SHORT PAPER

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Kinetic studies on the oxidation of some *para* and *meta*-substituted benzaldeydes by nicotinium dichromate†

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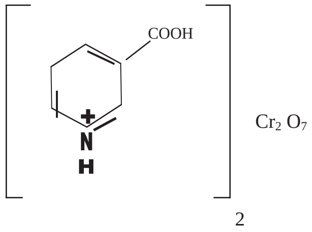
For the oxidation of *para*- and *meta*-substituted benzaldehydes by nicotinium electron releasing substituents retard and the electron withdrawing substituents enhance the rate of the reaction; from the kinetic data obtained activation parameters have been computed and a plausible mechanism has been proposed.

Keywords: para- and meta-benzaldehydes, nicotinum dichromate

Recently some neutral Cr(VI) reagents[1] have been developed for effective oxidation under mild conditions. Nicotinium dichromate (NDC) is an effective agent for the oxidisation of alcohols into carbonyl compounds.[2]



3- carboxy-pyridinium dichromate
(NDC)

The kinetics and mechanism of oxidation of aromatic aldehydes have been studied for number of oxidising agents, such as pyridinium fluorochromate in dimethyl sulfoxide,[3] pyridinium chlorochromate,[4] pyridinium fluorochromate in acetic acid – perchloric acid,[5] quinolinium chlorochromate,[6] quinolinium dichromate[7] and imidazolium dichromate[8] under different experimental conditions. It appears that no work has yet been done on ther oxidation of benzaldehydes by NDC from a kinetic view point. The present paper deals with the kinetics and mechanism of oxidation nine *para*- and *meta*- substituted benzaldehydes with NDC in an acidic medium.

Experimental

NDC was prepared by the reported method.[2] Some Benzaldehyde and substituted benzaldehydes were collected and purified before use. Acetic acid was refluxed over chromium trioxide for 6 h and then fractionated. All other chemicals used were of AnalaR grade. The solutions were prepared in triple-distilled water.

The reaction was carried out under first order conditions by maintaining the substrate concentration in excess over that of nicotinium dichromate. The kinetic measurements were made by estimating the aliquots of reaction mixtures for the oxidant iodometrically using starch as an indicator. The rate constants (k_1) evaluated from the linear plots of log [NDC] against time, by the least–squares method, were reproducible within ± 3%.

Reaction mixtures containing an excess of the oxidant over benzaldehyde were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unreacted oxidant proved that one mole of the oxidant consumes one mole of the substrate.

The product benzoic acids were identified by spot tests and IR spectral data.

Results and discussion

The first-order dependence of the reaction of benzaldehyde on NDC is obvious from the linearity of the plot of log [NDC] vs time. The reaction was found to be first-order in substrate as evidenced by the unit slope ($r = 0.997$) of the log–log plot of k_1 vs [aldehyde]. This was further well demonstrated by the constancy of the second-order rate constant $k_2 = k_1$ / [aldehyde] (Table 1).

The effect of acidity was studied by varying the concentration of perchloric acid and the rate constants were found to increase with the increase in the concentration of perchloric acid. The plot of log k vs log [H^+] gave a straight line with a slope of unity.

Table 1 Effect of concentration of reactants on reaction rates at 300K [H^+] = 1.50 mol dm^{-3} , 70% acetic acid – water(v/v)

10^2 [Benzaldehyde] /mol/dm^3	10^4 [NDC] /mol/dm^3	10^4 k_{obs} /s
2.0	7.50	3.43
2.0	10.00	3.60
2.0	12.50	3.38
2.0	15.00	3.27
2.0	20.00	3.51
1.5	10.00	2.75
2.5	10.00	4.26
3.0	10.00	5.13
3.5	10.00	6.02
4.0	10.00	6.76

The linear increase in rate with acidity suggests the involvement of protonated oxidant species in the rate determining step.[9] An attempt was made to correlate the rate data with the Hammett acidity function (H_0). Using H_0 values obtained by extrapolation from Wiberg's data,[10] plots of log k against H_0 were drawn which gave slopes far different from unity. Thus, under the present experimental conditions, it seemed reasonable to correlate the rate of the reaction with H^+ rather than with H_0.

The rate of the reaction increases with decreasing dielectric constant of the medium, suggesting ion–dipole interaction. The reaction mixture when allowed to stand with acrylonitrile does not induce polymerization suggesting the absence of a free radical mechanism. On the other hand, the addition of Mn^{2+} ions retarded the reaction rate indicating a two-electron transfer process in the reactions[11] (Table 2).

