

## **Research Articles**

### **KINETICS OF OXIDATION OF HALO-SUBSTITUTED MANDELIC ACIDS BY NICOTINIUM DICHROMATE**

**Shakuntala Mishra<sup>1</sup> and M.U. Khan<sup>2</sup>**

<sup>1</sup>Department of Chemistry, A.P.S. University, Rewa (M.P.)-486003, India.

<sup>2</sup>Retd. Principal Govt. P.G. College Budhar, Dist. Shahdol, (M.P.), India

<b>Received:</b> 12/10/2017	<b>Revised:</b> 02/11/2017	<b>Accepted:</b> 06/12/2017
-----------------------------	----------------------------	-----------------------------

#### **ABSTRACT**

The kinetics of para-halosubstituted mandelic acids by Nicotinium dichromate in aqueous acetic acid medium were investigated in presence of H<sub>2</sub>SO<sub>4</sub> at 303 and 308 K respectively. The velocity of the reaction was found to vary as first-order dependence of [NDC] and [H<sup>+</sup>] and fractional-order dependence on [substrates]. The complex nature of kinetics was observed between oxidant's active species and substrate. The primary salts had no effect on oxidation velocity. The reaction velocity accelerated with decrease in dielectric constant of the medium. The mole ratio 1:1 involved in the reaction, was determined stoichiometrically. The p-halo benzaldehydes were identified as end-products by existing standard methods. The various thermodynamic parameters were evaluated. The plausible scheme of mechanism and reactivity was proposed in conformity with the kinetic findings.

**Key words :** plausible, trend, versatile, polymerisation, conformity.

#### **INTRODUCTION**

The Nicotinium dichromate (NDC) is a tobacco alkaloid salt of Cr (VI) was first introduced by Lopez<sup>1</sup> et al. (1965) as an oxidant with two-electron system. A perusal of the literature shows that the reactivity of protonated species of NDC that attacks at negatively created centre of hydroxyl or carboxyl functional groups is limited and scanty. Its degradation action and hidden potentiality is little explored in the study of chemical reactions in acidic medium.

The hydroxyacids are bi-functional compounds containing carboxyl and hydroxyl functional groups (secondary alcoholic group) leads to different modes of

oxidation. The mechanistic steps suffer either a C–H cleavage or C–C fission depending upon the reaction conditions in above probe. The available survey pertaining to the previous work done on the oxidation of aromatic hydroxy acids by other oxidants such as halogens<sup>[2]</sup>, NBS<sup>[3]</sup>, CAB<sup>[4]</sup>, KMnO<sub>4</sub><sup>[5]</sup>, H<sub>2</sub>CrO<sub>4</sub><sup>[6]</sup>, K<sub>2</sub>CrO<sub>7</sub><sup>[7]</sup>, NCSA<sup>[8]</sup>, etc. have drawn considerable attention of several national and international laboratories. Although NDC has been used as a versatile oxidant in the oxidation kinetics of a number of compounds such as 2-naphthol<sup>9</sup>, Anthranyl styrlketone<sup>10</sup>, Anilines<sup>11</sup> etc. The ambiguity still exists in the mechanistic approaches in terms of reactivity, structural alternation, electronegativity, rate and equilibrium constant in this system. However no systematic kinetic probe has been documented with it. This prompted me to explore the kinetics of p-chloro, and p-bromo mandelic acids oxidation by NDC in acidic medium, which may help in understanding of the complex mechanism and other untraced side effect associated with the system.

## EXPERIMENTAL

All the chemicals required in this investigation were of standard analytical grade. The solution of NDC was prepared in 100% acetic acid (E. Merck) and standardized iodometrically<sup>12</sup> against standard sodium-thiosulfate, solution using starch as an indicator. The p-chloro and p-bromo mandelic acids solutions were prepared in requisite volume of CH<sub>3</sub>COOH- water mixture. The kinetic measurements were made under the condition [substrate] >> [NDC] [H<sup>+</sup>] at constant ionic strength. The solutions were kept in a reaction vessel maintained at constant temperature in a thermostat with an accuracy of  $\pm 0.1^{\circ}\text{C}$ . The progress of the reaction was monitored by withdrawing aliquotes at definite intervals of time and the unreacted NDC was estimated by titrating it against standard hypo- solution iodometrically. The experimental data obtained were fed into integration rate equation for evaluation of rate constant.

