Kinetics and Mechanism of Oxidation of Aromatic Aldehydes by Imidazolium Dichromate

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The kinetics of oxidation of *para* and *meta*-substituted benzaldehydes by imidazolium dichromate has been studied in 70% acetic acid-water medium. The order with respect to oxidant, substrate and $[H^+]$ is found to be unity. The rate increases with the increase in the percentage of acetic acid. An increase of ionic strength has an appreciable effect on the rate. The reaction does not induce polymerisation of acrylonitrile indicating the absence of free radical pathway. The retardation of the rate by the addition of Mn^{2+} ions confirms that a two electron transfer process is involved in the reaction. Electron releasing substituents retard the reaction rate and the electron withdrawing substituents enhance the rate of the reaction. From the kinetic data obtained, the activation paramters have been computed and a suitable mechanism has been proposed.

INTRODUCTION

Imidazolium dichromate is reported to be a neutral and mild oxidant for selective oxidations[1]. The kinetics of oxidation of α-hydroxy acids by imidazolium dichromate have been known[2]. The oxidation of aromatic aldehydes by various oxidants has been reported[3–7]. In this paper the oxidation of aromatic aldehydes by imidazolium dichromate in aqueous acetic acid in perchloric acid medium is reported.

EXPERIMENTAL

Imidazolium dichromate (IDC) was prepared as reported by Kim and Lhim[1]. A few substituted benzaldehydes were collected and purified before use. All other chemicals used were of AnalaR grade. Doubly distilled water was used throughout. Acetic acid was refluxed over chromic oxide for 6 h and then fractionated[8].

The reactions were followed under pseudo-first order conditions by maintaining the substrate concentration in excess over that of imidazolium dichromate. Known volumes of substrate, water and acetic acid were mixed to bring the percentage of acetic acid to the desired value and were thermostated. The reaction was started by adding the oxidant to the mixture. Aliquots were removed at definite time intervals and the unreacted imidazolium dichromate was estimated by

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standard iodometric titrations. The rate constants were determined by the least squares method.

The stoichiometric runs were carried out in the presence of excess imidazolium dichromate which reveals that two moles of the oxidant consume three moles of the substrate.

$$3ArCHO + 2Cr^{6+} \xrightarrow{H^+} 3ArCOOH + 2Cr^{3+}$$
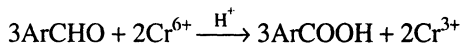
The stoichiometric amounts of substrate and oxidant were mixed at room temperature under kinetic conditions. After 24 h, the purified ether extract of the reaction mixture was evaporated. The product of oxidation of benzaldehyde by imidazolium dichromate was confirmed as benzoic acid, by m.p. and spectral analysis.

RESULTS AND DISCUSSION

The reaction is found to be first order with respect to the oxidant as evidenced by a good linearity in the plot of log [IDC] *vs* time. The pseudo-first order rate constants are found to be independent of the initial concentration of imidazolium dichromate. At constant [IDC], the rate constants increase with an increase in the concentration of substrate. A plot of log k *vs* log [substrate] gave a straight line with a slope of unity. This was further demonstrated by constancy of k_2 ($k_2 = k_{obs}/[S]$) (Table-1).

TABLE-1

RATE CONSTANT FOR THE OXIDATION OF BENZALDEHYDE
BY IMIDAZOLIUM DICHROMATE (IDC) AT 300 K

[Ben]10^2 M	[IDC]10^3 M	[KNO$_3$]10^4 M	[H$^+$] M	AcOH-H$_2$O % v/v	[Mn^{2+}]10^4 M	$k_{obs}10^4$ s^{-1}
2.0	1.0–2.5	–	1.60	70	–	2.16–1.90
1.50–3.00	1.0	–	1.60	70	–	1.55–3.24
2.0	1.0	0.0–6.00	1.60	70	–	2.30–1.25
2.0	1.0	–	1.34–2.14	70	–	1.82–3.14
2.0	1.0	–	1.60	60–75	–	1.16–3.59
2.0	1.0	–	1.60	70	0.0–4.50	2.30–1.13

