Kinetics of oxidation of phenoxyacetic acid by TPCC in aqueous aceticacid medium

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ABSTRACT

The kinetic of oxidation of phenoxyacetic acid and several Para and meta substituted phenoxyacetic acids by tetrakis (pyridine) cobalt (II) chromate (TPCC) in the presence of perchloric acid has been studied in aqueous acetic acid medium. The reaction shows unit order dependence each with respect to oxidant and substrate. The order with respect to hydrogen ion concentration is one. The rate of oxidation increases with increase in the percentage of acetic acid and increase in ionic strength has negligible effect on the rate. The addition of Al^{3+} ion had a noticeable catalytic effect on the reaction rate. In general, the electron releasing substituent accelerates the rate while electron attracting substituent retards the rate of reaction.

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INTRODUCTION

Tetrakis (pyridine) cobalt (II) chromate (TPCC) is one of the most versatile oxidant [1]. Although numerous studies have been devoted to the oxidation of alkenes by chromic acid and chromyl chloride, no kinetic study of TPCC oxidation of phenoxy acetic acid appeared. Studies reported so far on the kinetics of phenoxyacetic acid [2-5] to give diverse products, involving different intermediate in an aqueous medium. The use of an insulated acid substrate in a similar study is rare. We now report the oxidation of phenoxyacetic acid by tetrakis (pyridine) cobalt (II) chromate (TPCC).

MATERIALS AND METHODS

Reagents
Phenoxyacetic acid were prepared and purified by literature method [6]. TPCC was prepared by a known procedure [1] and its purity was determined by iodometric assay. Acetic acid was refluxed over chromium trioxide for 6 hours and then fractionated [7]. All other chemicals used were of AR grade. The solutions were prepared in triple distilled water.

Kinetic measurement
The reactions were followed under the conditions by maintaining always the substrate concentration in excess over that of TPCC. Known volumes of substrate, water and acetic acid were mixed to bring the percentage of acetic acid to the mixture and aliquots were removed at definite time intervals and the unreacted TPCC was estimated by standard iodometric titrations. Rate constants were calculated by the method of least squares.

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Stoichiometry
The reaction mixture containing excess of the oxidant over phenoxyacetic acid was kept at room temperature for sufficient length of time under the conditions employed for the kinetic runs. Estimation of unchanged oxidant showed that 1 mole of phenoxyacetic acid consumed 1 mole of TPCC.

Product analysis
 Phenoxyacetic acid (1 mol) was allowed to react with TPCC (1mol) under the conditions of kinetic measurement. After 24 hour the reaction mixture was extracted with ether and dried over anhydrous sodium sulphate. The ether layer was evaporated on a hot water bath to get solid product quinine was confirmed by TLC and infrared spectral data.

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RESULTS AND DISCUSSION

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The rate data and other experimental data were obtained for all the phenoxyacetic acids. Since the results are similar, only representative data are reproduced here. The reactions are of first order with respect to TPCC, as proved by the linearity of log [TPCC] against time. The reaction was found to be first order in phenoxyacetic acid as evidenced by the unit slope of log [S] against log k (Fig. 1)

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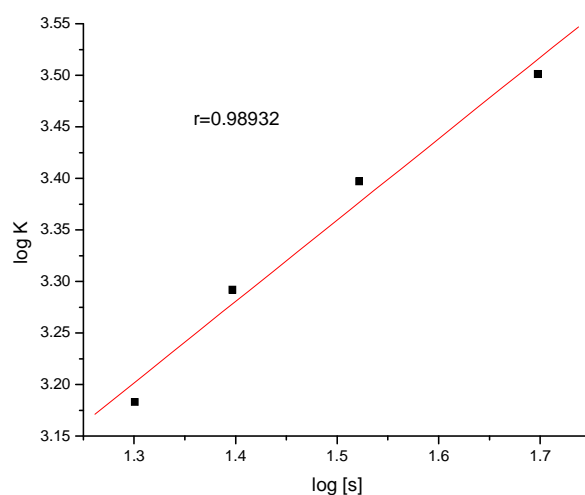
Fig.1. log [s] Vs log k

Table- 1 Effect of reactants on the reaction rate of oxidation of phenoxyacetic acid at 308K

