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Analytical and Kinetic Behaviour of N-Bromoimide-mercuric Acetate System towards Aromatic Aldehydes: A Mechanistic Study

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The oxidative kinetics of benzaldehydes, *viz.*, 4-bromo, 4-chloro, 4-methyl, 3-nitro benzaldehydes has been carried out by N-bromophthalimide in presence of excess of mercuric acetate in aqueous acetic acid medium. Results of detailed kinetic effects, *viz.*, solvent, temperature, concentration and salt effects, support the Michaelis. Menten type of mechanism. The stoichiometric ratio of N-bromophthalimide : benzaldehyde, was 1 : 1. The product of oxidation was benzoic acid, which was confirmed by HPLC and spot tests. Thermodynamic and activation parameters have been presented. Effect of substituents has been dealt with and order of reactivity established.

Key Words: N-Bromophthalimide, Benzaldehyde, Phthalimide, Kinetic study.

INTRODUCTION

The kinetics and mechanism of oxidation of benzaldehydes has been reported by various oxidants[1–8], *viz.*, permanganate, cerium(IV), chromic acid, vanadium(V), hexachloroirridate(IV), cobalt(III), manganese(III), bromine and diperiodatocuprate(III). A survey of literature on oxidation of benzaldehydes by various oxidants reveals that although the products of oxidation are benzoic acids, the oxidation takes place through one of the following mechanisms : (i) formation of ester intermediate between the substrate and the oxidant followed by the decomposition of the ester to give products[1–3]. (ii) Formation of free radicals due to fission of C—H bond followed by the reaction of the free radical with the oxidant to give products[4–10]. In continuation of our study on benzaldehydes[11], herein, the kinetic study of oxidation of benzaldehydes in aqueous acetic acid medium with N-bromophthalimide (NBP) in presence of mercuric acetate is reported. The various benzaldehydes studied are: 4-bromo benzaldehyde, 3-nitro benzaldehyde, 4-methyl benzaldehyde, 4-chloro benzaldehyde by NBP in aqueous acetic acid medium in presence of $Hg(OAc)_2$ in presence of excess of mercuric acetate.

EXPERIMENTAL

Under the conditions, [N-bromophthalimide] ≫ [benzaldehyde], stoichiometry has been carried out in the presence of excess of $Hg(OAc)_2$ in nitrogen atmosphere. The unreacted [NBP] was estimated iodometrically. The stoichiometry of the reaction was found to be that 1 mol of NBP was required to oxidize 1 mol of benzaldehyde. The stoichiometric equation is given as

$$PhCHO + NBP + H_2O \longrightarrow PhCOOH + NHP + HBr$$

The product of oxidation was found to be benzoic acid, which was detected by conventional tests and HPLC technique.

HPLC system used for the analysis of products was Shimadzu LC-10AT equipment with a dual piston-pump system, a solvent programmer and a Rheodyne injector model 7725 fitted with 20 μ loop. A prepacked octadecylsilyl silica gel ODS (mean particle size 5 μm) Hypersil column 25–0.46 cm was used. The column effluents were monitored at 280 nm, using variable wavelength SPD-10A UV-Visible detector equipped with 8 μL flow cell and attached to a C-R7Ae plus chromatopac integrator. Samples were eluted with aqueous solutions containing 10% (v/v) methanol and buffered with 10 mM KH_2PO_4 solution adjusted to pH 7. Before use the phosphate buffer was filtered through a millipore type HA 0.45 μm membrane filter. All the mobile phases were degassed using a vacuum pump. The solvent flow rate was kept constant at 0.5 mL/min and all the HPLC runs were carried out at ambient temperature.

RESULTS AND DISCUSSION

The reactions were conducted in 30% acetic acid medium under the conditions [NBP] ≪ [benzaldehyde] in the presence of excess of $Hg(OAc)_2$ under nitrogen atmosphere. The plot for log a/(a – x) *vs.* time was linear showing a first order dependence of rate on [NBP] (r = 0.99) (Fig. 1).

