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# Kinetics and Mechanistic Aspects of Oxidation of Acetophenones by N-Bromophthalimide in Presence of Mercuric Acetate

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The reactions of N-bromophthalimide (NBP) with acetophenones (ACP) have been studied in presence of excess of mercuric acetate in aqueous acetic acid medium. NBP acts as moderate oxidant with a redox potential of 1.09 V. The reaction kinetics were first order in [NBP] and fractional order in [acetophenone]. Variation of phthalimide, mercuric acetate and ionic strength had an insignificant effect on reaction rate. The solvent effect revealed a positive dielectric effect. The stoichiometric ratio of ACP : NBP was 1 : 2 and the products of oxidation were benzoic acid and formaldehyde. Hammetst plot of log k *vs.* $\sigma^+$ gave $\rho^+ = -0.52$ and Exner's plot gave isokinetic temperature $\beta = 263$ K. Thermodynamic and activation parameters have been evaluated and a mechanism consistent with the kinetic data has been proposed.

**Key Words: Kinetics, Oxidation, Acetophenones, N-Bromophthalimide, Mercuric acetate.**

## INTRODUCTION

In the recent past interest in chemistry of N-halo compounds has increased significantly[1-8]. The N-bromophthalimide (NBP) is a moderate oxidizing, two-electron oxidant with redox potential of 1.09 V[9-12].

## EXPERIMENTAL

Mercuric acetate, phthalimide, potassium iodide, sodium thiosulphate, potassium dichromate, potassium chloride, sodium hydrogen carbonate and other inorganic chemicals used were of highest purity or AnalaR grade. Sulphuric acid (E. Merck) was of highest purity and used as received. N-bromophthalimide (NBP) was obtained from Aldrich (USA) and used as received.

Acetophenone (E. Merck) and the other acetophenones, *viz.*, 4-chloroacetophenone, 4-nitro-acetophenone, 4-fluoro-acetophenone and 4-methylacetophenone (E. Merck) were distilled twice under reduced pressure. The present study of oxidation of acetophenones with NBP was carried out under pseudo first order conditions of [NBP] $\ll$ [ACP] in 30% AcOH in excess of mercuric acetate. The progress of the reaction was studied by monitoring the consumption of NBP

iodometrically. The pseudo-first order rate constants were calculated from the slope of plot of log a/(a – x) *vs.* time which was linear and passing through origin. The order in substrate [ACP] was obtained from the slopes of log k′ *vs.* log [ACP]. Absence of free radicals in the reaction mixture was identified by adding acrylamide or acrylonitrile to the reaction mixture which did not induce polymerization in the reaction mixture. Stoichiometric studies were carried out with the mixture containing acetophenone (0.001 M) and NBP (0.01 M) kept for 24 h at 25°C. The unconsumed NBP was then determined and it was found that 2 moles of oxidant were required to oxidize one mole of acetophenone. Under the conditions of [NBP] ≫ [ACP], the products of oxidation of acetophenone were found to be benzoic acid and formaldehyde which were confirmed by spot test, *viz.*, $NaHCO_3$ test for benzoic acid and chromotopic acid test for formaldehyde. The product benzoic acid was also determined quanlitatively by HPLC technique.

## RESULTS AND DISCUSSION

The plots of log a/(a – x) *vs.* time (where 'a' corresponds to the initial concentration and (a – x) corresponds to the concentration of NBP after time t)

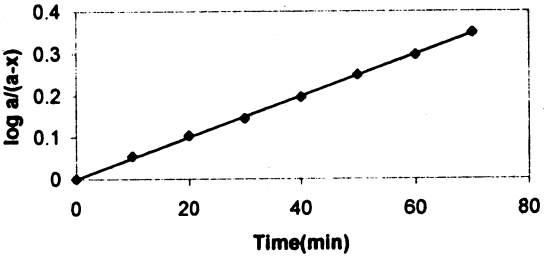



Fig. 1. Order in [NBP]

were linear (r = 0.98) passing through the origin indicating a first order dependence of rate on [NBP] (Fig. 1). From the slopes of the above plots the pseudo first order rate constants (k′) were evaluated and they were found to be independent of initial concentration of NBP, indicating that the reaction follows first order kinetics with respect to [NBP]. The plots of log k′ *vs.* log [ACP] were linear with slope = 0.21 (r = 0.99) indicating fractional order dependence of rate on [ACP] (Fig. 2).

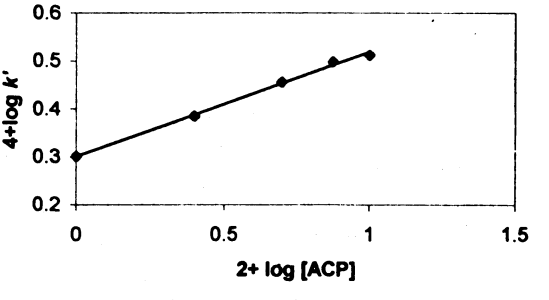



Fig. 2. Order in [ACP]

Lineweaver-Burk's plots of 1/k′ *vs.* 1/[ACP] (Fig. 3) were linear with positive slopes and intercepts on y-axis, indicating the formation of an intermediate comple. ; ior to rate limiting step.

