



LINEAR FREE-ENERGY RELATIONSHIPS IN CHROMIUM (VI) OXIDATION OF SOME *META*- AND *PARA* SUBSTITUTED PHENOLS IN AQUEOUS-ACID MEDIA : A KINETIC AND MECHANISTIC STUDY

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ABSTRACT

The kinetics of oxidation of a number of *meta*- and *para*- substituted phenols by isonicotinium dichromate(INDC) in the presence of oxalic acid in aqueous acetic acid medium have been investigated. The reaction is first order with respect to oxidant and substrate, but fractional order with respect to both $[H^+]$ ion and oxalic acid. Exner's plot gives a straight line with fine correlation coefficient, but the Hammett plot gives a curve that is concave downward instead of a straight line. The observed Hammett plot deviation has been accounted for suitably. From the kinetic data obtained the activation parameters have been computed using Eyring's plot and a suitable mechanism has been proposed. The oxidation product is p-benzoquinone. A suitable rate law is derived.

Keywords: Kinetics, Mechanism, Oxidation, Phenols, LFER, Isonicotinium dichromate.

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INTRODUCTION

Chromium(VI) compounds have been widely used in aqueous and non-aqueous media for the oxidation of variety of organic compound¹⁻¹¹. The behaviour of INDC as an oxidising agent has been reported recently¹²⁻¹³.

EXPERIMENTAL

Materials

INDC was prepared and purified as usual method. Purification of phenols were carried out by usual procedure and they were further purified by reduced pressured distillation, their physical constant coincided with literature values. All other chemical used were of AnalaR grade. Doubly distilled water was used throughout.

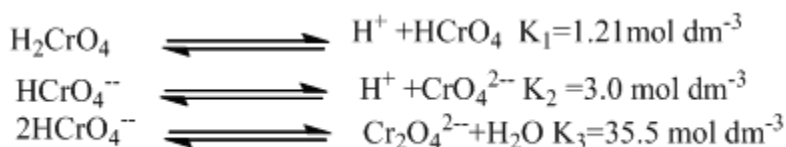
Stoichiometry and Product analysis

Solutions of phenol containing an excess of INDC were kept overnight at 30° C. Estimation of the remaining oxidant showed that the stoichiometry (Phenol : INDC) 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 pellet) was found to be p- benzoquinone.

RESULTS AND DISCUSSION

At fixed $[H^+]$ with [substrate] in excess, the plot of log(titre) against time was linear, indicating first order in INDC. The pseudo-first order rate constants were independent of the initial concentration of the oxidant (Table-1). From the observation it is clear that the reaction is showing first order dependence with respect to INDC and phenol. But the order in $[H^+]$ and [oxalic acid] are fractional. The above facts reveal that there is a combined effect of oxidant, oxalic acid and H^+ ion. The oxidation by Cr(VI) will vary with nature of Cr(VI) species used and solvent will play an important role on the rate of the reaction. In aqueous solution and in the absence of other ion the following equilibrium are

existing¹⁴(SCHEME-1) Here the dimerisation equilibrium is of considerable importance .In water the dichromate ion will be predominating species only when the concentration of Cr(VI) is greater than about 0.05 mol dm⁻³ .In this case ,as the concentration of Cr(VI) is less than 0.05 mol dm⁻³ monomeric form predominates and the active oxidising species is HCrO₄⁻.The reaction is acid catalysed one .The evolution of CO₂ confirms that oxalic acid one of the participants in the main reaction of co-oxidation process. Such a phenomenon of a ternary system was already established¹⁵.