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[PAA] x 10^2 mol dm^{-3}	[TPCC] x 10^3 mol dm^{-3}	[H$^+$] x 10^1 mol dm^{-3}	HOAc (%)	k_1 x 10^4 s^{-1}
2.0	2.0	3.0	70	3.15
3.0	2.0	3.0	70	4.00
4.0	2.0	3.0	70	5.09
5.0	2.0	3.0	70	6.55
3.0	0.50	3.0	70	5.08
3.0	0.75	3.0	70	4.39
3.0	1.00	3.0	70	4.00
3.0	1.25	3.0	70	2.51
3.0	2.0	1.5	70	2.62
3.0	2.0	3.0	70	4.00
3.0	2.0	4.5	70	4.57
3.0	2.0	6.0	70	5.03
3.0	2.0	3.0	70	4.00
3.0	2.0	3.0	75	4.25
3.0	2.0	3.0	80	4.50
3.0	2.0	3.0	85	5.56

At constant concentrations of the reactants, the reaction rate increased with the increase in the concentration of the hydrogen ion and the log k against log [H^+] was found to be linear with a slope of unity. The rate of oxidation of Phenoxyacetic acid is affected considerably by changing the solvent polarity of the acetic acid-water mixture. The rate of oxidation increases with the increase in the percentage of acetic acid. It is well known that the polarity of the solvent decreases, the rate of oxidation increases.

Increase in ionic strength of the 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 [9].   The reaction mixture, allowed to stand with acrylonitrile, did not induce polymerisation suggesting the absence of free radical mechanism. On the other hand, the additions of Mn^{2+} ions retard the rate of reaction. (Table. 2)

Table-2 Effect of Mn^{2+}, Al^{3+} and $NaClO_4$ on the reaction rate of phenoxyacetic acid at 308 K
[S]=3x10^{-2} mol dm^{-3}, [OX]=1x10^{-3} mol dm^{-3}, [Cat]=1x10^{-2} mol dm^{-3}, [H$^+$]=6x10^{-1} mol dm^{-3}

| [Mn^{2+}] x 10^2 mol dm^{-3}	[Al^{3+}] x 10^2 mol dm^{-3}	[$NaClO_4$] x 10^2 mol dm^{-3}	kx10^4 s^{-1}
1.00	-	-	3.31
2.00	-	-	3.25
3.00	-	-	3.06
4.00	-	-	2.92
-	1.00	-	3.04
-	2.00	-	3.48
-	3.00	-	3.83
-	4.00	-	4.05
-	-	1.00	3.14
-	-	2.00	3.12
-	-	3.00	3.10
-	-	4.00	2.83

EFFECT OF SUBSTITUENT ON THE REACTION RATE
The rates of oxidation of some substituted phenoxyacetic acids have been studied at four different temperatures viz 303,308,313and 318K. The activation parameters have been computed from a plot of ln k/T against 1/T using the Eyring's equation in Table 3. The entropies of activation $\Delta S^{\neq}$ are all high negative values indicating extensive solvation of the transition state over the reactants.

Table-3

S.No	Substituents	k x 10^4				$\Delta H\#$ KJmol^{-1}	$\Delta s\#$ Jmol^{-1}	$\Delta G\#$ KJmol^{-1}
		303K	308K	313K	318K			
1	H	3.16	4.00	5.50	6.02	33.01	-203.19	95.59
2	p-Cl	2.92	5.07	7.36	9.47	60.25	-113.44	95.19
3	p-CH3	3.14	3.89	4.32	5.12	22.62	-237.44	95.76
4	m-CH3	2.19	3.25	4.82	5.64	49.49	-151.59	96.18
5	p-NO2	0.63	1.00	1.81	2.84	81.29	-57.71	99.07
6	p-OCH3	2.59	3.70	4.88	5.87	41.28	-177.31	95.89
7	p-Br	2.10	2.82	3.27	4.35	34.78	-194.60	94.72
8	m-Cl	1.08	1.61	2.28	3.23	62.97	-113.54	97.94
9	m-OCH3	1.31	1.92	2.72	4.67	63.87	-108.97	97.43

