



## Kinetics and Mechanism of Oxidation of dibenzalacetone(DBA) by Isonicotinium dichromate in aqueous acetic acid medium -catalyzed by 1, 10-phenanthroline

An. Palaniappan<sup>a,\*</sup>, R. Udhayakumar<sup>b</sup>, S. Srinivasan<sup>a</sup>, and C. Raju<sup>a</sup>

<sup>a</sup>Department of Chemistry, Annamalai University, Annamalai Nagar – 608 002, India

<sup>b</sup>Department of Chemistry, Anna University of Technology, Tiruchirappalli-620 024, India

---

### ABSTRACT

The kinetics of the oxidation of dibenzalacetone (DBA) by isonicotinium dichromate (INDC), in acetic acid medium, catalysed by 1,10-phenanthroline has been investigated. The reaction shows fractional order dependence with respect to  $[H^+]$ , 1, 10-phenanthroline and first order dependence with respect to [oxidant] and [substrate]. The reactions are carried out for various substituents at different Concentration and at four different temperatures. Activation parameters have been calculated and a suitable mechanism has been proposed.

**Keywords:** Kinetics, oxidation, dibenzalacetone, INDC, perchloric acid, water.

---

### INTRODUCTION

Selective oxidation of organic compounds under aqueous [1] and non-aqueous [2] conditions is an important transformation in synthetic organic chemistry. Chromium compounds especially Cr (VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisable organic functional groups [3, 4]

Isonicotinium dichromate is one of the most versatile oxidant. Although numerous studies have been devoted to the oxidation [5-7] of alkenes by chromic acid and chromyl chloride [8] no kinetic study of INDC oxidation of dibenzalacetone,(DBA) has appeared. This investigation was undertaken to gain a clear understanding of the mechanism of the INDC oxidation of dibenzalacetone. Extensive kinetics and mechanistic studies on oxidation of organic compounds with chromium reagents revealed that such reaction ordinarily involves three – electron change where by Cr (VI) species are reduced to Cr (III). The objective of the present study is to ascertain the reaction pathway especially with respect to chromium.

### EXPERIMENTAL SECTION

#### Dibenzalacetone (DBA)

A cold solution of 25 g of NaOH in 25 mL of water and 20 mL of ethanol was placed in a 500 mL round bottomed flask equipped with mechanical stirrer and it was surrounded by ice water bath. The temperature of the solution was maintained at 20-25 °C and stirred vigorously. One half of previously prepared mixture of 26.5 g (25.5 mL, 0.25 mol) of pure benzaldehyde and 7.3 g (9.31 mL, 0.125 mol) of acetone were added. A flocculent precipitate was formed in 2-3 min. The remainder of the benzaldehyde acetone mixture was added after 15 min. The stirring was continued for a further 45 min. The precipitate was filtered at the pump and washed well with cold water to eliminate the alkali as completely as possible. The solid was dried at room temperature upon the filter paper to constant weight 27 g (93%) of crude dibenzalacetone[9] obtained was recrystallized from ethyl acetate (m.p.110 °C).

**Isonicotinium dichromate (INDC)**

Isonicotinic acid (7.38 g, 60 mmol) was added to chromium trioxide (12 g, 120 mmol) dissolved in water (12 ml) at 0-5 °C with stirring. After 15 min acetone (100 ml) was added to the resulting red- orange suspension and the mixture was stirred at 0-5 °C for 15 min. The product was filtered off and washed with acetone (50 ml) and dichloromethane (25 ml) affording isonicotinium dichromate (6 g)[10] as orange-yellow solid with m.p.250-251 °C.

**Acetic acid**

The procedure for the purification of acetic acid was essentially similar to that of Weissberger [11]. Glacial acetic acid (AR) was partially frozen and about [11] of the liquid were removed. The residue was melted and refluxed with chromium trioxide (30 g) and fractionally distilled. The portion distilling between 116-118 °C was collected, partially frozen and about half of the acid was discarded as liquid. The remaining residue was melted and fractionated again after treating with chromium trioxide (30 g).The fraction boiling at 117-118 °C was collected and kept in brown bottles. All other chemicals used were of AR grade (Fluka). Triply distilled water was used for the preparation of solutions.