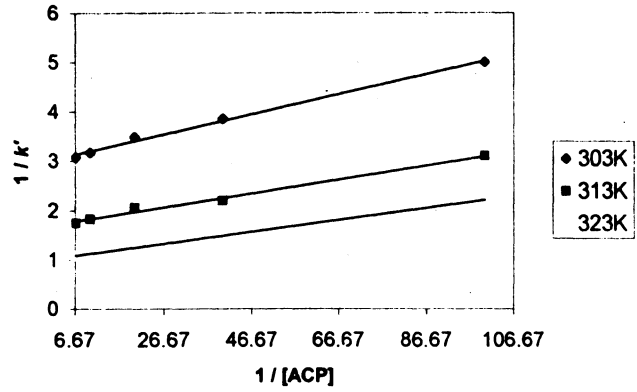



Fig. 3. Effect of [ACP] on NBP-ACP reaction and search for complex formation: a kinetic evidence

## Reactive Species and Mechanism

A perusal of literature reveals that the oxidizing species of NBP in acid solutions may be NBP, $Br^+$, $(NBPH)^+$, $H_2O^+Br$ according to the following equilibria:

$$NBP + H^+ \rightleftharpoons NHP + Br^+$$

$$NBP + H^+ \rightleftharpoons (NBPH)^+$$

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

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

The possibility of $(NBPH)^+$ to be the reactive species is ruled out on the basis of solvent and ionic strength effect studies which overrule the $[H_2SO_4]$ effect, as it had only a marginal effect on the reaction rate (Table-3). Since the reactions were conducted in the presence of excess of $Hg(OAc)_2$, as the added $Hg(OAc)_2$ eliminates $Br^-$ through complexation and thus any possible oxidation due to $Br_2$ could be ruled out.

The possibility of $Br^+$ and $H_2O^+Br$ being the reactive species could be ruled out as the reactions were carried out in the absence of mineral acid. Further the rate should have shown an inverse dependence on [Phthalimide] (Table-3), if HOBr were to be the reactive species. But in the present study such observation is not recorded, therefore free NBP is the probable oxidizing species under the present experimental conditions.

From the analysis of kinetic data and calculation of rate, it was observed that rate is first order in [NBP] and fractional order in [ACP]. These kinetic features suggest the formation of an intermediate adduct, *i.e.*, acetophenone-NBP complex prior to the rate limiting disproportionation step

The dielectric constant effect was studied by varying the composition of acetic

acid in the solvent mixture and it revealed that with the decrease in dielectric constant of the solvent, the rate of oxidation was decreased (Table-2) and the plot of log k′ *vs.* 1/D was linear with a negative slope indicating a rate limiting step with charge dispersal in the transition state.

TABLE-1
EFFECT OF SOLVENT ON THE RATE OF OXIDATION OF ACETOPHENONE

[ACP] = $1 \times 10^{-2}$ M $Hg(OAc)_2 = 2 \times 10^{-3}$ M
[NBP] = $1 \times 10^{-3}$ M Temp = 303 K

| % AcOH | Dielectric constant (D) | $10^3/D$ | $\frac{10^2(D-1)}{2D+1}$ | $10^5 \times k'$ ($s^{-1}$) | 5 + log k′ |
|---|---|---|---|---|---|
| 30 | 52.2 | 19.2 | 48.6 | 28.60 | 1.447 |
| 40 | 45.5 | 22.0 | 48.4 | 17.50 | 1.243 |
| 50 | 39.0 | 25.6 | 48.1 | 9.80 | 0.991 |
| 60 | 32.4 | 30.9 | 47.7 | 6.50 | 0.812 |
| 70 | 26.1 | 38.4 | 47.2 | 3.20 | 0.505 |

Further the plot of log k′ *vs.* (D – 1)/(2D + 1) was also found to be linear supporting the involvement of neutral molecules or dipoles in the reaction (Fig. 4 (a), (b)). In addition to this, the ionic strength of the medium had negligible effect on the reaction, which also further supports this contention.

