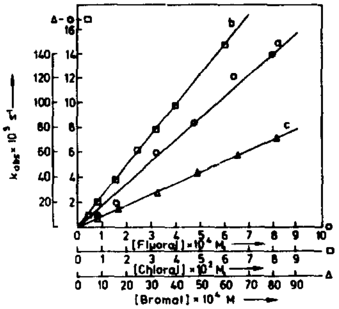


Figure 4 Plots of k_{obs} against [Substrate] for the oxidations of (a) fluoral, (b) chloral and (c) bromal

(a) $[Cr(VI)] = 1\,66 \times 10^{-4}\,M$ $[HClO_4] = 1\,M$, Temp = 40°C

(b) $[Cr(VI)] = 1\,66 \times 10^{-4}\,M$, $[HClO_4] = 2\,M$, Temp = 50°C

(c) $[Cr(VI)] = 1\,66 \times 10^{-4}\,M$ $[HClO_4] = 1\,M$ Temp = 35°C

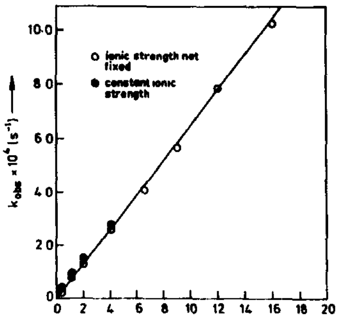


Figure 5 Acidity dependence of the chromium (VI) oxidation of benzaldehyde in aqueous perchloric acid medium

Plot of k_{obs} against $[H^+]$

$[Cr(VI)] = 1\,67 \times 10^{-3}\,M$

$[PhCHO] = 3\,0 \times 10^{-2}\,M$

Temperature = 40°C

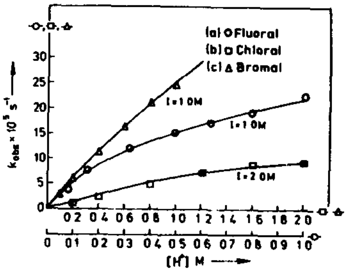


Figure 6 Variation of k_{obs} with acidity for the oxidations of (a) fluoral, (b) chloral and (c) bromal

(a) $[Cr(VI)] = 1{\cdot}66 \times 10^{-4}\,M$, $[Fluoral] = 6\,44 \times 10^{-4}\,M$ Temp = 40°C

(b) $[Cr(VI)] = 1\,66 \times 10^{-4}\,M$, $[Chloral] = 6\,00 \times 10^{-2}\,M$ Temp = 50°C

(c) $[Cr(VI)] = 1\,66 \times 10^{-4}\,M$ $[Bromal] = 3\,28 \times 10^{-3}\,M$ Temp = 35°C

Table 1. Determination of the values of k_{cor} at 40°C

(a) [PhCHO] = 2.08×10^{-2}M , [$HClO_4$] = 1M

(b)-(d) [CX_3CHO] = 1.0×10^{-2}M , [$HClO_4$] = 1M

[Cr(VI)] x 10^4M	[$HCrO_4^-$] x 10^4M	$k^a_{obs} \times 10^5 (s^{-1})$
6.66	11.51	6.40(3.70)
16.66	24.89	6.14(4.11)
33.33	42.31	5.04(3.98)
41.66	49.71	4.61(3.86)
50.00	56.53	4.26(3.76)

[Cr(VI)x10^4M	$k^b_{obs}x10^3 (s^{-1})$	$k^c_{obs}x10^5 (s^{-1})$	$k^d_{obs}x10^3 (s^{-1})$
16.66	1.75(1.17)	1.03(0.69)	1.40(0.94)
33.33	1.65(1.29)	0.95(0.75)	1.32(1.04)
41.66	1.52(1.27)	0.85(0.71)	1.25(1.05)
50.00	1.45(1.28)	0.80(0.71)	1.11(0.98)

Figures in the parentheses represent the values of k_{cor} for (a) benzaldehyde, (b) fluoral, (c) chloral and (d) bromal.

