Linear Free Energy Relationships in the Chromium(VI) Oxidation of Phenols

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Abstract. The kinetics of oxidation of phenol by nicotinium dichromate has been studied in 50 % acetic acid-water (*v/v*) medium. The reaction shows unit order dependence on 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 negligible effect on the reaction rate. In general, the electron withdrawing substituents enhance the rate of reaction. From the kinetic data obtained, the activation parameters have been calculated and a plausible mechanism has been proposed in accordance with multiparameter correlation analysis.

Keywords: linear free energy relationships, oxidation, phenols, activation parameters

INTRODUCTION

Nicotinium dichromate (NDC) is reported to be a mild oxidant for selective oxidations.[1] The oxidation of phenols by various oxidants has been reported.[2–6] Kinetics of oxidation of some organic substrates[7–9] by nicotinium dichromate has already been reported. In this paper, the oxidation of substituted phenols by nicotinium dichromate in aqueous acetic acid medium is reported.

EXPERIMENTAL

Nicotinium dichromate, $(C_6H_6O_2N^+)_2Cr_2O_7^{2-}$ was prepared by the reported procedure.[1] Commercial sample of phenols were collected and purified before use. All other chemicals were of AnalaR grade.

The reactions were carried out under pseudo-first order conditions by maintaining always the substrate concentration in excess over that of NDC. Known volumes of substrates, 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 decrease in [NDC] by digital photoelectric colorimeter (Equiptronics EQ 450) at 470 nm. The rate constants were obtained from the slope of the plot of log absorbance versus time by the least square method.

The stoichiometric runs were carried out in the presence of excess NDC which reveals that one mole of the oxidant consume one mole of the substrate confirming the stoichiometry of the reaction as 1:1. The reaction mixture from actual kinetic run with excess of oxidant after slight warming was kept for two days and extracted with chloroform and dried over anhydrous sodium sulphate. The chloroform layer was then evaporated and the solid on analysis through IR spectra 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 absorbance versus time (*r* = 0.992). The pseudo-first order rate constants were found to be independent of initial concentration of NDC. At constant [NDC], the rate constants increased with increase in the concentration of the substrate. A plot of log *k* versus log[substrate] gave a straight line with a slope of unity (*r* = 0.987). The constancy of $k_2 = k_1/[s]$ confirms the first order in the substrate.

Increase in the ionic strength of medium by adding sodium perchlorate has no effect on the reaction rate indicating the involvement of molecule in the rate determining step. The effect of acidity was studied by varying the concentration of perchloric acid and rate constants were found to increase with increase in the concentration of perchloric acid. Plot of log *k* versus

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Table 1. Rate constants for the oxidation of phenol by nicotinium dichromate at 313 K

$\dfrac{[s] \times 10^2}{\text{mol dm}^{-3}}$	$\dfrac{[O] \times 10^4}{\text{mol dm}^{-3}}$	$\dfrac{[H^+] \times 10}{\text{mol dm}^{-3}}$	$\dfrac{\text{AcOH}}{\%}$ (v/v)	$\dfrac{[NaClO_4] \times 10^4}{\text{mol dm}^{-3}}$	$\dfrac{[Mn^{II}] \times 10^2}{\text{mol dm}^{-3}}$	$\dfrac{k_1 \times 10^4}{\text{s}^{-1}}$
7.06−21.19	7.20	5.25	50	-	-	3.98−12.19
10.60	4.80−14.40	5.25	50	-	-	6.08−5.76
10.60	7.20	3.94−9.19	50	-	-	4.11−13.23
10.60	7.20	5.25	50−65	-	-	6.02−11.35
10.60	7.20	5.25	50	0.00−20.22	-	6.02−6.35
10.60	7.20	5.25	50	-	0.00−0.45	6.02−7.95

$\log[H^+]$ gave a straight line with slope of 1.43 ($r = 0.993$) indicating that the protonated species of the oxidant in the effective oxidant. Since, the plot of $\log k$ versus $\log[H^+]$ did not give and ideal slope of unity it is not possible to take the order with respect to $[H^+]$ as unity and it can be concluded that the reaction is simply an acid catalysed one. The rates were found to increase with increase in the percentage of acetic acid. A plot of $\log k$ versus inverse of dielectric constant is linear with a positive slope suggesting an interaction between a positive ion and a dipole. This is also confirms the involvement of protonated Cr^{VI} species in the rate determining step. The reaction mixture when allowed to stand acrylonitrile does not induce polymerization suggesting the absence of free radical pathway. The added Mn^{2+} ions had a noticeable catalytic effect on the reaction rate (Table 1).

Based on the above observations, the following mechanism (scheme 1) was proposed.

