

## Kinetics and Mechanism of Oxidation of Phenols by Pyridinium Dichromate

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The kinetics of oxidation of phenols by pyridinium dichromate (PDC) has been studied in 60% acetic acid-water (v/v) medium. The reaction shows unit order dependence each with respect to oxidant and substrate. The reaction is acid catalysed and the medium of low dielectric constant favours the reaction. Increase in ionic strength has no effect on the reaction rate. In the case of substituted phenols, the order with respect to substrate varies depending upon the nature of the substituent present in the ring. In general, the electron withdrawing substituents retard the reaction rate while the electron releasing substituents enhance the rate of the reaction. From the kinetic data obtained the activation parameters have been computed and a suitable mechanism has been proposed in accordance with multiparameter correlation analysis.

### INTRODUCTION

Pyridinium dichromate (PDC), one of the Cr(VI) compounds, is reported to be a neutral and mild oxidant for selective oxidation. Kinetics of oxidation of some organic substrates<sup>1-5</sup> by pyridinium dichromate have already been reported. The kinetics of chlorination of phenols by N-chloro-3-methyl-2,6-diphenylpiperidin-4-one<sup>6</sup> in aqueous ethanol medium has been studied extensively in our laboratory. Now we report the kinetics and mechanism of oxidation of phenol by pyridinium dichromate in acid medium.

### EXPERIMENTAL

Pyridinium dichromate was prepared as reported by Corey and Schmidt<sup>7</sup>. Commercial samples of phenols were collected and purified before use. All other chemicals used were of AR grade.

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

The stoichiometric runs were carried out in the presence of excess PDC which reveals that one mol of the oxidant consumes one mol of the substrate confirming the stoichiometry of the reaction as 1 : 1.

The reaction mixture from actual kinetic runs with excess of oxidant after slight warming was kept for two days and extracted with chloroform and dried over anhydrous sodium sulfate. The chloroform layer was then evaporated and the solid on analysis through IR spectra (KBr pellets) was found to be *p*-benzoquinone.

## RESULTS AND DISCUSSION

The reaction was found to be first order with respect to the oxidant as evidenced by a good linearity in the plot of  $\log [\text{PDC}]$  vs. time ( $r = 0.999$ ). The pseudo-first order rate constants were found to be independent of the initial concentration of PDC. At constant [PDC], the rate constants increased with increase in the concentration of substrate. A plot of  $\log k$  vs.  $\log [\text{substrate}]$  gave a straight line with a slope of unity ( $r = 0.978$ ). (Table-1)

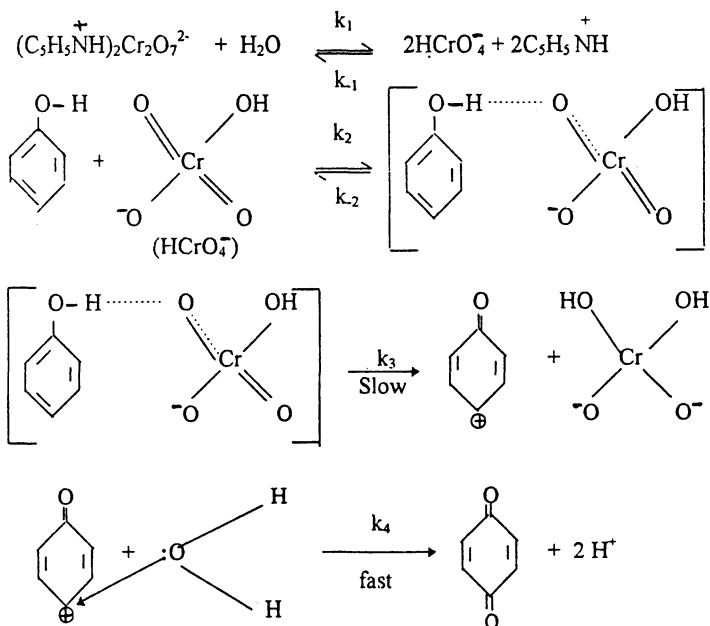
TABLE-1  
RATE CONSTANT FOR THE OXIDATION OF PHENOL BY PYRIDINIUM  
DICHROMATE AT 308 K

