



## KINETICS OF OXIDATION OF 2-NITRO BENZALDEHYDE BY PYRIDINIUM BROMOCHROMATE IN ACETIC ACID- WATER MIXTURE

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### ABSTRACT

Kinetics of oxidation of 2-nitrobenzaldehyde by pyridinium bromochromate (PBC) has been studied in acetic acid-perchloric acid medium. The product is 2-nitrobenzoic acid. The reaction shows first order dependence with respect to [PBC],  $[H^+]$  and Michaelis-Menten type kinetics with respect to [2-nitrobenzaldehyde]. The rate of oxidation decreases with increase in dielectric constant of solvent suggesting ion-dipole interaction. Activation parameters have been evaluated. A mechanism consistent with experimental observations has been proposed.

**Key words :** Kinetics, Oxidation, o-Nitrobenzaldehyde, Pyridinium bromochromate

### INTRODUCTION

Mahanti and Banerji<sup>1</sup> have reviewed synthetic, kinetic and mechanistic aspects of complexed Cr (VI) compounds. Pyridinium bromochromate<sup>2</sup> [PBC] is selective, effective and mild oxidizing and brominating agent of chromium (VI). It is used as an oxidant for oxidation of alcohols<sup>3</sup>, aliphatic aldehydes<sup>4</sup>, thio compounds<sup>5,6</sup> and amino acids<sup>7</sup> etc. Oxidation of aromatic aldehydes by PBC has not been studied so far. We report here the kinetics of oxidation of *ortho*-nitrobenzaldehyde in acetic acid-water-perchloric acid medium with PBC.

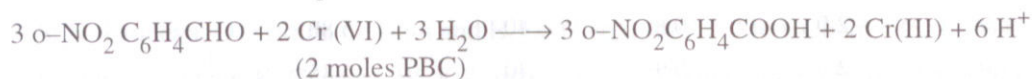
### EXPERIMENTAL

**Materials and Methods:** All chemicals used were of 'AnalaR' grade. Refluxing with chromium trioxide followed by distillation purified acetic acid. Deuterated 2-nitrobenzaldehyde was prepared in our lab. Purity of 2-nitrobenzaldehyde was checked by m.p. The stock solution of 2-nitrobenzaldehyde was prepared by dissolving known quantity in acetic acid and was estimated by sodium bisulfate and hydroxylamine hydrochloride<sup>8</sup>. PBC (mol.wt. =259.98) was prepared by reported method<sup>2</sup>. The orange solid, which separated out, was filtered, washed with water, dried in vacuum and crystallized from acetonitrile. Its purity was checked

iodometrically and by m. p. (428 K). Standard PBC solution was prepared in purified glacial acetic acid.

**Kinetic measurements:** The reactions were followed under pseudo first order conditions keeping a large excess ( $\times 10$ ) of the 2-nitrobenzaldehyde over PBC. A known volume of substrate, perchloric acid, water and acetic acid were mixed in reaction flask and kept in thermostat maintained at constant temperature ( $\pm 0.1$  K). The reaction was initiated by adding rapidly predetermined volume of PBC solution into the above reaction mixture. Aliquots (5.0 mL) were withdrawn at regular time intervals and added to 10 mL of 10 % potassium iodide solution. This was titrated against previously standardized sodium thiosulphate (hypo) using starch as an indicator. The rate constants were computed from the linear plots of  $\log [\text{hypo}]$  vs. time by least-square method. The results were reproducible to  $\pm 5$  %. Orders with respect to different reactants were determined by Oswald isolation method.

