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Kinetics and Mechanism of Oxidation of Some *meta*- and *para*- Substituted Phenoxyacetic Acids by N-Chloropiperazine-2,5-dione in Non-aqueous Medium

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The kinetics of oxidation of a number of *meta*- and *para*- substituted phenoxyacetic acids by N-chloropiperazine-2,5-dione (NCPD) have been studied in methanol medium. The reaction shows unit order dependence with respect to oxidant and the order with respect to substrate varies depending on the nature of the substituent present in the ring. The rate is showing an inverse order of dependence with respect to [TsOH]. The rate increases with decrease in the percentage of methanol. Increse in ionic strength has no effect on the reaction rate . From the kinetic data obtained the activation parameters have been computed and a suitable mechanism has been proposed in accordance with multiparameter correlation analysis.

Key words: Kinetics, Mechanism, Oxidation, Phenoxyacetic acids, n-Chloropiperazine-2,5-dione, Non-aqueous medium

INTRODUCTION

Kinetics of oxidation and halogenation of aromatic substrate using a variety of N-halo compounds have been reported earlier[1–3]. Kinetics of oxidation of phenoxyacetic acid using a variety of oxidants developed in our laboratories[4–6] gave interesting results, due to the difference in the product formation in each case of study. Now we report the kinetics and mechanism of oxidation of some *meta*- and *para*- substituted phenoxyacetic acids by N-chloropiperazine-2,5-dione (NCPD) in methanol medium.

EXPERIMENTAL

Piperazine-2,5-dione (PPD) was prepared as described by Vogel[7] and it was chlorinated to get N-chloropiperazine-2,5-dione by the usual procedure. Phenoxyacetic acid was prepared by the known method[8]. The phenoxyacetic acids were purified by repeated recrystallization in water to constant melting point. All chemicals used were of AR grade.

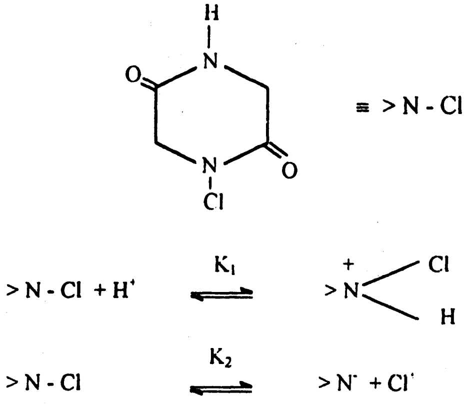
The reactions were followed under pseudo-first order conditions by maintaining the substrate concentration always in excess over that of NCPD. Known concentration of substrate, *p*-toluenesulphonic acid and methanol were mixed and thermostated. The reaction was started by adding the oxidant to the mixture and aliquots were removed at definite time intervals and the unreacted NCPD was estimated by standard iodometric titrations. The stoichiometric runs were carried out in the presence of excess of NCPD which reveals that one mole of the oxidant consumes one mole 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 sulphate. The chloroform layer was then evaporated and the solid on analysis through IR spectra (KBr pellets) was found to be *p*-benzoquinone.

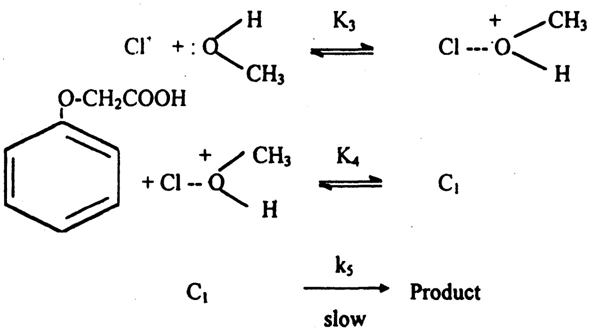
RESULTS AND DISCUSSION

The reaction was found to be first order with respect to the oxidant as evidenced by a good linearity in the plot of log [NCPD] *vs.* time (r = 0.995). The pseudo-first order rate constants were found to be independent of the initial concentration of NCPD. At constant [NCPD], the rate constants increased with increase in the cencentration of substrate. A plot of log k_1 *vs.* log [substrate] gave a straight line with a slope of 0.65 (Table-1) with Michaelis-Menton behaviour.

Increase in the ionic strength of medium by adding magnesium 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 *p*-toluenesulphonic acid and the rate constants were found to decrease with increase in the concentration of *p*-toluenesulphonic acid. The plot of log k_1 *vs.* log [TsOH] gave a straight line with a negative slope of –0.5234 (r = –0.996) indicating that the protonated species of the oxidant is not the effective oxidant. The rates were found to increase with decrease in the percentage of methanol, *i.e.*, with decrease in dielectric constant of the medium (Table-1). 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. Based on the above facts the following mechanism (Scheme-1) was proposed.