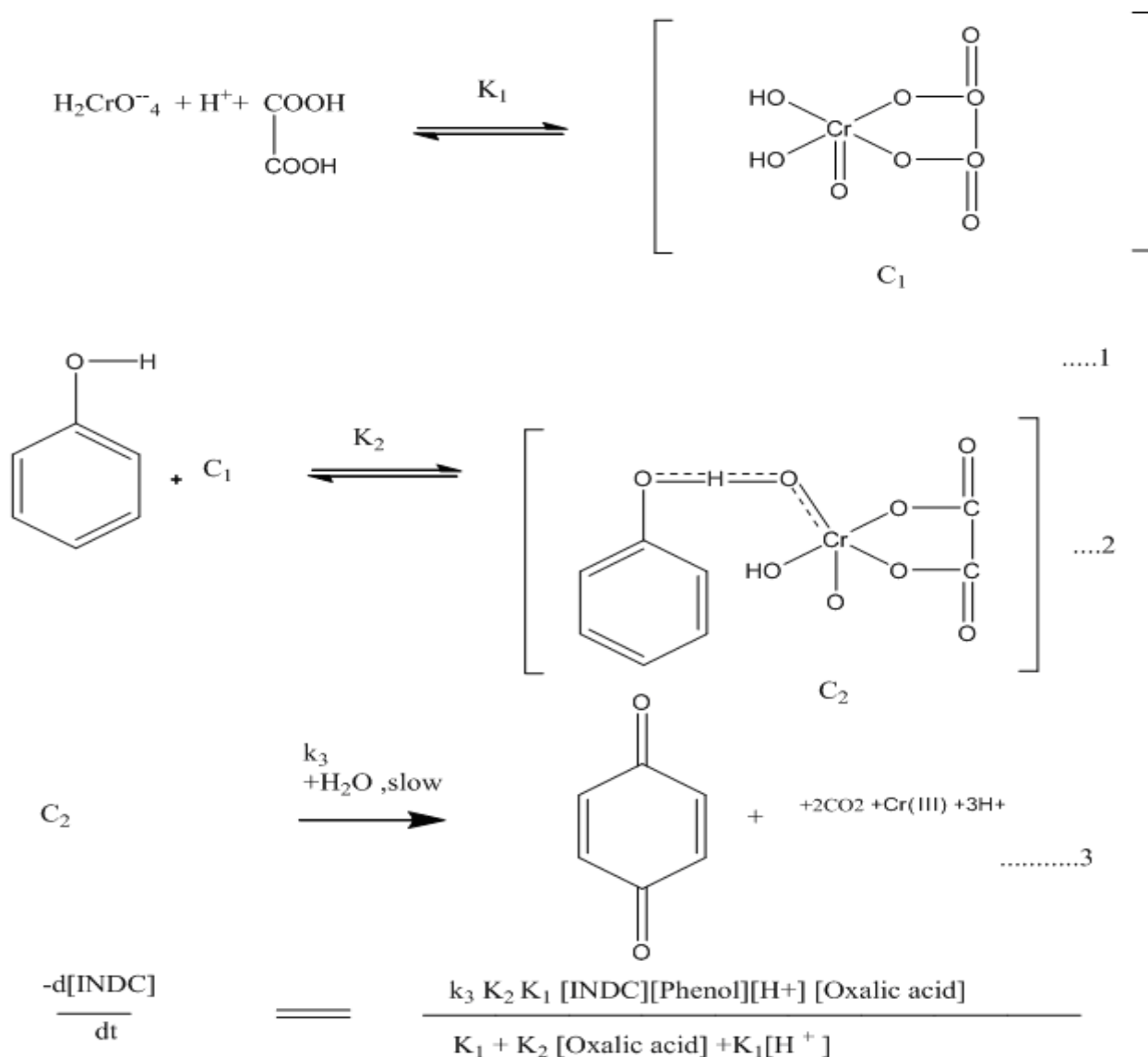
Scheme-1

The rate increases with decrease in the dielectric constant of the medium and increase in the ionic strength has negligible effect on the rate. The reaction did not induce polymerisation of acrylonitrile indicating the absence of free radical pathway. The addition of Mn²⁺ ion has a noticeable catalytic effect. The addition of Al³⁺ ion decrease the oxidation rate due to the formation of complex between Al³⁺ and oxalic acid(Table-2). Based on the above observations, a possible mechanism has been proposed (SCHEME-2).

In the proposed mechanism (SCHEME-2),If the rate of forward reaction of step(2) is greater than other steps, a zero order dependence on the substrate would be obtained; on the other hand If the it is lesser than other steps a unit order dependence on the substrate would be obtained; If the rate of the forward reaction of step (1) and step(2) are comparable values , a fractional order dependence on the substrate would result.¹⁶