**Product study and stoichiometry:** Product of the oxidation was identified as 2-nitrobenzoic acid. After completion of the reaction under kinetic conditions, the reaction mixture was treated with solid  $\text{NaHCO}_3$ . After complete neutralization, the reaction mixture was extracted with ether to remove unreacted 2-nitrobenzaldehyde. Aqueous layer was treated with concentrated hydrochloric acid. The solid obtained was filtered, washed with cold water, dried, weighed and identified as 2-nitrobenzoic acid by m. p. (mixed m. p.) and chemical test. Stoichiometric investigations revealed that 3 moles of 2-nitrobenzaldehyde consume 2 moles of PBC. Hence reaction can be represented as:



No polymerization of acrylonitrile was observed in the reaction mixture under inert atmosphere ( $\text{N}_2$ ). This suggests that free radicals are not formed in the reaction.

## RESULTS AND DISCUSSION

**Effect of oxidant:** The rate coefficients are independent of the initial concentration of PBC indicating that the reaction is first order with PBC (Table 1).

**Effect of pyridine:** Rate of reaction does not vary by addition of pyridine indicating that PBC solution does not hydrolyze. It also shows stability of the oxidant in reaction conditions.

**Effect of substrate:** The rate of oxidation increased on increasing the concentration of aldehyde (Table 1). Plot of  $1/k_{\text{obs}}$  vs.  $1/[\text{Aldehyde}]$  is linear ( $R^2 = 0.9887$ ) and makes a positive intercept on y-axis. This shows that Michaelis-Menten type kinetics is followed with respect to aldehyde. In the oxidation by PFC<sup>9,10</sup> in DMSO, Michaelis-Menten type kinetics were observed with respect to the aldehydes while in oxidation of substituted aromatic aldehydes by quinolinium bromochromate<sup>11</sup> in acetic acid-water, no Michaelis-Menten type kinetics were observed.

**Table 1: Variation of rate with oxidant concentration, substrate concentration, perchloric acid, solvent composition and temperature**

$10^3[\text{PBC}]$ $\text{mol dm}^{-3}$	$10^2[\text{substrate}]$ $\text{mol dm}^{-3}$	$[\text{H}^+]$ mol $\text{dm}^{-3}$	AcOH v/v %	$k_{\text{obs}} \times 10^5 \text{ s}^{-1}$	Temp K
0.5	2.0	1.0	40	7.65	308
1.0	2.0	1.0	40	6.95	
1.43	2.0	1.0	40	7.30	
2.0	2.0	1.0	40	7.74	
5.0	2.0	1.0	40	7.36	
2.0	1.0	1.0	40	5.00	308
2.0	2.0	1.0	40	7.72	
2.0	3.0	1.0	40	10.47	
2.0	4.0	1.0	40	12.74	
2.0	5.0	1.0	40	15.41	
2.0	6.0	1.0	40	17.66	
2.0	7.0	1.0	40	20.08	
2.0	2.0	0.6	40	4.15	308
2.0	2.0	0.7	40	4.75	
2.0	2.0	0.8	40	5.80	
2.0	2.0	0.9	40	6.85	
2.0	2.0	1.0	40	7.74	
2.0	2.0	1.0	30	9.81	308
2.0	2.0	1.0	35	8.58	
2.0	2.0	1.0	40	7.74	
2.0	2.0	1.0	45	6.37	
2.0	2.0	1.0	50	5.60	
2.0	2.0	1.0	40	3.29	9.77 <sup>#</sup> 293
2.0	2.0	1.0	40	5.94	13.77 <sup>#</sup> 303
2.0	2.0	1.0	40	7.74	16.33 <sup>#</sup> 308
2.0	2.0	1.0	40	9.59	19.91 <sup>#</sup> 313
2.0	2.0	1.0	40	12.53	24.78 <sup>#</sup> 318
				16.41	28.21 323

$\Delta E^* = 41.13 \pm 1.6 \text{ kJ mol}^{-1}$ ;  $\Delta S^* = -137.90 \pm 4.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $\Delta F^* = 41.78 \pm 1.7 \text{ kJ mol}^{-1}$

<sup>#</sup> Values indicate rate constants for benzaldehyde.



**Effect of ionic strength:** Rate does not depend on concentration of sodium sulphate and sodium perchlorate in the medium that the indicating interaction in rate-determining step is not of ion-ion type<sup>12</sup>.