Scheme-1 (Contd.)



Scheme 1

TABLE-1
RATE CONSTANT FOR THE OXIDATION OF PHENOXYACETIC ACID
BY NCPD AT 313 K

[PAA] (10^2 M)	[NCPD] (10^4 M)	[Mg(ClO_4)$_2$] (10^4 M)	[TsOH] (10^2 M)	Methanol-acetonitrile (% v/v)	K_1 (10^4 s^{-1})
2.00	7.50	—	12.50	100	3.0735
2.50	7.50	—	12.50	100	3.1411
3.00	7.50	—	12.50	100	3.7868
3.50	7.50	—	12.50	100	4.4555
2.50	5.00	—	12.50	100	3.0024
2.50	6.25	—	12.50	100	2.5310
2.50	7.50	—	12.50	100	3.1411
2.50	8.75	—	12.50	100	3.0597
2.50	7.50	2.50	12.50	100	1.9763
2.50	7.50	5.00	12.50	100	2.0253
2.50	7.50	7.50	12.50	100	2.1215
2.50	7.50	10.00	12.50	100	2.0986
2.50	7.50	—	10.00	100	3.5001
2.50	7.50	—	12.50	100	3.1411
2.50	7.50	—	15.00	100	2.9353
2.50	7.50	—	17.50	100	2.5785
2.50	7.50	—	12.50	100	3.1411
2.50	7.50	—	12.50	80	4.1995
2.50	7.50	—	12.50	75	4.9965
2.50	7.50	—	12.50	70	5.0643

Rate law: Rate of the reaction $= \dfrac{k_5K_4K_2K_3[NCPD]_t[PAA]}{\{1 + K_4[PAA]\}\{1 + K_1[H^+]\}}$

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 313 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.

TABLE-2
ACTIVATION PARAMETERS FOR THE OXIDATION OF *META*- AND *PARA*-SUBSTITUTED PHENOXYACETIC ACIDS BY NCPD

Substituents	Order with respect to substrate	$k_1 \times 10^4\ s^{-1}$ 308 K	313 K	318 K	323 K	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})
H	0.6506	1.1250	3.1411	4.6849	8.4669	104.4214	39.1786
m-CH_3	0.9231	0.1598	2.4177	6.6291	8.1059	210.3057	379.1109
p-CH_3	0.5466	1.6029	3.9989	5.5425	7.8349	81.8462	-34.1256
p-$C(CH_3)_3$	0.7772	0.8992	2.9870	5.5258	7.9044	121.0422	95.5004
p-OCH_3	0.1491	1.0225	2.7308	4.5002	6.4032	97.0384	-0.7524
p-Cl	0.2686	0.4225	0.5968	0.7632	0.9359	40.9976	-168.6498
p-NO_2	0.5548	1.4301	1.5120	1.6028	1.6685	14.9391	-253.9852

$\Delta G^{\#} = 92.1585$ kJ mol^{-1} at 313 K; $E_a = 116.6843$ kJ mol^{-1} at 313 K.

The rate of oxidation of the substituted phenoxyacetic acids has also been studied at four different temperatures, *viz.*, 308, 313, 318 and 323 K. The activation parameters were calculated using Eyring's plot[9] and the values are given in Table-2.

The plot of $\Delta H^{\#}$ *vs.* $\Delta S^{\#}$ (Isokinetic plot) gave a straight line with $r = 0.999$ (Fig. 1) and the isokinetic temperature $\beta = 402$ K is obtained. The genuine nature of the isokinetic relationship was verified by the Exner[10] criterion by plotting log $(k_2)_{323\,K}$ *vs.* log $(k_2)_{313\,K}$ which gave a straight line with $r = 0.9828$ (Fig. 2). The value of β was calculated from the equation,

$$\beta = \frac{T_1(1-q)}{(T_2/T_1) - q} \qquad (1)$$

where q is slope of Exner plot (slope = 1.1615) and $T_1 > T_2$. It is seen that the value of β is higher than the experimental temperature (313 K) indicating enthalpy control on the reactions. Such a good correlation indicates that all substituents follow a common mechanism.