Table 2. Effect of salts on pseudo-first-order rate constant at 40°C.

(a) [PhCHO] = $3.12x10^{-2}$M, [Cr(VI)] = $1.67x10^{-3}$M, [$HClO_4$] = 1M

(b) [PhCHO] = $2.08x10^{-2}$M, [Cr(VI)] = $1.67x10^{-3}$M, [$HClO_4$] = 1M

[$NaClO_4$] M	0.0	0.2	0.5	1.0	1.5	2.0	-
$k^a_{obs} \times 10^5 (s^{-1})$	9.21	9.30	9.51	0.98	10.5	11.1	-
[$MnSO_4$] x 10^3M	0.0	2.0	4.0	8.0	1.6	2.0	2.4
$k^b_{obs} \times 10^5 (s^{-1})$	6.28	3.99	3.38	3.17	2.88	2.5	2.1

shown in Figure 9. The slope (ρ) of the plot is 1.075 which is nearer that (1.05) reported[21] earlier in connection with the acid bromate oxidation of aromatic aldehydes. When the oxidations of benzaldehyde and different *para*-substituted benzaldehydes were determined in 15 % (v/v) acetic acid and at [Cr(VI)], [$HClO_4$] and temperature of 1.67×10^{-3}M, 1.0 M and 40°C respectively, the evidence for the formation of intermediate ester was quite significant in each reaction. The values of K'_e and k'_d in acetic acid medium were calculated from the double reciprocal plots (Figure 10). It has been reported[21] that electron withdrawing substituents facilitate the rate of oxidation of benzaldehyde by bromate ion, whereas electron donating substituents have opposite effect. The values of k'_d are 1.25×10^{-4}, 6.66×10^{-4}, 3.33×10^{-4} and 20.0×10^{-4}(s^{-1}) for the oxidations of *p*-OMe, *p*-H, *p*-Cl and *p*-NO_2 compounds whereas the corresponding values of K'_e are 18.1, 7.8, 12.8 and 6.0 (l mol^{-1}) respectively. Thus in the present study also the value of k'_d increases considerably when *p*-nitrobenzaldehyde is used and reverse is the case with *p*-methoxybenzaldehyde. The value of k'_d obtained in the oxidation of chlorosubstituted benzaldehyde lies in between the values of *p*-nitro- and *p*-methoxybenzaldehydes (Table 5). The values of disproportionation and equilibrium constants are found to be $2.8 \times 10^{-4} s^{-1}$ and 14.0 l mol^{-1} in the absence of acetic acid whereas those found in acetic acid medium are $6.66 \times 10^{-3} s^{-1}$ and 7.8 l mol^{-1} respectively. The results are to be expected since acetic acid is known to enhance the rate of chromic acid oxidation of organic compounds. An attempt was also made to correlate k'_d and K'_e with σ_p of different substituents. The plots of log k'_d (or log K'_e) against σ_p are not linear. Since σ_p values represent the sum of resonance (σ_R) and field effects (σ_I) and the values of σ_p and σ_R vary with the nature of the reaction and σ_I values are in variant throughout a wide variety of reaction series, correlations were tried using a special set of σ_p and σ_R called σ_p° and σ_R° which vary much less with the nature of the reaction. The values of σ_p°, σ_R° and σ_I along with the experimentally obtained k'_d and K'_e are recorded in Table 5. The plots of log k'_d (or log K'_e) against σ_p° or σ_I are non linear but good straight lines are obtained when plotted against σ_R° (Figure 11). However, the first Hammett plot of log k'_d against log K'_e (Figure 12) exhibits a linear relationship[25] with negative slope.