From the slopes of such plots, pseudo first order rate constants (k′) were evaluated. The rate constants (k′) have been found to increase with increase in [benzaldehyde] and the plots of log k′ *vs.* log [benzaldehyde] were linear with slope less than unity for all the benzaldehydes indicating a fractional order dependence of rate on [benzaldehyde]. Plots of 1/k′ *vs.* 1/[benzaldehyde] were linear with intercept on 1/k′ axis (Fig. 2). At constant [benzaldehyde] and [NBP], addition of KCl had negligible effect on the rate (Table-2). At constant [benzaldehyde] and [NBP], addition of $[H^+]$ decreased the rate of oxidation reaction (Table-2).

Variation of [phthalimide], the reduced product of NBP, [mercuric acetate] had

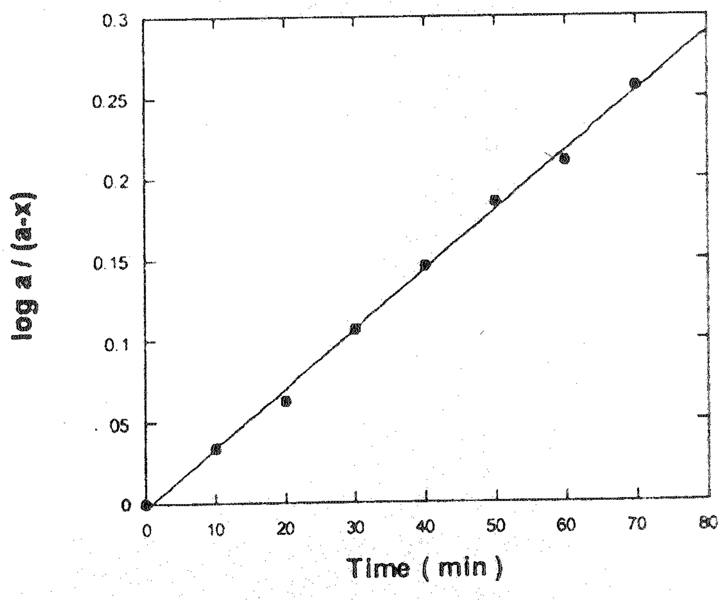


Fig. 1. Order in [NBP] in the oxidation of benzaldehyde by NBP in aqueous acetic acid medium.
$[NBP] = 1 \times 10^{-3}$ mol dm^{-3} ; $[benzaldehyde] = 1 \times 10^{-2}$ mol dm^{-3}
$[Hg(OAc)_2] = 2 \times 10^{-3}$ mol dm^{-3} ; [HOAc] = 30% (v/v); Temp = 303 K

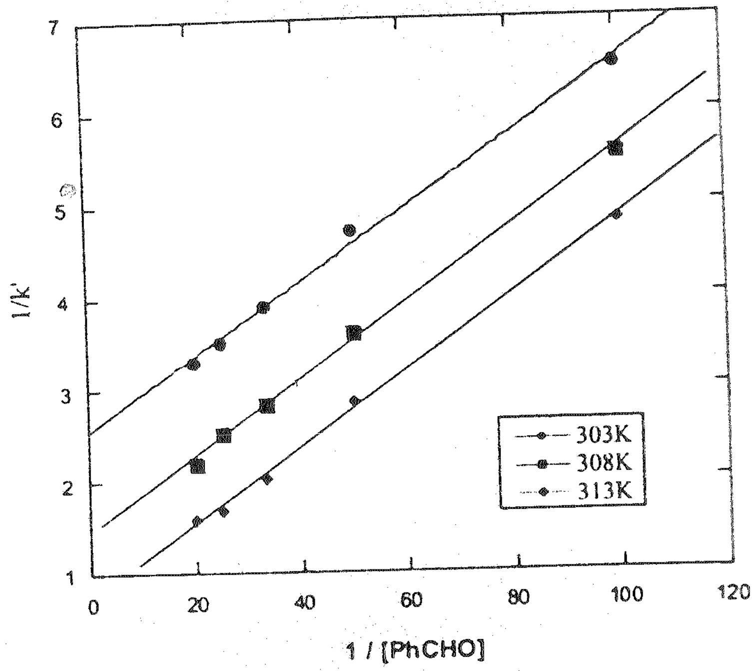


Fig. 2. Effect of [benzaldehyde] on k' in NBP-benzaldehyde [PhCHO] reaction at different temperatures and search for complex formation: A kinetic evidence
[NBP] = 1×10^{-3} mol dm^{-3}; [HOAc] = 30% (v/v); [Hg(OAc)$_2$] = 2×10^{-3} mol dm^{-3}

negligible effect on the rate (Table-2). An increase in acetic acid composition in the reaction mixture decreased the reaction rate at constant [benzaldehyde] [NBP] and ionic strength (Table-1, Figs. 3 and 4).

