

Kinetics and Mechanism of Oxidation of Phenoxyacetic Acids by Chromic Acid

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The kinetics of oxidation of phenoxyacetic acid and several *para*- and *meta*- substituted phenoxyacetic acids by chromic acid in presence of perchloric acid have been studied in 50% (v/v) aqueous acetic acid. The oxidation is fractional order (0.74) with respect to substrate. The increase in concentration of perchloric acid increases the rate of the oxidation with an order of 0.62 (fractional). The added Mn^{2+} decreases the rate considerably suggesting a two electron transfer at the rate limiting step. In general electron releasing substituents accelerate the rate while electron attracting groups retard the rate. A good correlation is found to exist between $\log k_2$ and Hammett constants.

INTRODUCTION

The reaction of insulated systems (containing groups or atoms between the reaction site and the bulk of the molecule) gained interest by us since *ortho*-substituted insulated compounds behaved like their *meta*- and *para*-substituted compounds in respect of the applicability of LFER. Thus we chose the carboxylic centre as the reaction site and followed esterification and ester hydrolysis studies.¹⁻⁵ Now it is thought of interest to change the reaction site in these substituted insulated compounds and hence the title study. These studies can also be described to (i) seek evidence for the valency shell expansion of sulphur and halogens (excepting fluorine) and (ii) to compare the difference in the electrical behaviour of various insulated groups. Though oxidation kinetics of this type of insulated acids is not widely reported, mention may be made of the work from our laboratories.⁶⁻⁸

EXPERIMENTAL

All the phenoxyacetic acids were prepared by the method of Koelsch⁹. All other chemicals used were of AR grade.

Kinetic measurements were carried out in 50% acetic acid and 50% water (v/v). The kinetics were followed by determining the unreacted [chromic acid] iodometrically at different time intervals. For all the runs good first order plots of \log [chromic acid] vs time with correlation coefficients (r) of at least 0.990 were obtained. The pseudo first order rate constants (k_{obs}) obtained by the method of least squares afforded the $K_{1.74}$ when divided by [Substrate].

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of [chromic acid] largely in excess over [substrate]. The estimation of unreacted [chromic acid] showed that one mole of chromic acid reacts with one mole of phenoxyacetic acid.

After about 70% completion of the reaction the reaction mixture in actual kinetic runs was ether extracted, ether evaporated and the residue was analysed by CO-TLC. Benzoquinone was found to be the product formed in the reaction.

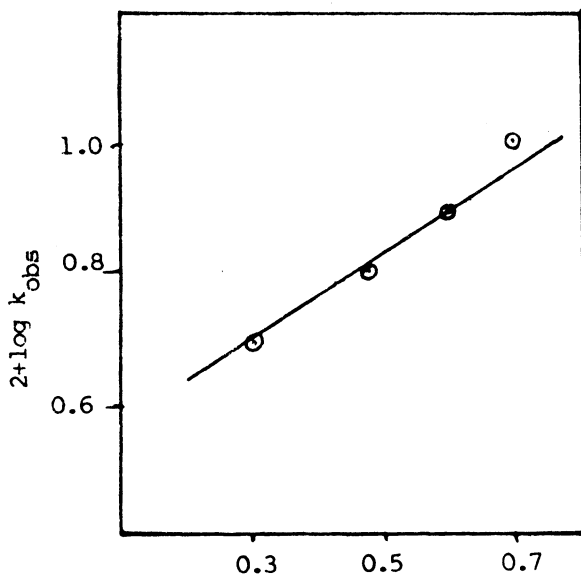
RESULTS AND DISCUSSION

The first order dependance of the reaction of chromic acid is obvious from the linearity of the plots of \log [chromic acid] vs time. The values ($K_{1.74}$) at different [phenoxyacetic acid] and [chromic acid] are listed in Table-1. The plot of $\log k_{\text{obs}}$ vs \log [substrate] (Fig. 1) is linear with a slope of 0.74 indicating a fractional order dependance on the substrate.

An increase in the concentration of perchloric acid increases the rate of oxidation with an order of 0.62. (Table-1). This is obvious from the linearity of the plot of \log [HClO_4] vs $\log k_{\text{obs}}$ with a slope of 0.62.