**Effect of solvent composition:** The rate of oxidation of aldehyde is affected considerably by changing solvent composition of acetic acid (Table 1). The rate of oxidation decreases with increase in volume percentage of acetic acid. The rate of oxidation depends on the polarity of medium. When the polarity of the solvent was increased, the rate decreased. In other words, a decrease in rate with increase in dielectric constant was observed. This is due to polar character of the transition state as compared to the reactants. The rate increases with the increase in mole fraction of water, which indicates the participation of water prior to rate determining step. This suggests involvement of hydrated aldehyde similar to aliphatic aldehydes<sup>13</sup>. The plot of  $\log k_1$  vs.  $1/D$  is linear indicating ion-dipole type interaction<sup>14</sup>. Similar phenomenon has been observed in the oxidation of substituted benzaldehyde by acid bromate<sup>15</sup>.

**Effect of perchloric acid:** Rate of reaction increased with the increase in perchloric acid concentration (Table 1). As there is no effect of ionic strength on rate of reaction; so ionic strength was not kept constant in these experiments. The plot of  $\log k_1$  vs.  $\log [H^+]$  is a straight line ( $R^2 = 0.9787$ ) with slope nearly one. Therefore order with respect to  $[H^+]$  ion is one. This suggests that  $[H^+]$  catalyses the oxidation reaction. In presence of acid, PBC may be protonated. A protonated Cr (VI) species is likely to be a better electrophile and oxidant compared to the neutral one. Ramakrishnan and Chockalingam<sup>16</sup> also suggested the reaction of hydrated benzaldehyde and protonated pyridinium fluorochromate in the oxidation of substituted benzaldehydes. In oxidation of benzaldehyde by Cr (VI)<sup>17</sup> and by bromine<sup>18</sup>, an involvement of hydrated benzaldehyde has also been suggested.

**Effect of temperature:** The rate of reaction increases on increasing the temperature. From the Arrhenius plot, activation parameters were evaluated and are summarized in Table 1. The entropy of activation is negative as expected for a bimolecular reaction. Glasstone<sup>12</sup> has pointed out that if entropy of activation is large and positive, the reaction will be normal and fast, but if it is negative, the reaction is slow. In our case, the value of entropy of activation falls under a category of slow reaction. Negative high values of entropy also suggests bimolecular reaction in the rate determining step in the presence of water as a solvent and the involvement of a proton transfer agent during the rate determining step. The high negative entropy of activation is probably due to the following factors:

