“Study on oxidation of some substituted aromatic alcohols by N-bromophthalimide benzhydrol by n-chlorosuccinimide in aqueous acetic acid medium”

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Abstract

The oxidation of para-methyl and para-chloro benzyl alcohols have been investigation at 308K by N-bromophthalimide in aqueous acetic acid medium. The reaction is first-order with respect to [NBP], [Substrate]. The $[H^+]$ has shown insignificant change in rate constant. The addition of reduced product phthalimide of the oxidant has shown slight retarding effect on the reaction rate whereas added primary salt show negligible effect. The reaction velocity accelerated with a decrease in dielectric constant of the medium. The corresponding benzaldehydes were identified as the main oxidation product of the reactions. The various activation parameters have been evaluated from Arrhenius plot by studying the reaction at different temperatures. A suitable mechanism consistent with the experimental findings has been proposed and appropriate rate law is deduced to account for the observed kinetic data.

Key Words : delocalization, probe, deterioration, exhibit, significance.

Introduction

N-bromophthalimide (NBP) halo-compound is known to be non-hazardous, versatile, oxidizing agent. It is economically cheap, stable and mild oxidant containing two acyl groups attached with > N-Br provides a large orbital for the electron de-localisation, that is, why, it is being used in kinetics, analytical and input technology. The kinetics of oxidation of substituted benzyl alcohols by CAT,[1] H_2O,[2] oxone,[3] etc. has already been reported by different authors by variety of oxidants. The NBP has been employed in the oxidation of hydroxyacids[4], benzhydrols[5], and amines[6]. However oxidation of p-substituted methyl and para-substituted chloro benzyl alcohols by NBP in aqueous acetic acid medium is not acclaimed so far and hence need for the probe.

Experimental

All the chemical used in the present text of investigation were of analytical grade. NBP was prepared in 100% acetic acid (BDH) and its purity was checked iodometrically. It was stored in Amber coloured flask to save it from the action of diffused day light which alters, appreciably its concentration. The substrates were prepared in acetic acid kinetics runs were carried out under pseudo-first order conditions [Substrates] >> [NBP]. Requisite amounts of para-substituted benzyl alcohols, acid, and aqueous acetic acid were taken in colouring glass reaction vessel placed in a thermostat with an accuracy $\pm 0.1^0$C maintained at the desired temperature for half an hour. The reaction was initiated by rapid addition of NBP solution and progress of the reaction was followed by estimating iodometrically, the amount of unconsumed NBP at regular intervals of time.

Results and Discussion

The kinetics data of para-methyl and para-chloro benzyl alcohols by NBP was collected of five-fold concentrations of the reactants keeping the other parameters constant. The oxidation proceeds smoothly at 308 K under the experimental conditions. The rate of reaction varies as a first power of [NBP]. The constancy of pseudo first-order rate constant at different [substrates] at constant

[NBP] was observed (Table-1) The plot of k^{-1} vs. $[\text{substrate}]^{-1}$ passes through the origin indicated first-order kinetics with substrates (Fig.1).

Table :1

Dependence of rate on the oxidation of p-substituted benzyl alcohols by NBP

10^3 [NBP] (mol dm^{-3}) = 2.50 (1, 2);
10^2 [H$^+$] (mol dm^{-3}) = 1.0 (1, 2,) ;
$CH_3COOH-H_2O$ %, (v/v) = 20 (1, 2) ;
Temp. K = 308 (1, 2).