The rate data for the oxidation of the substituted phenoxyacetic acids gave only a poor correlation with Hammett substituent constants σ^- value as well as σ^+ value at 313 K. Hence the rate data was subjected to multiple regression analysis using DSP equation. Along with Taft's equation[11], Swain's[12] dual

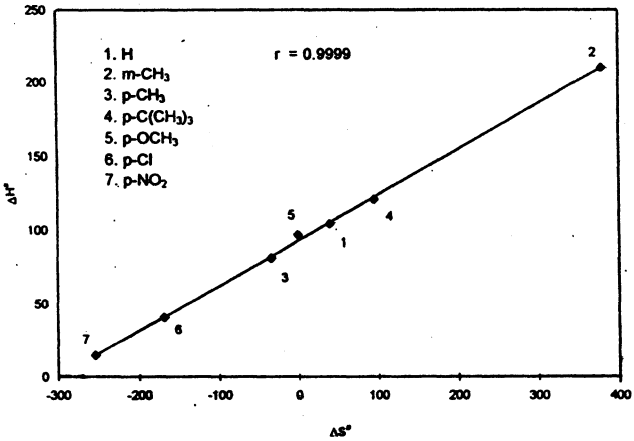


Fig. 1. Isokinetic plot for the reaction of NCPD with substituted phenoxyacetic acids

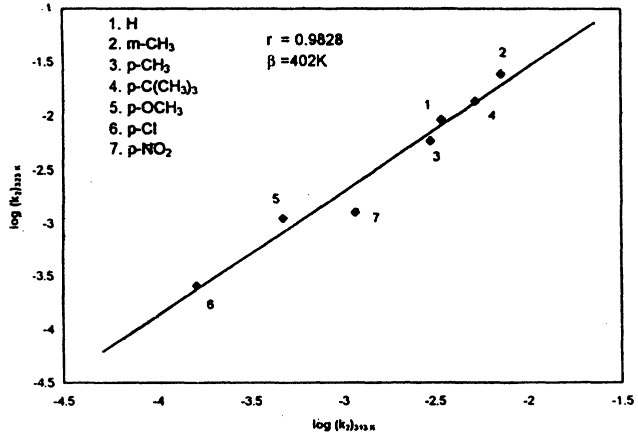


Fig. 2. Exner plot for the reaction of NCPD with substituted phenoxyacetic acids

substitutent 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_IF_R (Swain's treatment). The resuts of the multiple linear regression analysis with the statistical parameters f and ψ as the measure of goodness of fit[13, 14] are given in Table-3.

The reaction constants and the statistical data at four different temperatures for $\sigma_I\sigma_R^-$ parameters are given in Table-4.

The magnitude of ρ_R is higher than that of ρ_I in the case of *para*-substituted phenoxyacetic acids. Also the value of λ indicates that the reaction is more susceptible to resonance effect than field effects. Further percentage resonance character[15] (ρ_R) contributing to the total polar effect has been found to be 35–53% in the case of *para*-substituted phenoxyacetic acids. The magnitude of reaction constants remains unchanged with increase of temperature. Here it is interesting to find that though the reaction constant remains same, there is gradual increase in the field effect and decrease in the resonance effect leading to 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.

TABLE-3

RESULTS OF MULTIPLE REGRESSION ANALYSIS OF THE RATE DATA OF *PARA*-SUBSTITUTED PHENOXYACETIC ACIDS BY NCPD AT 313 K

Substituent constants	C	ρ_I	ρ_R	F	SE	R	f	ψ
$\sigma_I\sigma_R^0$	–2.4105	–1.3845	1.6933	84.6783	0.3106	0.9202	0.4254	0.6188
$\sigma_I\sigma_R^{(BA)}$	–2.4515	–1.3201	1.2088	76.5313	0.3844	0.8748	0.5538	0.7659
$\sigma_I\sigma_R^-$	–2.4290	–1.7839	1.3444	92.8244	0.2125	0.9634	0.2779	0.4233
$\sigma_I\sigma_R^+$	–2.4387	–1.2919	0.7226	72.1884	0.4184	0.8496	0.6206	0.8338
F_IF_R	–2.4558	–1.0409	0.3096	70.0039	0.4346	0.8366	0.6547	0.8657

TABLE-4

TEMPERATURE DEPENDENCE OF THE REACTION CONSTANTS FOR $\sigma_I\sigma_R^-$ PARAMETERS FOR NCPD OXIDATION OF *PARA*-SUBSTITUTED PHENOXY ACETIC ACIDS

T (K)	ρ_I	ρ_R	λ	P_R	f	ψ	SE	R
308	–1.2974	1.5179	–1.1699	53.9161	0.2121	0.3280	0.1494	0.9782
313	–1.7839	1.3444	–0.7536	42.9754	0.2779	0.4233	0.2125	0.9634
318	–1.8854	1.2031	–0.6381	38.9571	0.3153	0.4757	0.2429	0.9536
323	–2.1281	1.1774	–0.5532	35.1942	0.3047	0.4608	0.2582	0.9565

Note: The rate of p-C(CH$_3$)$_3$ and m-CH$_3$ substituted phenoxyacetic acids are not incorporated in the multiple regression analysis; f = S.E./root mean square; $\psi = n(RSS)/(n - m)(TSS)$; $\lambda = \rho_R/\rho_I$; F = 100 – (significance F × 100).

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