[Phenol] $10^2$ M	[PDC] $10^3$ M	[NaClO <sub>4</sub> ] $10^1$ M	[H <sup>+</sup> ] $10^1$ M	AcOH-H <sub>2</sub> O (% v/v)	[ACN] $10^2$ M	[Mn <sup>2+</sup> ] $10^2$ M	[Al <sup>3+</sup> ] $10^2$ M	$k_{\text{obs}} 10^4$ $s^{-1}$
3.0	1.0-2.25	—	2.19	60	—	—	—	4.62-5.07
3.0-6.75	1.0	—	2.19	60	—	—	—	4.62-11.22
3.0	1.0	0.0-2.79	2.19	60	—	—	—	4.62-4.96
3.0	1.0	—	2.19-4.93	60	—	—	—	4.62-15.43
3.0	1.0	—	2.19	30-70	—	—	—	1.71-8.13
3.0	1.0	—	2.19	60	0.0-2.5	—	—	4.62-4.59
3.0	1.0	—	2.19	60	—	0.0-2.0	—	4.62-8.12
3.0	1.0	—	2.19	60	—	—	0.0-5.0	4.62-9.25

Increase in the ionic strength of medium by adding sodium perchlorate has no effect on the reaction rate indicating the involvement of an ion and neutral molecule in the rate determining step. 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. Plot of  $\log k$  vs.  $\log [\text{H}^+]$  gave a straight line with the slope of 1.52 ( $r = 0.996$ ) indicating that the protonated species of the oxidant is the effective oxidant. Since the plot of  $\log k$  vs.  $\log [\text{H}^+]$  did not give an ideal slope of unity it is not possible to take the order with respect to  $[\text{H}^+]$  as unity, and it can be concluded that the reaction is simply an acid catalysed one. The rates were found to increase with the increase in the percentage of acetic acid, *i.e.*, with decrease in dielectric constant of the medium (Table-1). The enhanced oxidizing ability is attributed to the formation of acetochromate ion. The acetyl group enhances the electron accepting power of chromium thereby facilitating the reaction.

The added acrylonitrile had no effect on the reaction rate, *i.e.*, the reaction did not induce polymerization of acrylonitrile indicating the absence of free radical pathway. The added Mn<sup>2+</sup> ions had a noticeable catalytic effect on the reaction rate. Though the addition of Al<sup>3+</sup> ions showed a noticeable retarding influence on the rate, it was not possible to confirm three electron transfer process in this reaction, due to the absence of acrylonitrile effect (Table-1). Based on the above facts the following mechanism (Scheme-1) was proposed.

### Mechanism



Scheme 1

### Rate law

$$\text{Rate of the reaction} = k_3 \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} [\text{PDC}] [\text{Phenol}]$$

The rate of oxidation of some substituted phenols have been studied at five different temperatures, *viz.*, 303, 308, 313, 318 and 323 K. The activation parameters are calculated using Eyring's plot<sup>8</sup> and the values are given in Table-2. The fairly high values of enthalpy of activation ( $\Delta H^\ddagger$ ), free energy of activation ( $\Delta G^\ddagger$ ) and energy of activation ( $E_a$ ) indicate that the transition state is highly solvated. The negative values of the entropy of activation ( $\Delta S^\ddagger$ ) suggest 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. As ( $\Delta H^\ddagger$ ) and ( $\Delta S^\ddagger$ ) do not vary linearly no isokinetic relationship is observed. This indicates the absence of enthalpy-entropy compensation effect<sup>9</sup>. The plots of  $\log k_{308\text{ K}}$  *vs.*  $\log k_{303\text{ K}}$  and  $\log k_{313\text{ K}}$  *vs.*  $\log k_{303\text{ K}}$  gave straight lines with  $r = 0.999$ . Such a good correlation indicates that all the substituents follow a common mechanism.