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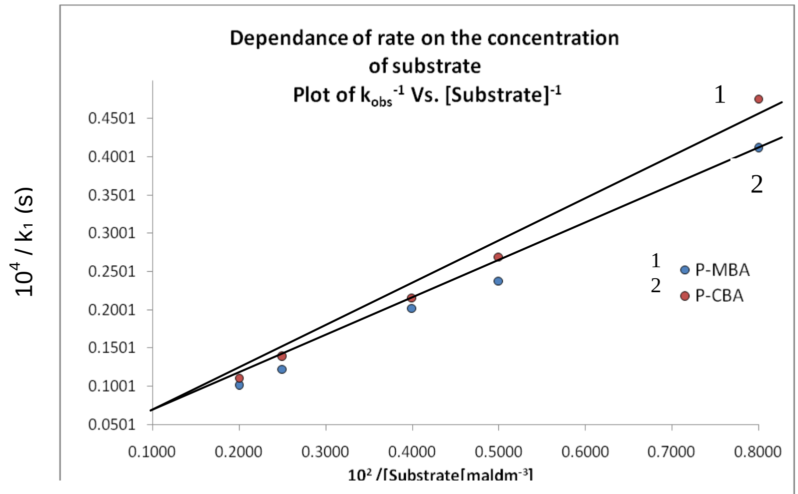
S.No.	**Concentration of substrate ×10^2 (mol dm^{-3})**	**Þ-methylbenzyl alcohols (1)**	**Þ-chlorobenzyl alcohols (2)**
		⟵ 10^4 k_1 s^{-1} ⟶	
1	1.25	2.43	2.10
2	2.00	4.21	3.71
3	2.50	4.95	4.63
4	3.33	-	6.09
5	4.00	8.17	7.20
6	5.00	9.90	9.00

1. p-methylbenzyl alcohol 2. p-chlorobenzyl alcohol



1. para-methyl benzylalcohol 2. para-chlorobenzyl alcohol

10^3 x [NBP] (mol dm^{-3}) = 2.50 (1, 2, 3) ;
10^2 x [H$^+$] (mol dm^{-3}) = 1.0 (1, 2, 3) ;
$HOAcH_2O$ % (v/v) = 20 (1, 2, 3) ;
Temp. K = 308 (1, 2, 3)

The order with respect to $[H^+]$ was found unity. The reaction was found acid catalysed. The reaction velocity increases with increases in dielectric constant of the medium (Table-2). The plot of log k Vs. 1/D was obtained linear with positive slope on y-axis (Fig.2). Addition of KCl and NaCl have no significant effect on the reaction, rate while addition of reductant product phthalimide retards the rate of oxidation. The end-products substituted benzaldehydes etc. have been identified by modern physical existing methods. The over all stoichiometric determination suggested 1:1 mole ratio involved in oxidation process under investigation.

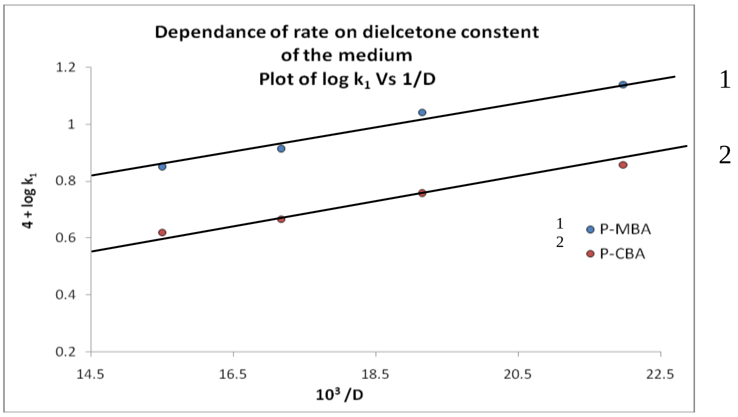
$$\phi\ C_6H_4CH_2OH + C_6H_4\ (CO)_2\ NBr \longrightarrow \phi\ C_6H_4CHO + C_6H_4\ (CO)_2\ NH + HBr$$

Table :2

Dependence of rate on dielectric constant of the medium

10^3 [NBP] (mol dm^{-3}) = 2.50 (1, 2);
10^2 [Substrate] (mol dm^{-3}) = 4.00 (1), 2.50 (2);
10^2 $[H^+]$ (mol dm^{-3}) = 1.0 (1, 2,) ;
Temp. K = 308 (1, 2)

S. No.	HOAc-H_2O % (v/v)	$\frac{10^3}{D}$	p-MBA (1)	p-CBA (2)
			⟵ 10^4 k_1 (s^{-1}) ⟶	
1	10	15.50	7.07	4.17
2	20	17.17	8.17	4.63
3	30	19.15	11.00	5.70
4	40	21.98	13.80	7.20