**Data and Kinetic measurement**

The reaction was carried out under pseudo-first order conditions by maintaining a large excess of dibenzalacetone over Cr (VI). The mixture was homogeneous throughout the course of the reaction. The reaction was followed titrimetrically. The rate constants were evaluated from log titre versus time plots. All rate constants are average of two or more determinations.

**Stoichiometry**

The reaction mixture containing excess of the oxidant over dibenzalacetone 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 dibenzalacetone consumed 1 mol of INDC.

**Product analysis**

Dibenzalacetone (1mole) was allowed to react with INDC (1mole) under the conditions of kinetic measurement. The mixture was neutralized with sodium bicarbonate solution and extracted with ether. The ether was evaporated and residue was crystallized several times from aqueous ethanol and the product was identified by IR as epoxide.

**RESULTS AND DISCUSSION****Effect of oxidant and substrate concentration on reaction rate**

The oxidation of dibenzalacetone by INDC was investigated at several concentrations of oxidant [INDC] (Table 1) and the [substrate]. The plot of log titre versus time was linear indicating the first order dependence on [INDC]. The values of pseudo-first order rate constant  $k_1$  were evaluated from the plot of log titre versus time following least square method (Fig. 1). The plot of log  $k$  versus log [substrate] is a straight line with slope equal to one showing first order dependence on [substrate].

Table – 1 Effect of reactants on the reaction rate of oxidation of dibenzalacetone at 308K

[S] x 10 <sup>2</sup> mol dm <sup>-3</sup>	[OX] x 10 <sup>3</sup> mol dm <sup>-3</sup>	[Cat] x 10 <sup>3</sup> mol dm <sup>-3</sup>	[H <sup>+</sup> ] x 10 <sup>1</sup> mol dm <sup>-3</sup>	$k_1$ x 10 <sup>4</sup> s <sup>-1</sup>
0.5	2.0	5.0	2.5	1.85
1.0	2.0	5.0	2.5	4.38
1.5	2.0	5.0	2.5	5.07
2.0	2.0	5.0	2.5	8.98
2.5	2.0	5.0	2.5	9.11
1.5	1.0	5.0	2.5	5.06
1.5	2.0	5.0	2.5	5.07
1.5	3.0	5.0	2.5	5.08
1.5	4.0	5.0	2.5	5.06
1.5	2.0	5.0	2.5	5.07
1.5	2.0	7.5	2.5	7.55
1.5	2.0	10.0	2.5	9.29
1.5	2.0	12.5	2.5	11.7
1.5	2.0	5.0	1.25	2.67
1.5	2.0	5.0	2.5	5.07
1.5	2.0	5.0	3.75	6.32
1.5	2.0	5.0	5.0	7.16
1.5	2.0	5.0	6.25	8.66

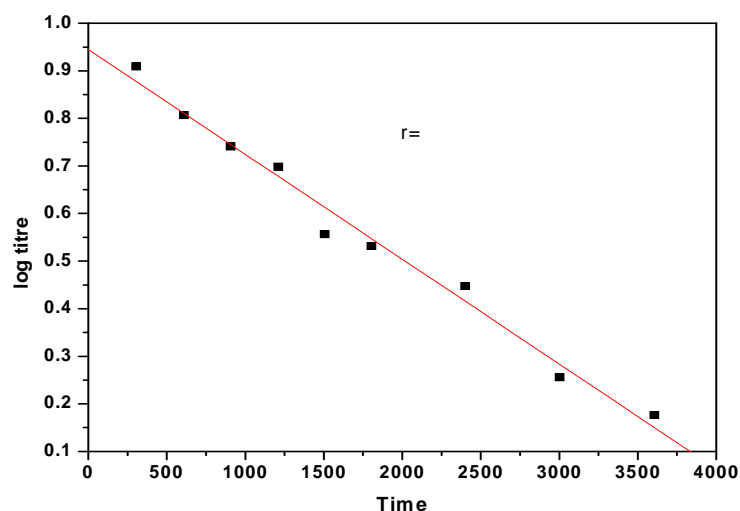
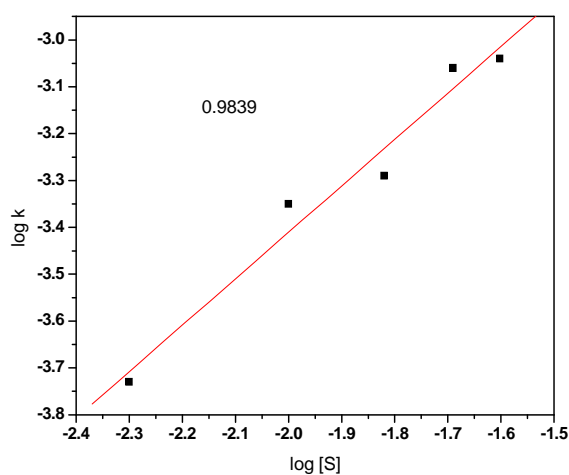