## RESULTS AND DISCUSSION:

All the reactions under investigation are homogeneous and characterized by induction period which can be accounted in terms of slow approach of the steady state. The probe indicated the first-order dependence of reaction rate on oxidant [NDC], while order varies from 1 to 0 for substrates (Table-1). The double reciprocal

plot drawn between  $k^{-1}$  vs.  $[\text{substrate}]^{-1}$  is linear with positive intercept on y-axis (Fig.1) provide confirmatory evidence about the formation of complex between oxidant's species  $\text{H}_2\text{CrO}_4$  and substrates. An increase in rate has been found proportionately to the increase in  $[\text{H}_2\text{SO}_4]$ . Thus showing first-order dependence in acid (Table-2 & Fig.2) The acid catalysis may be attributed to the protonated species of NDC which may exist in the solution and facilitates in complex formation. It is observed that rate of reaction increases with diminishing in dielectric constant of the medium.

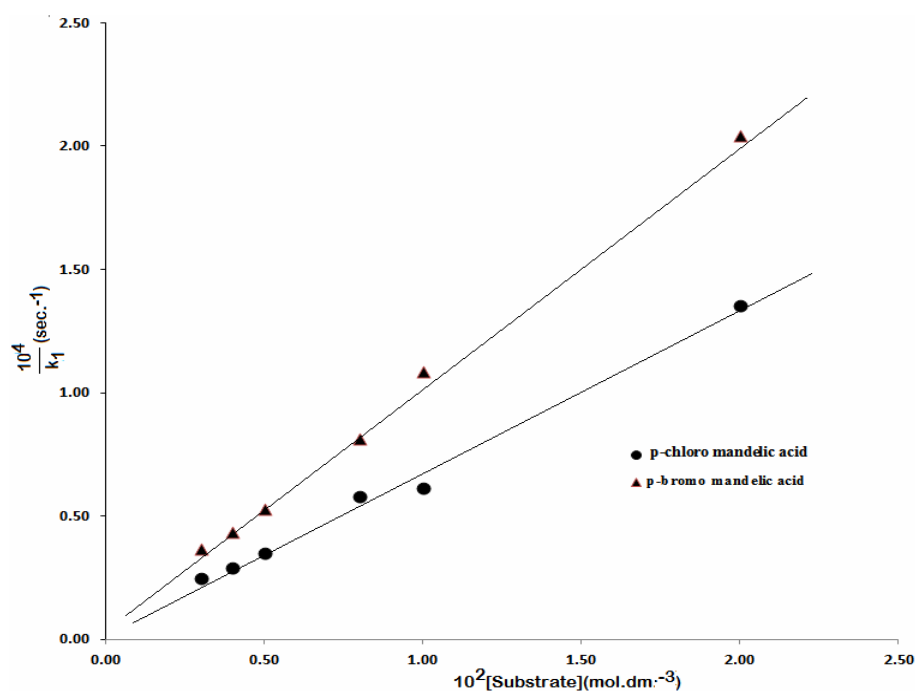


Fig.1

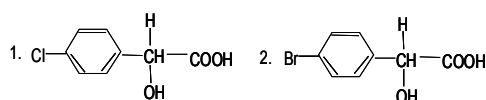
The additions of foreign catalysts  $\text{Cu}^{++}$  ions indicate an increase in reaction velocity whereas  $\text{Mn}^{++}$  ions show retardation trend. The study failed completely to induce the polymerisation of olefinic monomer acrylonitrile in the present system suggests that ionic mechanism is operative and rules out the existence of free radicals in the system.