TABLE-1
EFFECT OF SOLVENT ON k' IN THE OXIDATION OF BENZALDEHYDE BY NBP IN AQUEOUS ACETIC ACID MEDIUM

[PhCHO] = 1×10^{-2} mol dm^{-3}
[Hg(OAc)$_2$] = 2×10^{-3} mol dm^{-3}
[NBP] = 1×10^{-3} mol dm^{-3}
Temp = 303 K

AcOH (%)	Dielectric constant, D	10^3/D	10^2(D-1)/(2D + 1)	10^5 k' (s^{-1})	5 + log k'
30	52.2	19.2	48.6	9.89	0.995
40	45.5	22.0	48.4	9.00	0.954
50	39.0	25.6	48.1	8.15	0.911
60	32.4	30.9	47.7	7.15	0.854
70	26.1	38.4	47.2	6.00	0.778

The absence of free radicals in the reaction system was confirmed by adding acrylamide or acrylonitrile which were not polymerised.

Reactive Species and Mechanism

N-bromophthalimide (NBP) like other N-halomides exists in various forms in acid medium, *i.e.*, free NBP, protonated NBP, *i.e.*, (NBPH)$^+$, HOBr and H_2O^+Br according to the following equilibrium:

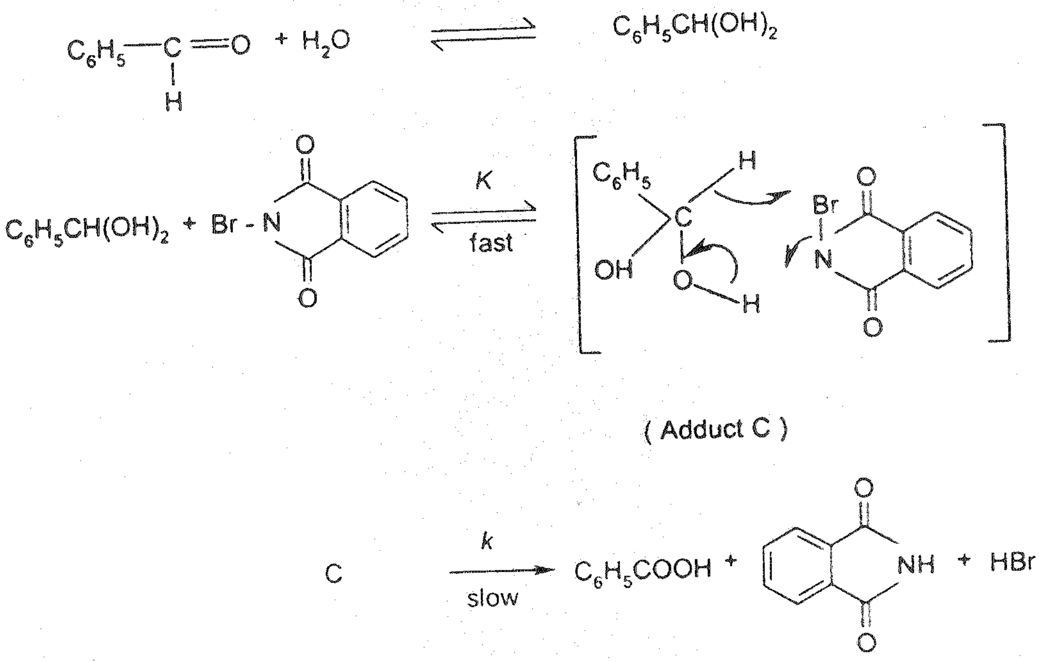
$$\text{NBP} + \text{H}^+ \rightleftharpoons \text{NHP} + \text{Br}^+$$