To have an idea about the order with respect to each of the substituents, the order with respect to each of the substrates has been studied at 308 K and the results are given in Table-2. It is interesting to note that the order with respect to substrate changes depending upon the nature of the substituent present in the benzene ring. For electron releasing substituents, *viz.*, *p*-CH<sub>3</sub>, *p*-OCH<sub>3</sub>, *p*-C(CH<sub>3</sub>)<sub>3</sub>, *m*-CH<sub>3</sub> and *m*-Cl show a unit order dependence on the reaction rate and

for less electron withdrawing groups, viz., *p*-Cl and *p*-Br, the order with respect to substrate was found to be fractional. For high electron withdrawing substituents, viz., *p*-NO<sub>2</sub>, *m*-NO<sub>2</sub> and *p*-COOH the order with respect to substrate was found to be zero.

TABLE-2  
ACTIVATION PARAMETERS FOR THE OXIDATION OF PHENOLS BY PDC

Substituents	Order with respect to substrate	$k_{\text{obs}} 10^4 \text{ s}^{-1}$					$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ JK <sup>-1</sup> mol <sup>-1</sup>
		303 K	308 K	313 K	318 K	323 K		
H	1	3.25	4.62	7.48	10.53	15.49	61.71	79.31
<i>p</i> -CH <sub>3</sub>	1	11.26	16.68	23.62	31.69	42.66	51.27	103.01
<i>p</i> -OCH <sub>3</sub>	1	8.90	2.84	19.86	26.85	39.09	57.61	84.29
<i>p</i> -C(CH <sub>3</sub> ) <sub>3</sub>	1	68.46	91.08	127.90	175.10	237.40	48.51	97.49
<i>m</i> -CH <sub>3</sub>	1	10.79	15.84	21.71	30.60	42.20	52.53	99.35
<i>p</i> -Cl	0.76	2.71	3.93	5.43	7.85	10.81	53.72	107.04
<i>p</i> -Br	0.86	2.12	2.99	4.19	5.78	7.92	51.04	117.90
<i>p</i> -NO <sub>2</sub>	0	0.10	0.14	0.20	0.29	0.38	51.52	141.43
<i>p</i> -COOH	0	0.10	0.15	0.22	0.34	0.48	61.40	109.05
<i>m</i> -Cl	1	0.19	0.27	0.40	0.57	0.81	56.75	119.21
<i>m</i> -NO <sub>2</sub>	0	0.04	0.06	0.08	0.11	0.15	47.02	163.13

$\Delta G^\ddagger = 86 \pm 6 \text{ kJ mol}^{-1}$  at 308 K;  $E_a = 64 \pm 6 \text{ kJ mol}^{-1}$  at 308 K.

The variation in the order of dependence with respect to different substituted phenols is explained by invoking different rate controlling steps in the mechanism. In the mechanism if  $k_2 \gg k_1, k_{-1}, k_{-2}$ , the order with respect to substrate will be zero. If on the other hand  $k_2 \ll k_1, k_{-1}, k_{-2}, k_3$ , a unit order dependence with respect to substrate will be obtained. If  $k_1$  and  $k_2$  are comparable values, i.e.,  $k_1 \approx k_2$  a fractional order dependence on the substrate will be obtained.