TABLE 1

(Substrate) $\times 10^2$ M	(Oxidant) $\times 10^4$ M	(HClO_4) $\times 10$ M	(NaClO_4) $\times 10^2$ M	(MnSO_4) $\times 10^4$ M	% of Acetic acid-water	Tempe- rature	$k_{\text{obs}} \times 10^5 \text{ Sec}^{-1}$
2.00	10.0	1.0	—	—	50-50	303 K	4.98
3.00	10.0	1.0	—	—	50-50	303 K	6.33
4.00	10.0	1.0	—	—	50-50	303 K	7.80
5.00	10.0	1.0	—	—	50-50	303 K	9.88
4.00	5.0	1.0	—	—	50-50	303 K	8.38
4.00	15.0	1.0	—	—	50-50	303 K	7.71
4.00	20.0	1.0	—	—	50-50	303 K	7.30
1.00	10.0	2.0	—	—	50-50	303 K	6.38
1.00	10.0	3.0	—	—	50-50	303 K	8.01
1.00	10.0	4.0	—	—	50-50	303 K	11.70
1.00	10.0	1.0	—	—	30-70	303 K	1.78
1.00	10.0	1.0	—	—	40-60	303 K	3.23
1.00	10.0	1.0	—	—	60-40	303 K	9.54
1.00	10.0	1.0	—	—	80-20	303 K	14.04
1.00	10.0	1.0	1	—	50-50	303 K	3.03
1.00	10.0	1.0	2	—	50-50	303 K	3.13
1.00	10.0	1.0	3	—	50-50	303 K	4.09
1.00	10.0	1.0	4	—	50-50	303 K	3.94
2.00	10.0	1.0	—	5	50-50	303 K	4.19
2.00	10.0	1.0	—	10	50-50	303 K	3.92
2.00	10.0	1.0	—	15	50-50	303 K	3.62
2.00	10.0	1.0	—	20	50-50	303 K	3.31



$r = 0.99$; Slope = 0.74

Plot of $5 + \log [\text{Substrate}]$ vs. $2 + \log k_{\text{obs}}$

Fig. 1

The rates at different solvent compositions (Table-1) show that the reaction is facilitated by an increase in the polarity and /or nucleophilicity of the medium suggesting polar rate limiting transition state. The reaction does not show any salt effect as evident from the rate constants (Table-1), at different ionic strengths (maintained by adding NaClO₄). The added Mn²⁺ retards the rate of the oxidation (Table 1) considerably showing that the rate determining step involves a two electron transfer

The rate constants for chromic acid oxidation: of substituted phenoxyacetic acids at different temperatures and the slope and intercept of the Eyring's plot are listed in Table-2. The negative entropy of activation (ΔS^\ddagger) values indicate that there is more orderliness in the rate determining transition state relative to the reactants. The data in Table-2 reveal that the electron releasing substituents enhance the rate, while electron withdrawing substituents retard it. The plot of $\log K_{1.74}$ (40°C) vs σ is also linear, affording a ρ value of -1.344 . This suggests that the phenoxyacetic acid molecule becomes electron deficient in the rate limiting step. This is in consonance with the proposed mechanism.

The reaction series generally obey the isokinetic relationship as shown by a typical linearity of the plot of $\log k_{1.74}(30^\circ\text{C})$ vs $\log k_{1.74}(50^\circ\text{C})$ ¹⁰. Such a correlation indicates that all the esters undergo oxidation through the same mechanism¹¹. The plot of ΔS^\ddagger and ΔH^\ddagger gives a straight line (Correlation coefficient $r = 0.874$) and from the slope, the isokinetic temperature is found to be 294.1 K.