Increase in the ionic strength of the medium by adding potassium nitrate had no effect on the reaction rate consistent with the involvement of an ion and neutral molecule in the rate determining step. The rate of the reaction increases with an increase in [H$^+$], suggesting that the reaction is acid-catalysed. The plot of log k vs log [H$^+$] is linear with unit slope, indicating a first order dependence on acidity. The rate of the reaction increases with decreasing dielectric constant of the medium, suggesting the ion-dipole interaction. In case of addition of MnSO$_4$, the rate decreases considerably which may be taken as evidence for a two-electron process[9]. The possibility of radical involvement in the reaction is ruled out as the addition of acrylonitrile to the reaction mixture developed no turbidity (Table-1).

The rates of oxidation of some substituted benzaldehydes have been studied at three different temperatures, $viz.$, 300, 308 and 313 K. The activation parameters have been computed from a plot of ln k_2/T vs $1/T$ using Eyring's equation. (Table-2). A plot of $\Delta H^\#$ vs $\Delta S^\#$ (isokinetic plot) gives a straight line with the correlation coefficient $(r = 0.971)$[10, 11]. The plot of log $k_{300 K}$ vs log $k_{313 K}$ gives a straigth line with r = 0.985. Such a good correlation indicates that all the substituents follow a common mechanism[12]. The near constancy of $\Delta G^\#$ values shows the operation of similar mechanism.
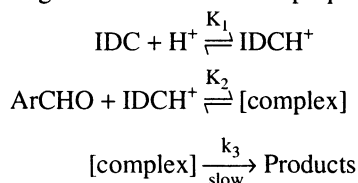
TABLE-2

THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF $PARA$-AND $META$ SUBSTITUTED BENZALDEHYDES BY IMIDAZOLIUM DICHROMATE

Substituents	k_{obs} 10^4 (s^{-1})			$\Delta H^\#$	$-\Delta S^\#$	$\Delta G^\#$
	300 K	308 K	313 K	kJ mol^{-1}	J K^{-1}mol^{-1}	kJ mol^{-1} at 308 K
H	2.30	3.08	4.65	33.61	153.91	81.01
p-CH$_3$	1.69	2.51	4.07	43.29	120.91	80.53
p-OCH$_3$	1.04	1.30	2.15	33.28	158.45	82.08
p-Cl	3.67	4.20	6.45	23.84	179.39	79.09
p-Br	2.65	3.60	5.20	37.54	156.25	85.66
p-NO$_2$	8.25	9.36	10.86	18.11	208.16	82.22
m-CH$_3$	1.54	2.38	3.31	42.77	143.14	86.86
m-Cl	3.75	4.47	5.86	23.32	200.67	85.13
m-NO$_2$	7.80	8.65	10.23	13.38	227.66	83.50

The rate data for oxidation of the $para$ and $meta$-substituted benzaldehydes give a good correlation (r = 0.989, $\rho = + 0.64$) with the Hammett σ-value at 308 K. Similar phenomenon has been observed in the oxidation of substituted benzaldehydes by PFC[13]. The positive ρ value indicates that electron-withdrawing substituents increase the rate of oxidation and electron-releasing substituents decrease the rate.

Mechanism of Rate Law

It is shown that the reaction is first order dependent on oxidant, substrate and [H$^+$]. The ionic strength of the medium has moderate effect on the reaction rate, but increases with the decreasing dielectric constant of the medium. Based on the above facts, the following mechanism has been proposed.

$$IDC + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} IDCH^+$$

$$ArCHO + IDCH^+ \underset{}{\overset{K_2}{\rightleftharpoons}} [complex]$$

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

The above mechanism leads to the following rate law:

$$Rate = k_3[complex]$$

$$Rate = K_1K_2k_3 \, [ArCHO][IDC][H^+]$$

This rate law explains all the experimental data observed.

Conclusion

The oxidation of aromatic aldehydes by imidazolium dichromate in aqueous acetic acid medium leads to the formation of a complex giving benzoic acid as the final product. The reaction follows a simple order kinetics. The substituent effect have also been studied. The mechanism proposed for this oxidation kinetics is in accordance with the observed kinetic data.

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