Fig.1 log titre versus time (seconds)

**Effect of  $[H^+]$  and catalyst concentration on reaction rate**

The rate constants were found to increase with increase in  $[H^+]$  as shown in Table 1 and the plot of  $\log k_1$  against  $\log [H^+]$  gave a straight line with the slope less than one. The reaction rate were also measured at the different initial concentration of 1, 10-phenanthroline and the rate constant was found to increase with the concentration of 1, 10-phenanthroline. The plot of  $\log k$  versus  $\log [\text{catalyst}]$  was linear with the slope less than one.

Fig. 2.  $\log [S]$  versus  $\log k$ **Effect of  $Mn^{2+}$ ,  $Al^{3+}$  and  $NaClO_4$  on the reaction rate of dibenzalacetone**

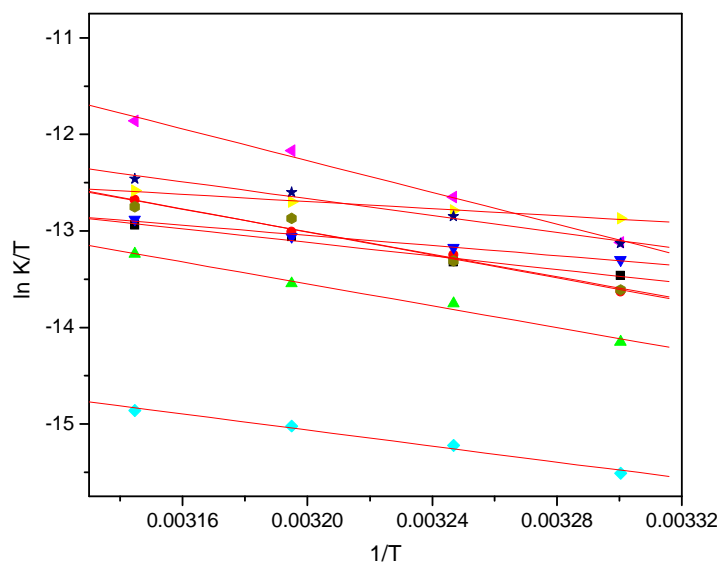
To analyze the number of electrons involved in the oxidation process, the reaction rate was followed by varying the concentration of  $[Mn^{2+}]$ ,  $[Al^{3+}]$  and it is shown in Table 2. The rates were found to increase with increase in the percentage of acetic acid. Depressed reactivity observed in the presence of  $Mn^{2+}$  clearly indicated the involvement of intermediate valence states of Chromium, particularly Cr (IV). With the increase in the concentration of  $Al^{3+}$  the rate of reaction decreases indicating the three electron transfer in the reaction, Addition of  $NaClO_4$  has catalytic effect on the reaction rate.

**Table – 2 Effect of Mn<sup>2+</sup>, Al<sup>3+</sup> and NaClO<sub>4</sub> on the reaction rate of dibenzalacetone at 308 K**

[S] = 1.5 × 10 <sup>-2</sup> mol dm <sup>-3</sup> , [OX] = 2.0 × 10 <sup>-3</sup> mol dm <sup>-3</sup>		[H <sup>+</sup> ] = 2.5 × 10 <sup>-1</sup> mol dm <sup>-3</sup> [cat] = 5.0 × 10 <sup>-3</sup> mol dm <sup>-3</sup>	
[Mn <sup>2+</sup> ] × 10 <sup>3</sup> mol dm <sup>-3</sup>	[Al <sup>3+</sup> ] × 10 <sup>3</sup> mol dm <sup>-3</sup>	[NaClO <sub>4</sub> ] × 10 <sup>3</sup> mol dm <sup>-3</sup>	k × 10 <sup>4</sup> s <sup>-1</sup>
2.5	-	-	4.98
5.0	-	-	4.53
7.5	-	-	4.25
10.0	-	-	4.01
-	2.5	-	4.99
-	5.0	-	4.72
-	7.5	-	4.53
-	10.0	-	4.31
-	-	2.5	5.07
-	-	5.0	5.18
-	-	7.5	5.22
-	-	10.0	5.32