$$\text{NBP} + \text{H}^+ \rightleftharpoons (\text{NBPH})^+$$

$$NBP + H_2O \rightleftharpoons HOBr + NHP$$

$$HOBr + H^+ \rightleftharpoons (H_2O^+Br)$$

The rate of oxidation of benzaldehydes by NBP was found to decrease with the increase in [H^+] (Table-2). On the basis of this the possibility of $(NBPH)^+$ as the reactive species could be ruled out in the oxidation of benzaldehydes by NBP. Br^+ and $(H_2OBr)^+$ cannot be the reactive species as the reactions were carried out in the absence of mineral acid. If HOBr were to be the reactive species, the rate should have indicated inverse dependence on [NHP] (phthalimide) (Table-2), which is not observed in the present investigation. We, therefore, assume that free NBP could be the most probable oxidizing species under the experimental conditions employed.



Scheme

TABLE-2

EFFECT OF IONIC STRENGTH (KCl), [H^+], PHTHALIMIDE (NHP), MERCURIC ACETATE ON k′ IN THE OXIDATION OF BENZALDEHYDE BY NBP

$10^2 \times [A]$ (mol dm^{-3})	A = KCl, $10^4 \times k'$ (s^{-1})	A = H_2SO_4 $10^4 \times k'$ (s^{-1})	A = NHP $10^4 \times k'$ (s^{-1})	$10^2 \times [Hg(OAc)_2]$ (mol dm^{-3})	$10^4 \times k'$ (s^{-1})
0.00	1.32	13.2	1.32	2.00	1.32
1.00	1.25	8.67	1.34	3.00	1.20
2.00	1.19	7.71	1.42	4.00	1.18
3.00	1.06	7.25	1.50	5.00	1.12
4.00	1.00	6.75	1.55	6.00	1.08

The rate showed a first order dependence on [NBP] and fractional order dependence on [benzaldehyde], which indicates that the reaction proceeds through the formation of an adduct in the pre-equilibrium step. This adduct dissociates in a slow rate-determining step to give final products. On the basis of observed kinetic results the mechanism of oxidation of benzaldehyde by NBP can be written as:

The effect of solvent was studied and this effect supported the participation of neutral molecules (benzaldehyde and NBP) in the reaction. The plot of log k′ *vs.* 1/D was found to be linear with negative slope and a plot of log k′ *vs.* (D – 1)/(2D + 1) was found to be linear with positive slope (Figs. 3 and 4) which supports the above proposition. The insignificant salt effect (Table-2) was observed which suggests that the reaction involved neutral molecular species.