Benzaldehyde-d_1 was oxidized under the same conditions as for the oxidation of ordinary benzaldehyde in perchloric acid medium. The pseudo-first-order rate constants decreased in benzaldehyde-d_1 than in benzaldehyde. The isotope effect, k_H/k_D decreases considerably in solutions of high acidity[7]. Since the reaction was carried out at [H^+] = 1.0 M, the present

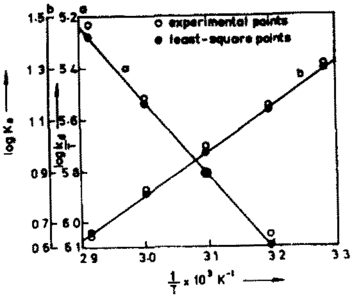


Figure 7 Variation of electron-transfer constants and equilibrium constants with temperatures Plots of (a) log k_e/T against $1/T$ (b) log K_e against $1/T$

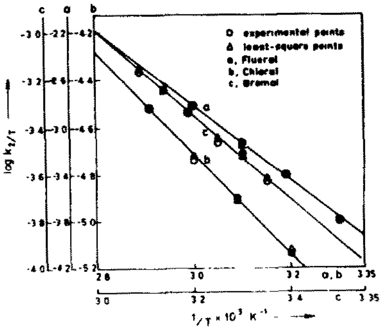


Figure 8 Plots of log k_2/T against $1/T$

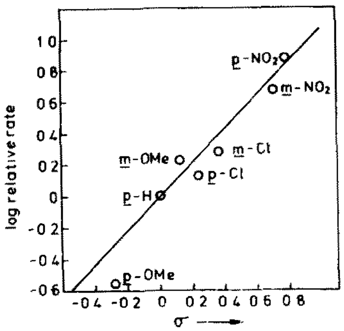


Figure 9 Plots of log relative rates against the Hammett σ values

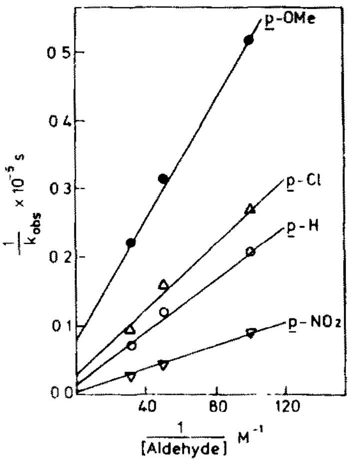


Figure 10 Plots of reciprocal of the first order rate constants against reciprocal of aldehyde concentrations

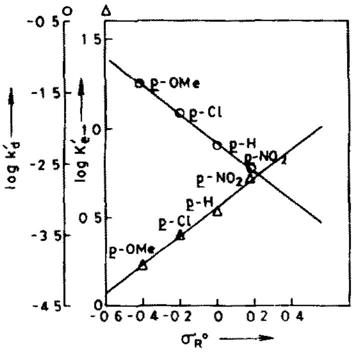


Figure 11 Plots of (a) log k'_d against σ_R° and (b) log K'_e against σ_R°

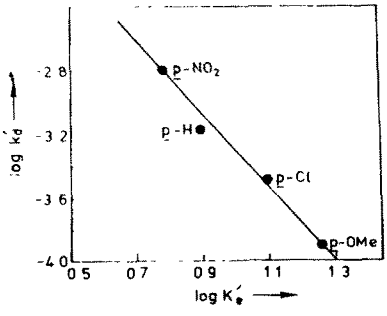


Figure 12 Linear free energy relationship The first Hammett plot of log k'_d against log K'_e

Table 3. Activation parameters of the reactions involving some aliphatic aldehydes and chromium (VI) in perchloric acid medium.

Aldehydes	Fluoral	Chloral	Bromal
$\Delta H^{\ddagger}$ ($kJmol^{-1}$)	63.1	41.8	34.8
$-\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	61.7	161.9	150.1

Table 4. Effect of substituents on the oxidation of benzaldehyde in 90 % (v/v) acetic acid.