**Effect of Temperature**

Kinetics of oxidation of dibenzalacetone and other substituted dibenzalacetone by INDC was carried out under pseudo-first order conditions. From a series of kinetic runs the rate constants *k* were estimated for some substituted dibenzalacetone at four different temperatures, viz. 303, 308, 313 and 318 K. The thermodynamic parameters were calculated using the Eyring's plot (Fig. 3) and the values are given in the Table 3.

**Fig. 3** The Eyring's Plot**Table – 3 Rate constant and activation parameters of dibenzalacetone**

[S] = 1.5 × 10<sup>-2</sup> mol dm<sup>-3</sup>  
[Phen] = 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>

[OX] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>  
[H<sup>+</sup>] = 6.0 × 10<sup>-1</sup> mol dm<sup>-3</sup>

substrate	k <sub>1</sub> × 10 <sup>5</sup> S <sup>-1</sup>				(ΔH <sup>#</sup> ) kJmol <sup>-1</sup>	(ΔG <sup>#</sup> ) kJmol <sup>-1</sup>	-(ΔS <sup>#</sup> ) Jmol <sup>-1</sup>	r
	303 K	308 K	313K	318 K				
H	43.1	50.8	66.6	76.3	29.18	94.90	-213.38	0.989
m-CH <sub>3</sub>	36.6	54.4	70.1	99.4	49.55	94.90	-147.25	0.997
m-NO <sub>2</sub>	21.7	32.9	41.1	56.5	21.12	94.58	-238.51	0.992
p-Cl	50.8	58.7	66.3	80.9	20.96	94.59	-239.05	0.989
p-NO <sub>2</sub>	5.55	7.57	9.36	11.2	34.53	99.96	-212.45	0.992
p-OCH <sub>3</sub>	60.7	98.4	162	226	68.36	93.30	-80.98	0.996
m-OCH <sub>3</sub>	77.9	85.8	95.5	109	15.37	93.62	-254.06	0.994
P-CH <sub>3</sub>	37.2	50.9	80.9	92.1	48.51	94.90	-150.60	0.981
P-Br	60.1	80.7	106	123	36.31	93.84	-186.81	0.991

The rate data for the oxidation of substituted dibenzalacetone gave only poor correlation with Hammett and Brown plot at 313K. This may be due to nature of the substituent.

The fairly high values of enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) indicate that the transition state is highly solvated. The negative values of the entropy of activation ( $\Delta S^\ddagger$ ) suggest extensive solvation of the transition state over the reactants.

It also reveals that the rate-determining step is less disorderly oriented relative to the reactants. As  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  do not vary linearly, no isokinetic relationship is observed. This indicates the absence of enthalpy entropy compensation effect [12].

Exner [13] criticized the validity of such a linear correlation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , as these quantities are dependent on each other. When the measurements at two different temperatures have been made, the data can be analyzed by the following equation.

$$\log(k)_{T_2} = a + b \log(k)_{T_1} \text{ where } T_2 > T_1$$

The plots of  $\log k_{\text{obs}}$  (303 K) versus  $\log k_{\text{obs}}$  (313 K) ( $r = 0.995$ ) and  $\log k_{\text{obs}}$  (303 K) versus  $\log k_{\text{obs}}$  (318 K) give straight lines with  $r = 0.993$  (Fig. 4). Such a good correlation indicates that all the substituent follow a common mechanism of oxidation.