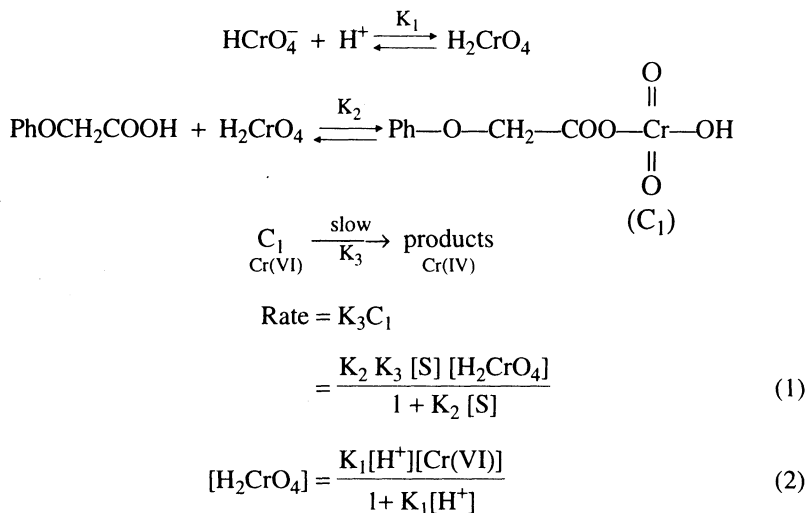
TABLE 2
EFFECT OF SUBSTITUENTS ON THE REACTION RATE

No.	Substituent	$k_{1.74} \times 10^6 \text{M}^{-1} \text{S}^{-1}$			$\Delta H^\#$	$-\Delta S^\#$
		303 K	313 K	323 K	kJmol^{-1}	$\text{JK}^{-1} \text{mol}^{-1}$
1.	-H	900	1250	1600	20.35	236.17
2.	<i>p</i> -OCH ₃	2060	2250	2470	4.76	316.48
3.	<i>p</i> -CH ₃	1370	1880	2210	13.46	254.80
4.	<i>p</i> -C ₂ H ₅	1390	1690	2060	13.44	255.42
5.	<i>p</i> -Br	350	460	560	16.02	258.26
6.	<i>p</i> -Cl	370	530	690	23.42	233.54
7.	<i>m</i> -CH ₃	1040	1311	2970	39.85	171.54
8.	<i>m</i> -C ₂ H ₅	940	1170	1460	15.38	252.43
9.	<i>m</i> -Br	200	310	430	28.79	267.12
10.	<i>m</i> -NO ₂	63	120	180	40.00	192.88

[Substrate] = 2×10^{-2} M M [Oxidant] = 1×10^{-3} M

[HClO₄] = 1×10^{-1} MM [Solvent] = Acetic acid – water 50% (v/v)

Mechanism and rate law



Substituting [H₂CrO₄] in equation (1)

$$\text{Rate} = \frac{K_1 K_2 K_3 [\text{S}] [\text{Cr(VI)}] [\text{H}^+]}{1 + K_2 [\text{S}] \quad 1 + K_1 [\text{H}^+]}$$

$$= \frac{K_1 K_2 k_3 [\text{S}] [\text{Cr(VI)}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_2 [\text{S}] + K_2 K_1 [\text{S}] [\text{H}^+]}$$

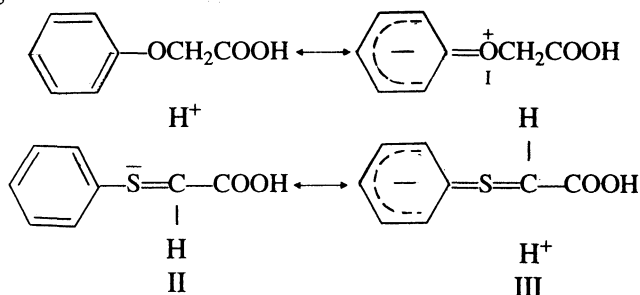
Since $K_2K_1[S][H^+]$ is negligible when compared to other terms,

$$\text{Rate} = \frac{K_1K_2K_3[S][Cr(VI)][H^+]}{1 + K_2[S] + K_1[H^+]}$$

The rate equation well explains the observed orders with respect to oxidant, substrate and H^+ .

It is interesting to note that when we carried out the same reaction with S-phenylmercaptoacetic acid,¹² there is an appreciable activity even with very low concentration of perchloric acid.

Thus at 30°C, $k_{\text{obs}} = 4.47 \times 10^{-4}$ [Oxidant] = 1×10^{-4} M; [Substrate] = 1×10^{-2} M; $[HClO_4] = 1 \times 10^{-4}$ M]. The sluggish nature of phenoxyacetic acid in comparison with its sulphur analogue is quite understandable if we invoke the following structural elucidations.



Structures II and III are hyperconjugated structures made possible by the valency shell expansion of sulphur. The ability of sulphur to expand its valency shell in this compound has been discussed by our earlier kinetic studies.^{13,14}

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