$[HClO_4] = 1.0 \times 10^{-1}M$, Temperature = 30°C

Substituent	σ	$k_2 \times 10^3$ ($l.mol^{-1}s^{-1}$)	Relative rate
p-H	0.00	6.10	1.00
p-NO_2	0.78	46.20	7.57
p-Cl	0.23	8.42	1.38
p-OMe	-0.27	1.72	0.28
m-NO_2	0.71	28.40	4.65
m-Cl	0.37	11.60	1.90
m-OMe	0.12	10.50	1.72

Table 5. Variation of k_d' and K_e' with σ_p^o , σ_R^o and σ_I of different reactions in 15 % (v/v) acetic acid at 40°C. $[Cr(VI)] = 1.66 \times 10^{-3}M$, $[HClO_4] = 1.0\,M$

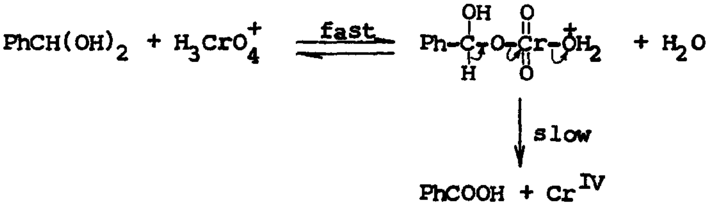
Substituent	σ_p^o	σ_R^o	σ_I	$k_d' \times 10^4 (s^{-1})$	K_e' ($l.mol^{-1}$)
p-H	0	0	0	6.66	7.8
p-NO_2	0.83	0.19	0.64	20.0	6.0
p-Cl	0.27	-0.20	0.47	3.33	12.8
p-OMe	-0.15	-0.41	0.26	1.25	18.1

value of 3.5 as against that reported[9] (k_H/k_D = 4.3) in much lower acidity (0.1 M) is not unexpected. It is pertinent to mention that isotope effects of 6.8, 5.0 and 7.9 in the oxidations of formaldehyde[7], acetaldehyde[26] and pivaldehyde[13] respectively have been noticed. Thus both aromatic and aliphatic aldehydes react by the same mechanism in which carbon-hydrogen bond is cleaved.

DISCUSSION

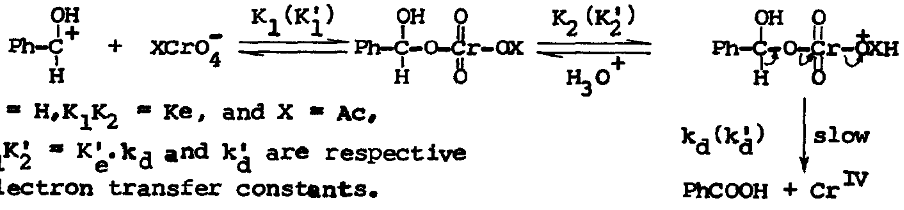
The principal observation made in the oxidations of some aromatic aldehydes is that the reaction is initiated through the intermediate formation of an ester between the reactants. Both kinetic and spectrophotometric results support this. Although some aliphatic aldehydes undergo a reversible hydration in neutral aqueous solutions to form gemdiols, the possibility that aromatic aldehydes are also hydrated cannot be totally ignored. The second order dependence of $[H^+]$ on rate may be explained on the assumption that protonated chromic acid ($H_3CrO_4^+$) reacts with hydrated benzaldehyde to give an ester which then decomposes to give the products.

Scheme 1



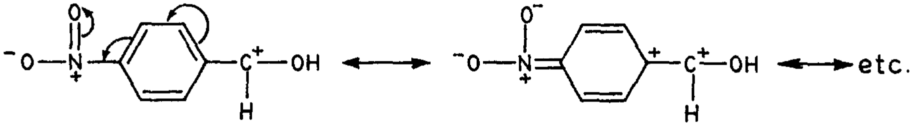
Alternatively free benzaldehyde may also be protonated and the protonated aldehyde reacts with $HCrO_4^-$ to give an intermediate ester which on further protonation gives protonated ester in fast steps. There is literature evidence[27] to indicate that aromatic aldehydes can accept proton to give protonated aldehydes. The protonated ester is capable of an internal two electron transfer oxidation-reduction reaction to give products as shown below.