Rate law

$$\text{Rate of reaction} = K_1 K_2 k_3 [\text{NDC}][\text{Phenol}]$$
$$= \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} k_3 [\text{NDC}][\text{Phenol}]$$
$$= -\frac{d[\text{NDC}]}{dt} = k_3 K_2 K_1 [\text{NDC}][\text{Phenol}]$$

Effect of substituents

The rate constant k_1 was estimated for the substituted phenols at five different temperatures *viz.,* 303, 308, 313, 318 and 323 K in order to calculate the thermodynamic parameters. The thermodynamic parameters were calculated using Eyring's plot[10] and the values are given in table 2. The enthalpies of activation ($\Delta H^{\#}$) values are very low indicating a concerted mechanism as proposed. The negative values of the entropies of activation ($\Delta S^{\#}$) suggested that the transition state formed was consider-

Mechanism

$$(C_6H_5O_2N^+H)_2Cr_2O_7^{2-} + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} 2HCrO_4^- + 2C_6H_5O_2N^+H$$
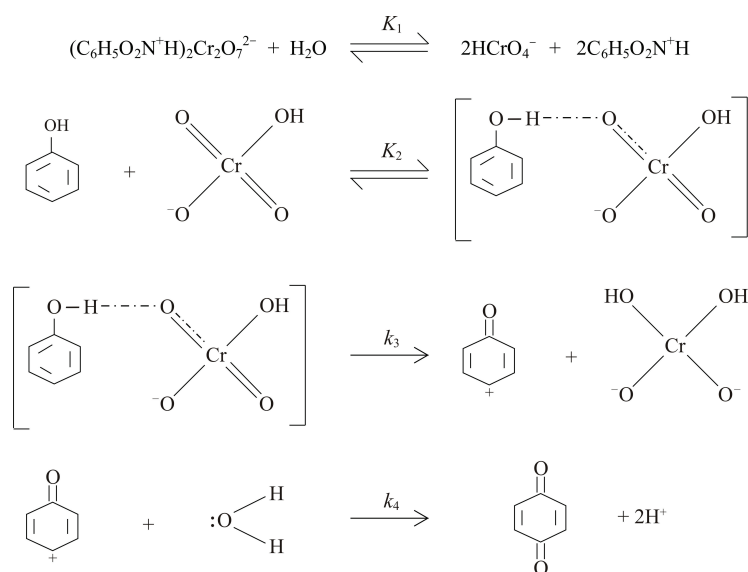
Scheme 1.

Table 2. Thermodynamic parameters for the oxidation of *para*- and *meta*- phenols by NDC calculated from Eyring's plot

S. No.	Substituent	Order w.r.t. substrate	$\dfrac{k_1 \times 10^4}{\text{s}^{-1}}$					$\dfrac{\Delta H^{\#}}{\text{kJmol}^{-1}}$	$\dfrac{-\Delta S^{\#}}{\text{JK}^{-1}\text{mol}^{-1}}$	$\dfrac{\Delta G(313\text{K})}{\text{kJmol}^{-1}}$	$\dfrac{E_a(313\text{K})}{\text{kJmol}^{-1}}$	r
			303K	308K	313K	318K	323K					
1	-H	1.01	3.74	4.75	6.02	7.57	9.69	16.77	162.62	67.67	19.37	0.999
2	*p*-CH$_3$	0.98	16.45	22.64	31.18	43.14	60.10	22.81	137.35	65.80	25.41	0.998
3	*p*-OCH$_3$	0.91	19.11	27.02	39.82	57.01	79.92	25.47	128.00	65.55	28.07	0.998
4	*p*-Cl	0.93	1.02	1.17	1.35	1.56	1.81	10.39	188.36	69.35	12.99	0.997
5	*p*-Br	0.88	2.48	3.21	4.18	5.49	7.18	18.76	157.55	68.07	21.36	0.997
6	*p*-NO$_2$	0.82	0.06	0.10	0.14	0.20	0.27	26.16	146.33	71.96	28.76	0.996
7	*p*-COOH	0.86	0.06	0.13	0.19	0.30	0.43	27.92	139.43	71.56	30.52	0.998
8	*m*-CH$_3$	1.09	8.65	10.66	13.11	16.28	20.31	15.02	165.37	66.78	17.62	0.997
9	*m*-Cl	0.95	0.04	0.05	0.06	0.07	0.08	12.05	194.45	72.91	14.65	0.998
10	*m*-NO$_2$	0.87	0.33	0.40	0.47	0.56	0.68	12.54	185.31	70.54	15.14	0.996
11	*m*-Br	0.90	0.62	0.72	0.85	1.02	1.20	11.77	185.64	69.87	14.37	0.997

Table 3. Temperature dependence of the reaction constants for $F_I F_R$ parameters for NDC oxidation of *para*- substituted phenols

Temperature / K	ρ_I	ρ_R	λ	P_R	S. E.	R	f	Ψ
303	-1.1045	-0.7405	0.6704	40.14	0.2525	0.9883	0.0098	0.1806
308	-1.0954	-0.7350	0.6710	40.16	0.2582	0.9876	0.0108	0.1860
313	-1.0751	-0.7459	0.6938	40.96	0.2728	0.9862	0.0125	0.1955
318	-1.0717	-0.7545	0.7040	41.32	0.3033	0.9833	0.0166	0.2153
323	-1.0851	-0.7620	0.7022	41.25	0.3279	0.9810	0.0200	0.2294