Table: 1

**Dependence of rate on variation of concentration of Substrates**

$10^3 \times [\text{NDC}] (\text{mol dm}^{-3})$	= 2.00 (1, 2) ;
$10^2 \times [\text{H}^+] (\text{mol dm}^{-3})$	= 1.0 (1, 2) ;
HOAc-H <sub>2</sub> O %, (v/v)	= 20 (1, 2) ;
Temperature K	= 303 (1), 308 (2)

S. No.	[Substrates] $\times 10^2$ (mol dm <sup>-3</sup> )	p-chloro mandelic acid (1)	p-bromo mandelic acid (2)
		$\longleftrightarrow 10^4 k (\text{s}^{-1}) \longrightarrow$	
1.	0.50	0.74	0.49
2.	1.00	1.63	0.92
3.	1.25	1.73	1.23
4.	2.00	2.86	1.90
5.	2.50	3.47	2.31
6.	3.33	4.05	2.72



le: 2

**Dependence of rate on the concentration of Sulphuric acid**

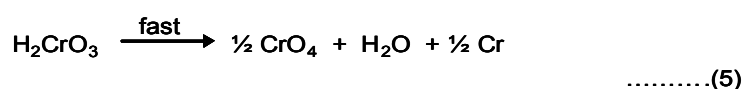
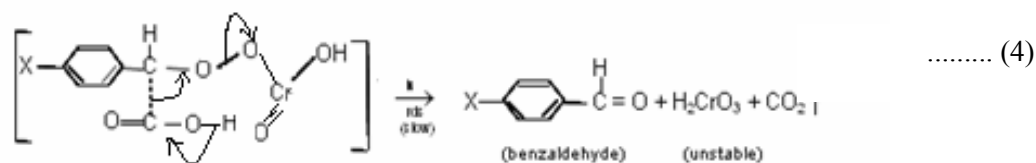
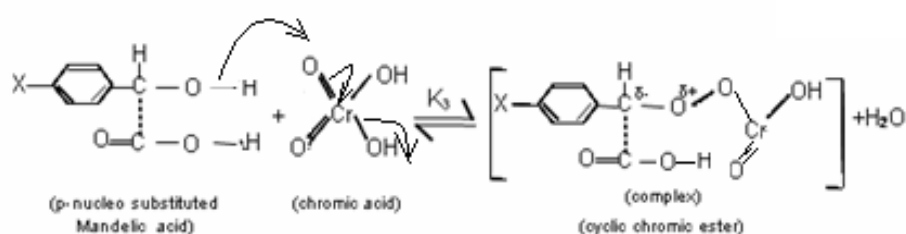
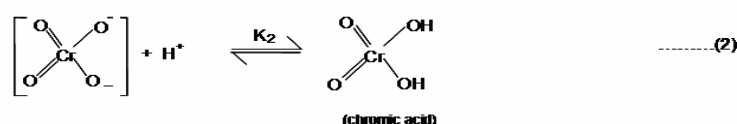
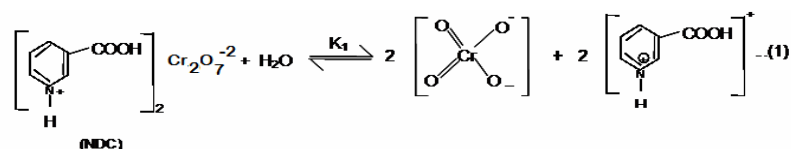
$10^3 \times [\text{NDC}] (\text{mol dm}^{-3})$	= 2.00 (1, 2) ;
$10^2 \times [\text{Substrate}] (\text{mol dm}^{-3})$	= 1.0 (1, 2) ;
HOAc-H <sub>2</sub> O %, (v/v)	= 20 (1, 2) ;
Temperature K	= 303 (1), 308 (2)

S. No.	[H <sup>+</sup> ] $\times 10^2$ (mol dm <sup>-3</sup> )	p-chloro mandelic acid (1)	p-bromo mandelic acid (2)
		$\longleftrightarrow 10^4 k (\text{s}^{-1}) \longrightarrow$	
1.	0.50	1.20	1.10
2.	1.00	2.26	1.82
3.	1.25	2.86	2.32
4.	2.00	4.52	3.71
5.	2.50	5.61	4.62

The stoichiometric measurement indicated mole ratio 1:1 for oxidant and substrate under study. The p-chloro and p-bromobenzaldehydes were isolated as the corresponding main (characterized) oxidation products of the reactions, identified chromatographically and also by existing conventional methods.