Scheme 2

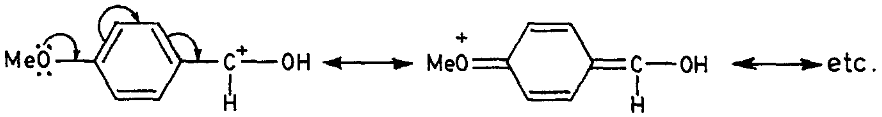


X = H, K_1K_2 = Ke, and X = Ac,
$K_1'K_2'$ = K_e'. k_d and k_d' are respective electron transfer constants.

Thus when the reaction was studied in perchloric acid medium, acid chromate ion ($HCrO_4^-$) attacks the protonated aldehyde whereas in perchloric acid-acetic acid medium the attacking species will be acetyl chromate ion ($AcO\,CrO_2O^-$). Since ^-OAc is a better leaving group than OH^- the elimination of HOAc from the protonated ester (formed between protonated aldehyde and acetyl chromate ion followed by protonation as mentioned in scheme 2) becomes easier than that of H_2O thereby increasing the rate in perchloric acetic-acid medium than in perchloric acid medium only. Structures (I-IV) may be considered in explaining the aforementioned schemes (1 and 2).



I II



III IV

The species having two positive charges on adjacent carbon atoms (Structure II generated from I through resonance) should be unfavourable. In structure I and II the C^+(benzylic) is never neutralised by electromeric shift. So it is always available for ester formation with $HCrO_4^-$. But in case of p-methoxy compound C^+(benzylic) is neutralised by electromeric shift (as shown in IV) thereby diminishing the attack of $HCrO_4^-$ to form the chromate ester. This has been found to be true experimentally.

Chromium (IV) formed in the slow step is unstable, which disproportionates or reacts rapidly with chromium (VI) to form chromium (V). There are convincing evidences in the literature[28] which indicate that chromium(V) is formed during the oxidation of some alcohols, oxalic acid and α-hydroxy acid by chromium (VI). Chromium (V) being a stronger oxidant than chromium (VI), rapidly oxidizes reactive reductant.

$$PhCH(OH)_2 + Cr(V) \longrightarrow PhCOOH + Cr(III)$$

The observation made in this study is however reminiscent of the effect noted in the vanadium(V) oxidation[29] of aromatic aldehydes where an intermediate complex was formed between reactive vanadium(V) and benzaldehyde prior to electron transfer in perchloric acid medium. Consequently the observation that an intermediate ester between reactive chromium(VI) species and aldehyde is formed in the present study is not unexpected. Recently it has been shown[21] that benzaldehyde is also oxidized by bromate ion in the acid medium through the initial formation of an ester. The values of $\Delta H^{\neq}$ and $-\Delta S^{\neq}$ for the oxidation of benzaldehyde by bromate ion are 57.8 kJ mol^{-1} and 133.2 JK^{-1}mol^{-1} respectively as compared to the respective values of 55.8 kJ mol^{-1} and 135.3 JK^{-1}mol^{-1} in the present reaction. Again in the oxidations of some aliphatic aldehydes by chromium(VI) in acid medium, the kinetic evidence for intermediate ester formation in each reaction was found to be quite insignificant[13,26]. The result is to be expected since in aliphatic aldehydes the generation of $R\overset{+}{C}HOH$ will be less favourable due to the presence of alkyl groups attached to -CHO group. Moreover, the aliphatic aldehydes are known to be partially hydrated[13] in aqueous solution whereas in solutions of aromatic aldehydes the concentrations of hydrates are known to be small, the equilibrium being strongly in favour of free aldehydes. Consequently the generation of $\overset{+}{C}$(benzylic) in aromatic aldehydes and its subsequent reaction with acid chromate ion or acetyl chromate ion in perchloric acid medium will be much more favourable than those of the aliphatic aldehydes. Again, in the chromic acid oxidation of some ketones it has been shown[30] that chromic acid attacks the enol rather than the ketone form of the substrate. The attack of chromic acid on the enol is a concerted process perhaps base catalyzed which immediately gives an intermediate chromate ester. The latter then hydrolyzes to give products of oxidation. All these lend further support to the ester formation mechanism suggested in the oxidations of some aromatic aldehydes.

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