When Effect of substituent on the reaction rate

In the reaction the order of reactivity of substituted phenols are m-NH₂ > m-CH₃ > p-C(CH₃) > p-CH₃ m-OCH₃ > p-Cl > p-Br > p-OCH₃ > p-COOH > p-NO₂ > m-NO₂ (Table-3).The variation in the respect of different substituted phenols are explained by invoking different rate controlling step in the proposed mechanism .The activation parameters are calculated using Eyring's plot and the values are given in Table-3.The fairly high value of ΔH[#],ΔG[#] and E_a indicate that the transition state is highly solvated .The negative value of entropy of activation(ΔS[#]) suggested that extensive solvation of the transition state over the reactants. As ΔH[#] vs. ΔS[#] do not vary linearly no isokinetic relationship is observed. This indicates the absence of enthalpy –entropy compensation effect¹⁷ . Exner¹⁸⁻¹⁹ criticized the validity of such linear correlation between ΔH[#] and ΔS[#].As these quantities are dependent on each other when measurements are made ,the experimental data can be treated by the following equation²⁰⁻²¹ log(k)_{T2} = a+ b log (k)_{T1} where T₂ > T₁ the plot of log k_(318K) vs. log k_(308K); log k_(313K) vs. log k_(308K) and log k_(318K) vs. log k_(313K) gave a straight lines with r=0.99 (Fig-1) . Such a good correlation indicates that all the substituents follow a common mechanism . When Hammett equation was applied to this reaction system with the usual substituent constants, no linear correlation was obtained; instead a curve concave downward was obtained. An attempt was made to correlate the log k values with substituent constant σ⁺ and σ^o ²²⁻²³. In both case large deviations were noted in Hammett plot. Hence the deviation from linearity in Hammett's plot is not due to change in σ. The curvature may be due to any one of the following two factors (i) a gradual change in the reaction mechanism when one passes from electron-donating to electron withdrawing substituent (ii) a change in the rate determining steps with change in the nature of substituent. The observed curvature in the Hammett's plot may be attributed to the change in rate determining step. Since Michaelis-Menten plot with some of the substrates (p-CH₃ , m-NH₂ , p-COOH , p-OCH₃, and m-OCH₃) yields some definite intercept confirming the complex formed, which subsequently decomposes in a slow rate determining step to give product . This further confirmed by the shape (concave downward) of the Hammett curve (Fig-2), which indicates that the reaction series is following a common mechanism with the different rate determining step. If a curve (concave upward) results ,the reaction should be following a different mechanism²⁴.



Scheme-2

Table-1

[Phenol] (10 ² M)	[INDC] (10 ³ M)	[H ⁺] (10M)	[Oxalic] (10 ³ M)	[NaClO ₄] (10 ⁴ M)	H ₂ O- CH ₃ COOH (% v/v)	k ₁ (10 ⁴ s ⁻¹)
3.00	1.00	1.00	5.00	-	70-30	1.54
4.00	1.00	1.00	5.00	-	70-30	2.40
5.00	1.00	1.00	5.00	-	70-30	2.83
6.00	1.00	1.00	5.00	-	70-30	3.21
4.00	0.50	1.00	5.00	-	70-30	2.39
4.00	1.00	1.00	5.00	-	70-30	2.40
4.00	1.50	1.00	5.00	-	70-30	2.43

4.00	2.00	1.00	5.00	-	70-30	2.41
4.00	1.00	0.05	5.00	-	70-30	2.21
4.00	1.00	0.10	5.00	-	70-30	2.40
4.00	1.00	0.20	5.00	-	70-30	3.02
4.00	1.00	0.30	5.00	-	70-30	3.23
4.00	1.00	1.00	2.50	-	70-30	1.80
4.00	1.00	1.00	5.00	-	70-30	2.40
4.00	1.00	1.00	10.00	-	70-30	3.48
4.00	1.00	1.00	15.00	-	70-30	3.96
4.00	1.00	1.00	5.00	2.50	70-30	2.39
4.00	1.00	1.00	5.00	5.00	70-30	2.39
4.00	1.00	1.00	5.00	7.50	70-30	2.41
4.00	1.00	1.00	5.00	10.00	70-30	2.41
4.00	1.00	1.00	5.00	-	70-30	2.40
4.00	1.00	1.00	5.00	-	60-40	2.72
4.00	1.00	1.00	5.00	-	50-50	2.98
4.00	1.00	1.00	5.00	-	30-70	3.51

Table-2
[phenol]= 4.0×10^{-2} M, [H⁺]= 1.0×10^{-3} M, [INDC]= 1.0×10^{-3} M, Temperature: 308K
[oxalic]= 5.0×10^{-3} M, Solvent: 70% H₂O-CH₃COOH(v/v)

[Mn ²⁺] (10 ⁴ M)	[Ar ³⁺] (10 ⁴ M)	[acrylonitrile](10 ⁴ M)	k ₁ s ⁻¹
2.50	-	-	2.43
5.00	-	-	2.49
7.50	-	-	2.99
10.00	-	-	3.22
-	2.50	-	2.38
-	5.00	-	1.95
-	7.50	-	1.18
-	10.00	-	1.11
-	-	2.50	2.41
-	--	5.00	2.38
-	-	7.50	2.43
-	-	10.00	2.44

Table-3 :Activation parameters for the oxidation of meta- and para- substituted Phenols by Isonicotinium dichromate