**Mechanism**

Based on experimental findings a plausible mechanism for the kinetics exploration of p-halo substituted mandelic acids with NDC has been proposed in the following steps :



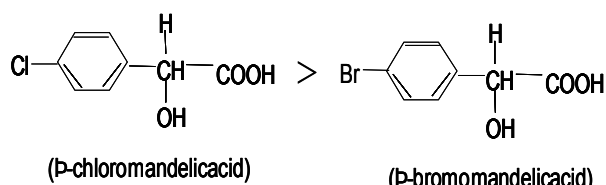
where, X = -Cl and -Br for corresponding p-halo substituted mandelic acids.

Taking into consideration, the various steps involved in the proposed scheme of mechanism, the final rate equation could be derived as :

$$k_{\text{obs}} = \frac{K_1 K_2 k [\text{XMA}] [\text{H}^+]}{[\text{Nicotinic acid}] K_1 + K_1 [\text{H}^+] + K_1 K_3 [\text{XMA}] + [\text{H}^+]} \quad (6)$$

The validity of rate law was tested by making some assumptions. The intercept on Y-axis of double reciprocal plot drawn between  $1/k_{\text{obs}}$  vs.  $1/[\text{X-MA}]$  (Fig.1) explains clearly the first to fractional order and illustrated complex mechanism of the reactions.

The observed order of reactivity among the substrates studied was found as:



The above order of the reactivity also supports the rate determining decarboxylation involving cleavage of  $C_1 - C_2$  bond as the transition state here is electron deficient. The  $C_1$  is site of oxidation whereas  $C_2$  the site of decarboxylation. The electron attracting groups such as  $-Cl$  and  $-Br$  retard the rate of oxidation due to destabilization of transition state. Similar trend was also observed in  $Ce(IV)^{13}$ , Chromic acid<sup>6</sup> and  $NDC^{14}$  oxidation of mandelic acids. The thermodynamic values of parameters are well in accordance with the reactivity trend. The high negative value of  $\Delta S^\ddagger$  ( $-76.90$  to  $-60.94 \text{ JK}^{-1} \text{ mol}^{-1}$ ) suggests the ability of  $H_2CrO_4^-$  to react with substrates. The  $\Delta G^\ddagger$  is approximately constant ( $84.10$  to  $87.72 \text{ kJ mol}^{-1}$ ) indicate that the similar mechanism prevails in the system. The iso-kinetic temperature  $\beta$  is  $321.3 \text{ K}$  well above the experimental temperature obviously suggests that the reactions are enthalpy controlled.

## REFERENCES

1. Lopez, C., Gonzalez, C., Cossio, F.P. and Palmo, C. : Synth. commun. 15, 1197 (1965).
2. Tapodi, H.P., Shanker, R. and Bakore, G.V. : Indian J. Chem., 19, 330, (1980).
3. Bishnoi, M.L., Negi, S.C. and Banerji, K.K. : Indian J. Chem., 25, 660, (1986).
4. Mathur, A.K., Sharma, V. and Banerji, K.K. : Indian J. Chem., 27, 123, (1988).
5. Bakore, G.V., Shanker, R. and Goyal, U. : Indian J. Chem., 1, 331, (1963).
6. Sundaram, S. and Venkatasubramanian, N. : Curr. Sci., 33, 646, (1967).
7. Saran, N.K., Acharya, R.C. and Rao, S.R. : J. Indian Chem. Soc., 62, 747, (1985).
8. Singh, V.P., Khan, M.U., Chauhan, D.B.S. and Verma, J.K. : Oxid. Commun. 20(1), 124-131, (1997).
9. Vellaisamg, M., Suryakala, K. and Ravishanker, M. : J. Chem. Pharm. Res, 3(5), 678-681 (2011).
10. Palaniappan, A.N., Vaideki, S., ShriNivasan, S., and Raju, C. : J. Chem. Pharm. Res., 4(1), 640-647 (2012).
11. Durvas, S., Bhuraneshwani, Kuppanagounder, and Elango, K.P. : J. Indian Chem. Soc., 60(b), 1105-1111, (2003).
12. Barkat, M.A. and Abdel Wahab, W.F. : Analyst, Chem. 26, (1954).
13. Dayal, R. and Bakore, G.V. : J. Indian Chem. SOC., 49, 1093, (1972).
14. Soni, Mamta, Mishra, Shakuntala, and Khan, M.U. : J. Chemtracks, 16(1), 73-78, (2014).