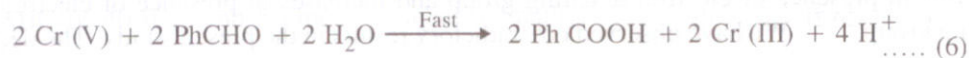
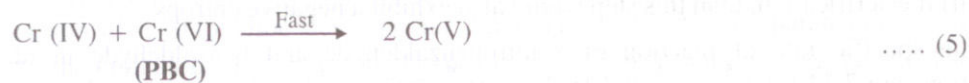
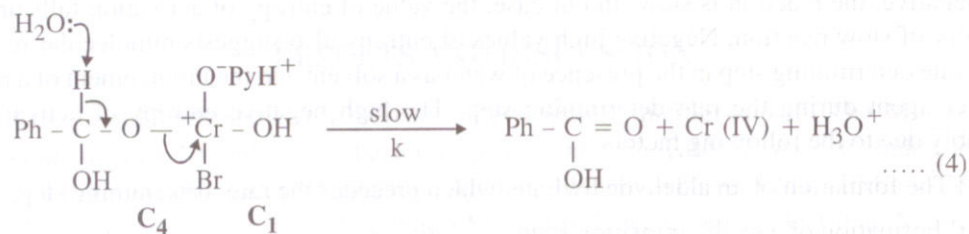
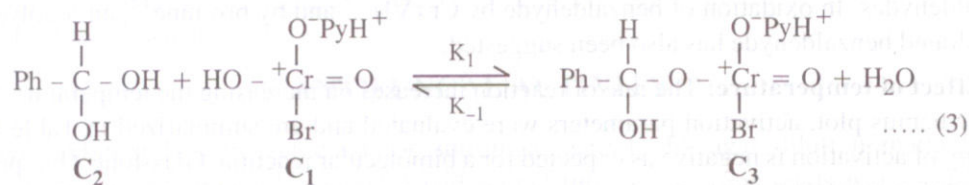
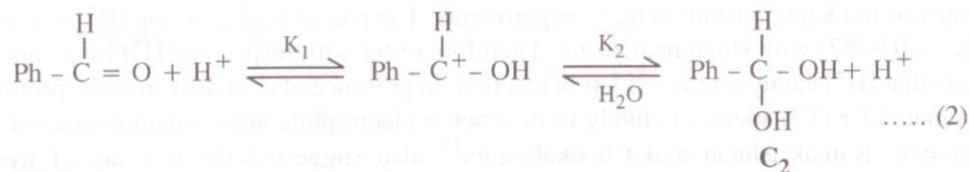
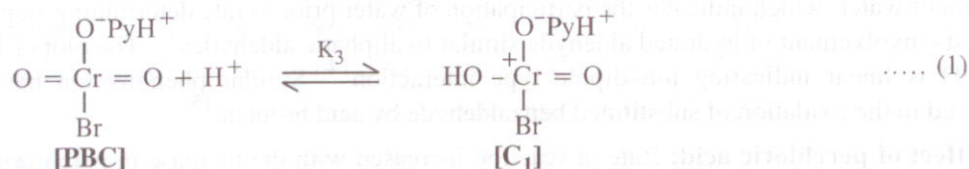
- (i) The formation of an aldehyde hydrate, which precedes the rate-determining step.
- (ii) Formation of a cyclic transition state
- (iii) if esterification, than this step would also exhibit a negative entropy<sup>19</sup>.

The specific rate of reaction of 2-nitrobenzaldehyde and benzaldehyde in identical conditions are  $7.74 \times 10^{-5} \text{ sec}^{-1}$  and  $16.33 \times 10^{-5}$ , respectively. The rate of oxidation usually decreases in presence of electron donating group and increases in presence of electron withdrawing group<sup>20,21</sup>. We have observed contradictory results in the present study. The decrease

in rate in case of 2-nitrobenzaldehyde suggests that electron-withdrawing group does not facilitate the rate of oxidation. Further the slow rate may be a case of steric effect by *ortho*-substituent. As reported earlier by Banerji et. al<sup>1</sup>, that the oxidation of *ortho* compounds showed a correlation with Tafts  $\sigma_1$ ,  $\sigma_{R+}$  and Charton's steric parameters.

The above result suggests that the oxidation proceed through intermediate complex of the hydrated aldehyde and protonated PBC. The entropy of activation and energy of activation indicate that the C-H bond is cleaved in the rate-determining step. The probable mechanism of oxidation is as shown here.

Considering all these experimental data, the following reaction scheme may be suggested:





The above mechanism leads to the rate equation—

$$\text{Rate} = -\frac{d[\text{PBC}]}{dt} \propto [\text{C}_4]$$

$$= k [\text{C}_4]$$

$$\text{Rate} = \frac{k K_1 K_2 [\text{PhCHO}] [\text{H}^+] [\text{PBC}]}{K_m + K_2 [\text{PhCHO}]}$$

$$= k_{\text{obs}} [\text{PBC}]$$

$$\text{Where } K_m = \frac{k_{-1} + k_1}{k_1}$$

$$\text{and } k_{\text{obs}} = \frac{k K_1 K_2 [\text{PhCHO}] [\text{H}^+]}{K_m + K_2 [\text{PhCHO}]}$$

This rate law is consistent with all the observed experimental results.

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