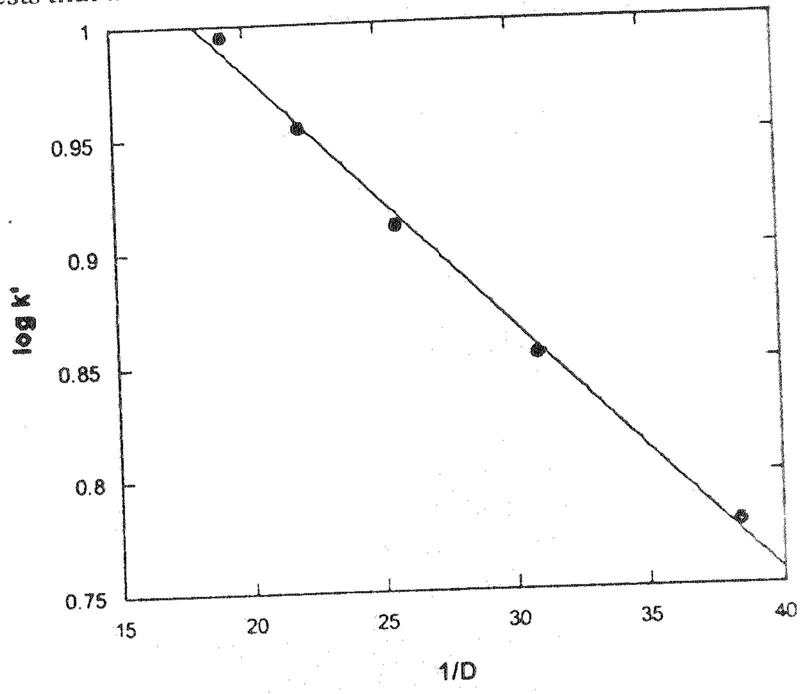


Fig. 3. Effect of solvent-Amis plot

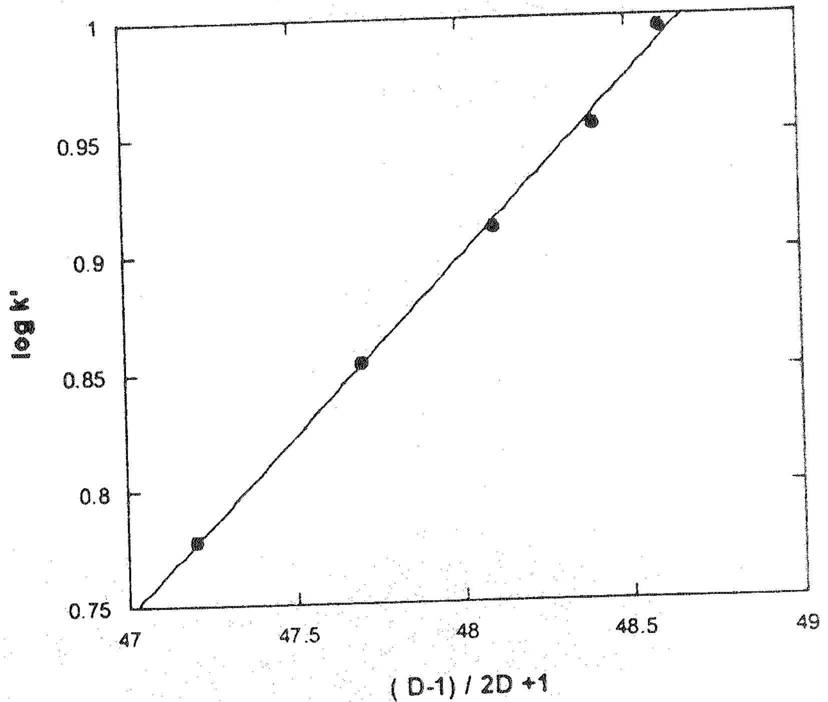


Fig. 4. Kirkwood plot

At constant ionic strength the rate law from the above mechanism is given as

$$\frac{-d[\text{NBP}]}{dt} = \text{rate} = \frac{kK[\text{benzaldehyde}][\text{NBP}]}{1 + K[\text{benzaldehyde}]} \quad (1)$$

$$\frac{\text{rate}}{[\text{NBP}]} = \frac{kK[\text{benzaldehyde}]}{1 + K[\text{benzaldehyde}]} \quad (2)$$

Reciprocal of equation (2) gives

$$\frac{[\text{NBP}]}{\text{rate}} = \frac{1}{kK[\text{benzaldehyde}]} + \frac{1}{k} \quad (3)$$

According to eqn. (3) plots of [NBP]/rate *vs.* 1/[benzaldehyde] should be linear with positive slope and intercepts on Y-axis. These types of plots have been observed in the present study supporting the proposed mechanism. From the intercepts and slopes of these plots at various temperatures k and K were calculated and presented in Exner's plot of log $k_{313\,K}$ *vs.* log $k_{303\,K}$ which was linear and isokinetic temperature $\beta = 289.9$ K and $r = 0.95$ was obtained, which was less than the experimental range (303–313 K) predicting the existence of an isokinetic relationship and it is an enthalpy controlled reaction.

The effect of substituents was studied and Hammett plot of log k *vs.* σ was linear with negative slope ($\rho = -0.422$, $r = 0.83$), indicating the presence of high electron charge density at the reaction site and the electron donating groups accelerate the rate of reaction The rate of oxidation of benzaldehydes was found to be in the order of 4-methyl benzaldehyde > benzaldehyde > 4-chloro benzaldehyde > 4-bromo benzaldehyde > 3-nitro benzaldehyde.

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