1. para-methyl benzylalcohol 2. para-chlorobenzyl alcohol

Fig. 2

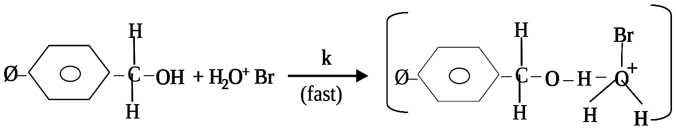
10^3 x [NBP] (mol dm^{-3}) = 2.50 (1, 2, 3) ;
10^2 x [Substrate] (mol dm^{-3}) = 4.00 (10) 2.50 (2,3) ;
10^2 x [H$^+$] (mol dm^{-3}) = 1.0 (1, 2, 3) ;
Temp. K = 308 (1, 2, 3)

Mechanism

Under the experimental condition, H_2O^+Br has been regarded as the powerful prime reactive oxidizing species of NBP, ruling out Br_2 and HOBr by certain experimental reasons. The effective species H_2O^+Br has also been earlier reported by a couple of researchers in NBP oxidations of aliphatic alcohols[7], benzhydrols, and hydroxy acids[8]. The scheme of mechanism was proposed as :

$$\text{NBP} + H_2O \overset{K_1}{\rightleftharpoons} \text{HOBr} + \text{Phthalimide} \quad .....(1)$$

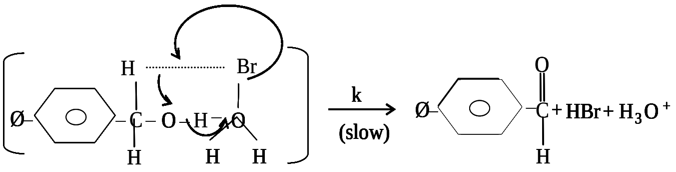
$$\text{HOBr} + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+\,Br \quad .... (2)$$



……. (3)

(Substrate)

Where, Ø = -Cl – CH_3



….. (4)

(products)

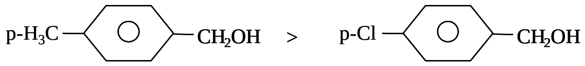
$$\text{The derived rate law} = \frac{k\,k_1\,k_2\,[\text{substrate}]\,[H^+]}{[Ph] + k_1}$$

where S = substrate

which explain all the experimental facts.

It is well known fact that electron releasing group (CH_3) accelerate the rate while electrons withdrawing group like Cl electron retarded the rate of oxidation. The introduction of substituents o different nature in aromatic ring exhibiting inductive and +M and --M effects causes about order of reactivity which is further supported by the energy of activation (Ea) which depends upon the tendency of substitutents group two release of withdraw electrons. . (Ea= 40.01, and 43.31 kJ mole $^{-1}$ for 1,2 respectively).

The observed reactivity for the present to investigation was found as :



The dielectric constant of the medium explains the reaction between two dipoles in the rate determining step, which is in good agreement with Kirkwood theory[9]. The high positive[10] values of free energy of activation (85.76 and 85.77 KJ mole for 1,2) indicate that similar mechanism prevails in the system shows that the reaction is enthalpy controlled.

The value of isokinetic temperature β (322 K) evaluated is above the experimental temperature the value of σ , para-substituted benzyl alcohol obey Hemmat equation.

$$\log \frac{k}{k_o} = \sigma p$$

The methyl group attached to the benzene ring alters the stability of the carbocation by dispersing or intensifying the positive charge depending upon its electron releasing or electron withdrawing nature. The inductive effect stabilized the developing the positive charge in the transition state and thus leads to a faster reaction. Hence the order of reactivity.

Conclusion

1. The study will furnished an ampoule of precious wealth of formation about the nature, stages of reaction with various environmental changes occurring during the interaction in the oxidant substrate system.
2. The fruitful outcome of the kinetic studies can be suitably applied in the field of pharmaceuticals, dyes radioactivity, thermogravimetry, biochemistry[11-18], Hi-tech, pharmacodynamics, pharmacokinetics, electronegativity and also in MO theory.
3. The kinetic study has shed recently a new light in calculating the growth of malignacy in carcinoma, blood circulation[16] in body and in biochemical reaction occurring in bio-system.[19-21]
4. The technique has proved very useful in calculating beats/ pulses in diffusion of pool of blood in cardiac disease through semipermeable membrane.
5. This work can better and suitably be utilized in same branches of science to which kinetics is relevant are organic chemistry, Bacterial growth, flow process, Chemical engineering, Electrochemistry.

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