Substituents	303K k ₁ × 10 ⁴ s ⁻¹	308K k ₁ × 10 ⁴ s ⁻¹	313K k ₁ × 10 ⁴ s ⁻¹	318K k ₁ × 10 ⁴ s ⁻¹	ΔH [#] kJ mol ⁻¹	ΔS [#] KJ mol ⁻¹	order
<i>m</i> -CH ₃	7.14	16.89	23.14	32.57	75.72	-52.17	0.00
<i>p</i> -C(CH ₃) ₃	5.71	14.31	25.57	37.57	208.91	401.22	1.00
<i>p</i> -CH ₃	5.97	6.57	7.06	7.89	11.95	-136.30	0.32
<i>m</i> -NH ₂	1.95	28.10	37.53	46.72	25.58	-191.19	0.43
<i>p</i> -NO ₂	0.03	0.04	0.042	0.044	8.32	-75.24	0.00
<i>m</i> -NO ₂	0.01	0.018	0.022	0.024	21.59	-112.16	0.00
<i>p</i> -COOH	0.15	0.212	0.22	0.26	24.29	-143.17	0.20
<i>p</i> -Cl	0.67	1.82	2.52	3.25	79.22	-23.45	1.00
<i>p</i> -Br	1.47	1.57	2.59	3.61	50.44	-106.59	1.00
<i>p</i> -OCH ₃	0.26	0.26	0.26	0.27	14.87	-73.91	0.54
<i>m</i> -OCH ₃	3.18	3.51	3.61	3.82	11.33	-58.53	0.40

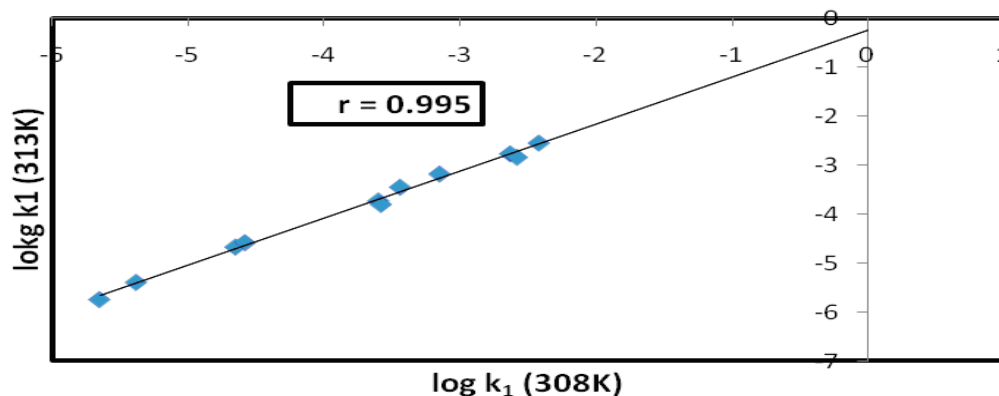


Fig.-1: Exner Plot

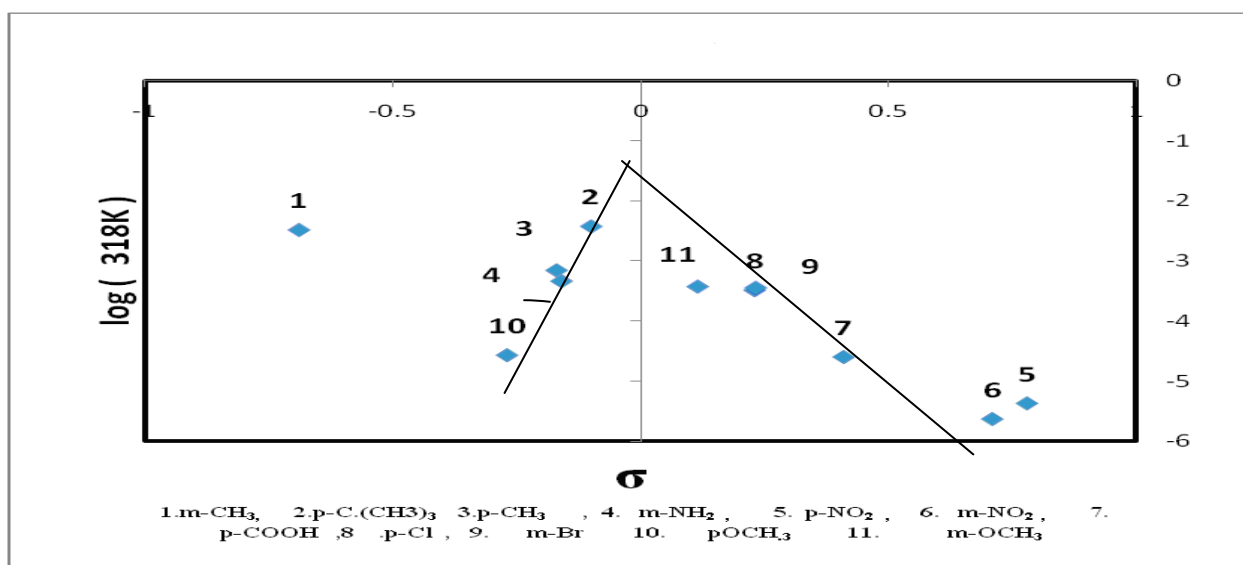


Fig.-2: Hammett Plot

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