Effect of substituent on the reaction rate

The rates of oxidation of some substituted benzaldehydes were studied at three different temperatures viz., 300, 310 and 320 K. The activation parameters have been computed from a plot of ln k_2/T vs $1/T$ using Eyring's equation (Table 3). The enthalpy of activation, $\Delta H^{\#}$, values are very low suggesting a concerted

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Effect of acidity, solvent composition, $[Mn^{2+}]$ on the reaction rate for benzaldehyde at 300K $[NDC] = 1.0 \times 10^{-3}$ mol/dm^3; [Aldehyde] = 2.0×10^{-2} mol/dm^3

$[HClO_4]$ mol/dm^3	10^4 k_{obs} /s	% of Acetic acid v/v	10^4 k_{obs} /s	$10^4[Mn^{2+}]$ mol/dm^3	10^4 k_{obs} /s
1.25	2.82	60	2.74	0.00	3.60
1.50	3.60	65	3.25	1.25	2.31
1.75	4.12	70	3.60	2.50	2.18
2.00	4.90	75	5.13	3.75	2.10
2.25	5.62	–	–	5.00	2.03
2.50	6.17	–	–	6.25	1.97

Table 3 Thermodynamic parameters for the oxidation of *para-* and *meta-* substituted benzaldehydes by nicotinium dichromate

$[NDC] = 1.0 \times 10^{-3}$ mol dm^{-3}; [aldehyde] = 2.0×10^{-2} mol/dm^3
$[H^+] = 1.50$ mol/dm^3, 70% Acetic acid – water(v/v)

Substituents	10^3 k_{obs}/s			$\Delta H^{\#}$ kJ/mol	$\Delta S^{\#}$ J/mol/K	$\Delta G^{\#}$ kJ/mol
	300 K	310 K	320 K			
H	0.36	0.51	0.70	25	200	84
p-CH_3	0.30	0.38	0.42	11	240	84
p-OCH_3	0.25	0.34	0.40	17	220	84
p-C1	0.47	0.60	0.69	13	230	83
p-Br	0.44	0.55	0.76	21	210	83
p-NO_2	1.00	1.07	1.16	3.3	280	87
m-CH_3	0.33	0.38	0.42	7.9	250	84
m-C1	0.60	0.71	0.88	13	230	82
m-NO_2	0.87	0.94	1.02	3.7	260	81

mechanism as proposed.[12] The entropies of activation, $\Delta S^{\#}$, are all high negative values indicating extensive solvation of the transition state over the reactants. It also reveals that the rate determining state is less disorderly oriented relative to the reactants. The free energy of activation, $\Delta G^{\#}$, is nearly constant, 84.00 ± 3 kJ/mol supporting a unified mechanism with all the benzaldehydes studied. A plot of $\Delta H^{\#}$ *vs* $\Delta S^{\#}$ gave a straight line with a correlation coefficient ($r = 0.980$).[13,14] Exner[15] criticised the validity of such linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ as these quantities are dependent on each other. When measurements at two different temperatures have been made the experimental data can be treated by the following equation,

$$\log (k_1)_T = a + b \log (k_1)_T$$

where $T_2 > T_1$.

Thus a good correlation co-efficient ($r = 0.984$) was obtained for a plot $\log k_{310K}$ vs $\log k_{300K}$. This serves as an argument that all the substituents follow a common mechanism.

The rate data for oxidation of the *para* and *meta-* substituted benzaldehydes give a good correlation ($r = 0.996$, $\rho = +0.55$) with the Hammett σ value at 300K. Similar phenomenon has been observed in the oxidation of substituted benzaldehydes by pyridinium fluorochromate[5].

Mechanism and rate law

It is clear that the reaction shows a first-order dependence on oxidant and substrate. The reaction rate increases with the decreasing dielectric constant of the medium. Based on the above facts, the following mechanism is proposed.

$$\text{NDC} + H^+ \xrightleftharpoons{K_1} \text{NDCH}^+$$

$$\text{ArCHO} + \text{NDCH}^+ \xrightleftharpoons{K_2} [\text{complex}]$$

$$[\text{complex}] \xrightarrow[\text{slow}]{k_3} \text{Products}$$

The above mechanism leads to the following rate law,
Rate = k_3 [complex]
Rate = K_1K_2 k_3 [ArCHO][NDC]$[H^+]$
This rate law explained the experimental data obtained.

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