TABLE-3  
RESULTS OF MULTIPLE REGRESSION ANALYSIS OF THE RATE DATA OF  
PARA-SUBSTITUTED PHENOLS BY PDC AT 308 K

Substituent constants	C	$\rho_I$	$\rho_R$	F	SE	R	f	$\Psi$
$\sigma_I \sigma_R^0$	-3.4138	-1.7792	-2.8797	17.75	0.3304	0.9480	0.0236	0.3764
$\sigma_I \sigma_R^{(BA)}$	-3.3866	-1.8209	-2.2159	10.19	0.4206	0.9143	0.0300	0.4792
$\sigma_I \sigma_R^-$	-3.3362	-1.2619	-2.0477	24.35	0.2861	0.9613	0.0204	0.3259
$\sigma_I \sigma_R^+$	-3.4379	-1.8355	-1.3860	8.21	0.4596	0.8967	0.0328	0.5236
$F_1 F_R$	-3.7530	-0.1642	-0.7606	2.31	0.7077	0.7318	0.0505	0.8064

The rate data for the oxidation of the substituted phenols gave a fair correlation ( $r = 0.939$ ) with Hammett  $\sigma$  value at 308 K. Hence the rate data was subjected to multiple regression analysis using DSP equation. Along with Taft's equation<sup>10</sup>, Swain's<sup>11</sup> dual substituent parameters equation was also considered in the multiple regression analysis. The results of the correlation analysis at five different combinations indicate that the data correlates well with  $\sigma_I \sigma_R^-$  values when compared with  $\sigma_I \sigma_R^0$ ,  $\sigma_I \sigma_R^{(BA)}$ ,  $\sigma_I \sigma_R^+$  and  $F_1 F_R$  (Swain's treatment). From the rate data for the oxidation of phenols by PDC at 308 K it is clear that the better

correlation exists with  $\sigma_I\sigma_R^-$  values. The results of the multiple linear regression analysis with the statistical parameters, the standard error (SE), the coefficient of multiple correlation (R) and the parameters  $f$  and  $\Psi$  as the measure of goodness of fit<sup>12, 13</sup> are given in Table-3.

The reaction constants and the statistical data at the five different temperatures for  $\sigma_I\sigma_R^-$  parameters are given in Table-4. The magnitude of  $\rho_R$  is higher than that of  $\rho_I$  in the case of *para*-substituted phenols. Also the value of  $\lambda$  ( $\lambda = \rho_R/\rho_I$ ) indicates that the reaction is more susceptible to resonance effects than field effects. Further percentage resonance character<sup>14</sup> contributing to the total polar effect has been found to be around 61% in the case of *para*-substituted phenols. The magnitude of reaction constants remains unchanged with the increase of temperature. Here it is interesting to find that even though the reaction constant remains the same, there is a gradual increase in the field effect and decrease in the resonance effect leading to a gradual decrease in the value of  $\lambda$  when the temperature is increased. Hence it is obvious from the data that as the temperature is raised the reaction is more susceptible to field effect than resonance effects.

TABLE-4  
TEMPERATURE DEPENDENCE OF THE REACTION CONSTANTS FOR  
 $\sigma_I\sigma_R^-$  PARAMETERS

T (K)	$\rho_I$	$\rho_R$	$\lambda$	$P_S$	$f$	$\Psi$	SE	R
303	-1.2442	-2.0567	1.65	62.31	0.0193	0.3332	0.2930	0.9995
308	-1.2619	-2.0477	1.62	61.87	0.0204	0.3259	0.2861	0.9613
313	-1.3210	-2.0466	1.55	60.77	0.0217	0.3148	0.2787	0.9639
318	-1.3086	-2.0028	1.53	60.48	0.0224	0.3049	0.2644	0.9662
323	-1.3382	-2.0165	1.51	60.11	0.0233	0.2896	0.2530	0.9696

Note: The rate of *p*-C(CH<sub>3</sub>)<sub>3</sub>, *m*-Cl, *m*-CH<sub>3</sub> and *m*-NO<sub>2</sub> substituted phenols are not incorporated in the multiple regression analysis;  $f = \text{S.E./root mean square}$ ;  $\Psi = [n(1 - r^2)/(n - 2)]^{1/2}$ .

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