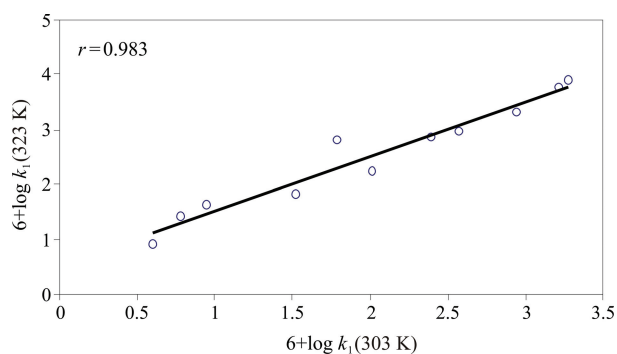**Figure 1.** Plot of log k_1(323 K) *versus* log k_1(303 K) for the oxidation of phenols by NDC at 313K. Numbers correspond to compounds in Table 2.

ably rigid, resulting in a reduction in the degrees of freedom of the molecules. The constancy of the $\Delta G^{\#}$ values indicated a common mechanism for the oxidation of all the substrates. As $\Delta H^{\#}$ and $\Delta S^{\#}$ do not vary linearly no isokinetic relationship is observed. This indicated that the absence of enthalpy-entropy compensation effect.[11] Exner[12] criticised the validity of such linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ as these quantities are dependent on each other. When the measurements at two different temperatures have been made. The data can be analysed the following equation.[13]

$$\log k_1\left(T_2\right) = a + b\log k_1\left(T_1\right) \qquad \text{where } T_2 > T_1$$

The plot of log k (323K) versus log k (303K) (Figure 1) gave a straight line with $r = 0.988$ 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 substrate has been studied at 313 K and results are given in Table 2. It is interesting to note that all the substituted phenols show a unit order dependence on the reaction rate. The electron releasing groups enhance and electron withdrawing groups retard the reaction rate.
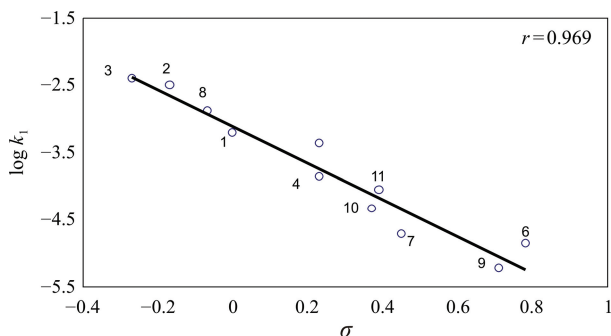

Figure 2. Plot of log k_1 *versus* σ for the oxidation of phenols by NDC at 313K. Numbers correspond to compounds in Table 2.

The rate data for the oxidation of the substituted phenols gave a fair correlation (r = 0.969) with Hammett σ value at 313 K (Figure 2). Hence the rate data was subjected to multiple regression analysis using dual substituent parameter equation. Along with Taft's equation[14], Swain's dual substituent parameter equation was also considered in the multiple regression analysis. The results of the correlation analysis at five different temperatures indicate that the data correlate well with F_IF_R (Swain) values when compared with $\sigma_I\sigma_R^{\,o}$, $\sigma_I\sigma_R^{\,(BA)}$, $\sigma_I\sigma_R^{\,-}$ and $\sigma_I\sigma_R^{\,+}$. The table 3 also contains standard error of estimate (S. E.) the coefficient of multiple correlation (R) and the statistical parameters f and λ as the measure of goodness of fit.[15]

The temperature dependence

The reaction constants and the statistical data at five different temperatures for F_IF_R parameters are given in Table 3. The values of λ calculated by the expression, ρ_R/ρ_I are also given in Table 3. The values of *para*-compounds indicate the greater importance of the field effect than the resonance effect further percentage resonance character contributing to the polar effect has been found to be around 40 % 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 decrease in the value of λ, 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 effect.

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SAŽETAK

Odnosi linearne slobodne energije u krom(VI) oksidaciji fenola

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Kinetika oksidacije fenola nikotinijevim dikromatom je istražena u mediju 50 %-tne octene kiseline-vode (*v*/*v*). Reakcija pokazuje brzinu reakcije prvog reda u ovisnosti prema oksidansu i prema supstratu. Reakcija je kiselo katalizirana i medij niske dielektrične konstante favorizira reakciju. Porast ionske jakosti ima neznatan učinak na brzinu reakcije. Generalno, supstituenti koji izvlače elektrone ubrzavaju reakciju. Iz dobivenih kinetičkih podataka, izračunati su aktivacijski parametri i predložen je mogući mehanizam u skladu s multiparametarskom korelacijskom analizom.