The plot of logk_{303} against log $k_{308,318}$ gave a straight line with r = 0.9817 and 0.9904 (Fig.2). Such a good correlation indicates that all the substituents follow common mechanism
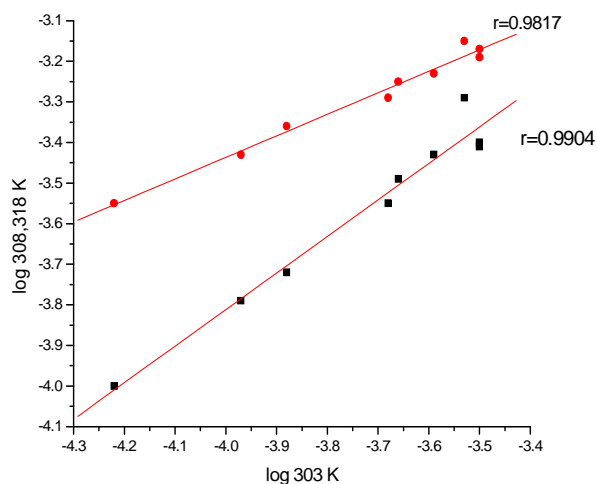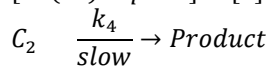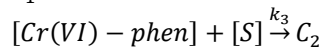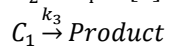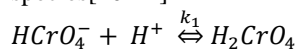
Fig.2 log 303 k Vs log 308,318k

The plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ gave straight line with correlation (r=0.998; Fig 3)
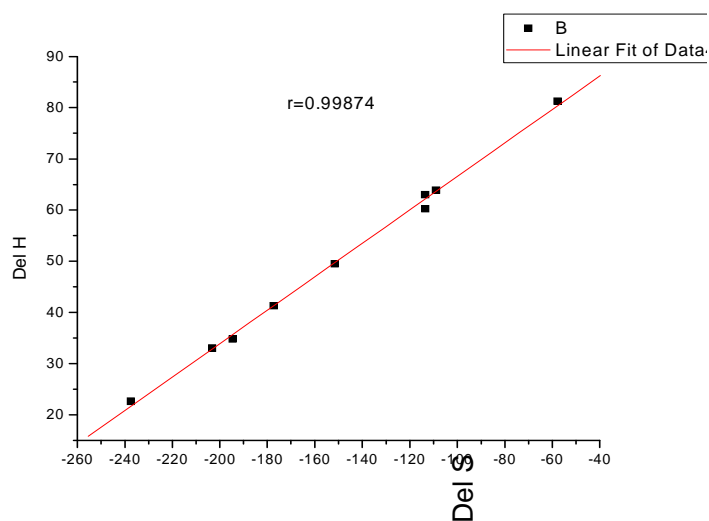
Fig3. log $\Delta S^{\neq}$ Vs log$\Delta H^{\neq}$

Mechanism
Tetrakis pyridine cobalt (II) dichromate in aqueous acetic acid medium yields $HCrO_4^-$ is the effective oxidising species[10-11]

$$HCrO_4^- + H^+ \overset{k_1}{\Longleftrightarrow} H_2CrO_4$$

$$H_2CrO_4 + [S] \overset{k_2}{\Longleftrightarrow} Complex\ 1$$

$$C_1 \overset{k_3}{\rightarrow} Product$$

$$[Cr(VI) - phen] + [S] \overset{k_3}{\rightarrow} C_2$$

$$C_2 \quad \frac{k_4}{slow} \rightarrow Product$$

Rate $= K_3 C_1$
$= k_2 k_3 [H_2\ Cr_2O_4][S]$
$= k_1 k_2 k_3 [HCrO_4^-\ ][S]\ [H^+]$
$= k_1 k_2 k_3 [S]\ [H^+]$

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CONCLUSION

The title oxidation reaction studies revealed that, order with respect to oxidant, substrate and H^+ followed unit order dependence. Addition of perchloric acid enhances the rate of the reaction. The negative value of $\Delta S^{\neq}$ and a positive magnitude of $\Delta H^{\neq}$ shown the possible to form the intermediate complex.

Correlation of isokinetic plot indicates that all the substituents undergo a common mechanism pathway.

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