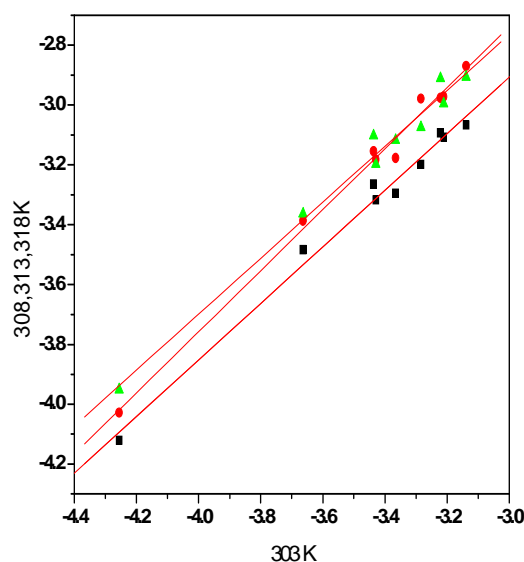
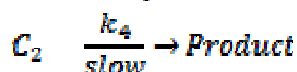
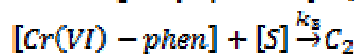
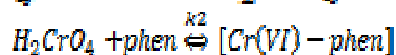


Fig. 4 The Exner Plot

#### Mechanism and rate law

Isonicotinium dichromate in aqueous acetic acid medium yields  $\text{HCrO}_4^-$  is the effective oxidizing species [14].



$$\text{Rate} = k_4 \text{C}_2$$

$$= k_3 k_4 [\text{C}_1] [\text{S}]$$

$$= \frac{k_2 k_3 k_4 [\text{S}] [\text{phen}] [\text{Cr(VI)}]}{[1 + k_2 [\text{phen}]]}$$

$$= \frac{k_1 k_2 k_3 k_4 [\text{S}] [\text{H}^+] [\text{phen}] [\text{Cr(VI)}]}{\{1 + k_1 [\text{H}^+]\} \{1 + k_2 [\text{phen}]\}}$$

$$k_{\text{obs}} = \frac{k_1 k_2 k_3 k_4 [\text{S}] [\text{H}^+] [\text{phen}]}{\{1 + k_1 [\text{H}^+]\} \{1 + k_2 [\text{phen}]\}}$$

[S] = [DBA], [Phen] = [1,10-phenanthroline]

### CONCLUSION

The title oxidation studies revealed that order with respect to oxidant, substrate followed unit order dependence and fractional order dependence with respect to  $[H^+]$ , 1, 10-Phenanthroline. Addition of perchloric acid and 1, 10-Phenanthroline enhances the rate of reaction. The negative value of  $\Delta S^\ddagger$  and small positive magnitude of  $\Delta H^\ddagger$  shown the possibility to form the intermediate complex. Correlation of Isokinetic plot indicates that all the substituents undergo a common mechanism pathway.

### REFERENCES

- [1] J Dharma Raja; K Krishnasamy; M Shanmugam. *E-Journal of Chemistry.*, **2008**, 5, 754.
- [2] Pravesh Kumar; Dinesh Panday; Seema Kothari. *Croat Chem Acta.*, **2011**, 84 53.
- [3] G Mangalam; S Meenakshisundaram. *J Chem Soc.*, **1991**, 68, 77.
- [4] S Kabilan; M Uma; K Krishnasamy; P Sankar. *J Indian Council Chem.*, **1994**,10, 21.
- [5] F Mares; J. Rocek; J. Sicher. *Coll. of Czech. Chem. Commun.*, **1961**, 26, 2355.
- [6] J. Rocek; F. Mares. *Coll. of Czech. Chem. Commun.*, **1959**, 24, 2741.
- [7] DD Sung; PA Nadar. *Bull. Korean Chem. Soc.*, **1999**, 20, 1487.
- [8] F. Freeman; NJ Yamachika. *Tetrahedron Letters.*, **1969**, 41, 3615.
- [9] RE Lutz; TA Martin; JE Codington; TM Amacker; RK Allison; NH Leaks; RJ Rowlett Jr; JD Smith; JW Wilson. *J. Org. Chem.*, **1949**, 14, 993.
- [10] C Lopez; A Gonzalez; FD Cossio; C Palomo. *Synth. Commun.*, **1985**, 15,1197.
- [11] A Weissberger; ES Proskauer. *Organic solvents physical properties and Method of Purifications*. 2<sup>nd</sup> edition, Interscience publishers Ltd., London,**1955**, 390.
- [12] MG Alder; JE Lefter. *J. Am. Chem. Soc.* **1954**, 76, 1425.
- [13] O Exner; *Coll Czech. Chem. Commun.*, **1964**, 29, 1094.
- [14] AN Palaniappan; C Raju; S srinivasan. *Oxidation.commun*, **2010**, 33, 77