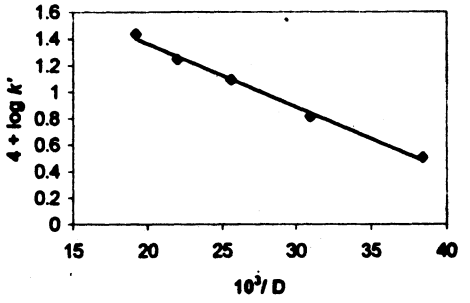



Fig. 4 (a) Amis plot of effect of solvent on reaction rate

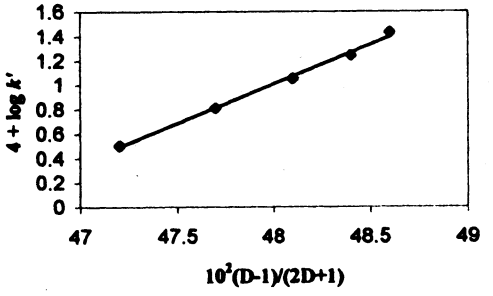
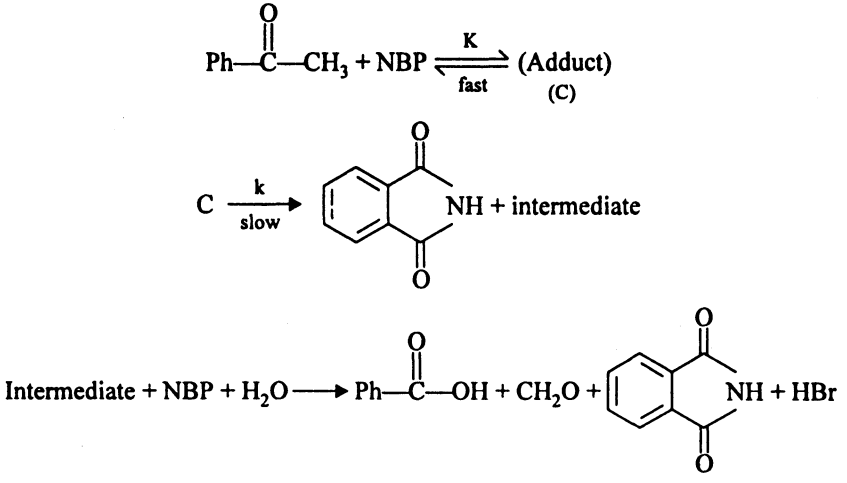



Fig. 4 (b) Kirkwood plot

**Evidence for keto form to be the reactive species and not the enol form**

The kinetics of oxidation and enolization of acetophenones are quite different. Enolization is an acid catalyzed reaction and is favoured by increase in the proportion of acetic acid in the solvent mixture, whereas oxidation is independent of these variations. Hence both reactions cannot have the same mechanism. The present kinetic study of oxidation of acetophenones is not an acid catalyzed reaction and the reaction rate is not favoured by the increase in acetic acid in the solvent mixture. Therefore keto form of acetophenone is the most probable oxidizing species and not the enol form.

From the foregoing kinetic features and discussion most probable mechanism for the oxidation of acetophenone by NBP could be given as shown in **Scheme-1.**




**Scheme-1**

The rate law for the above mechanism can be given as,

$$\frac{-d[NBP]}{dt} = k' = \frac{kK[acetophenone][NBP]}{1 + K[acetophenone]}$$

$$\frac{1}{k'} = \frac{1}{kK[acetophenone]} + \frac{1}{k}$$

From the above equation, it is evident that the plots of 1/k′, *vs.* 1/[ACP] should be linear and which is observed in case of all the acetophenones studied at three temperatures,; thus confirming the proposed mechanism. From the intercept and slope values of the plot 1/k′ *vs.* 1/[ACP] at different temperatures, the values of formation constant K and disproportionation constant k have been evaluated. From these values at various temperatures, activation parameters were calculated (Table-2).

The effect of substituents was studied to find the electronic and steric effects on the rate of oxidation and to support the proposed mechanism. The Hammett plot of log k *vs.* $\sigma^+$ is linear and $\rho^+$ value obtained is –0.52 (r = 0.980) indicating the presence of high electron charge density at the reaction site and the reaction is accelerated by electron donating substituents, which is observed in the

acetophenone series. The order of reactivity among the various acetophenones studied is 4-methyl- ACP > ACP > 4-chloro-ACP > 4-flouro-ACP > 4-nitro-ACP.

TABLE-2
DISPROPORTIONATION CONSTANT (k), FORMATION CONSTANT (K) AND ACTIVATION PARAMETERS FOR NBP-ACETOPHENONE REACTIONS IN AQUEOUS ACETIC ACID MEDIUM

$[NBP] = 1 \times 10^{-3}$ mol dm$^{-3}$ Temp. = 303 K
$[Hg(OAc)_2] = 2 \times 10^{-3}$ mol dm$^{-3}$ [HOAc] = 30% (v/v)

| Substrate | k ($s^{-1}$) | K ($mol^{-1}$ $dm^{-3}$) | $E_a$ | $\Delta H^{\neq}$ (kJ $mol^{-1}$) | $\Delta G^{\neq}$ | $-\Delta S^{\neq}$ (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|---|---|
| Acetophenone | 3.33 | 23.4 | 34.47 | 31.96 | 73.39 | 136 |
| 4-Nitro-acetophenone | 2.86 | 50.0 | 25.72 | 23.19 | 74.12 | 168 |
| 4-Methyl-acetophenone | 5.00 | 15.0 | 18.23 | 15.71 | 72.34 | 186 |
| 4-Fluoro-acetophenone | 3.03 | 42.0 | 21.16 | 18.64 | 74.06 | 182 |
| 4-Chloro-acetophenone | 3.12 | 36.0 | 28.36 | 25.84 | 74.00 | 159 |

The validity of isokinetic phenomenon is checked by taking Exner's plot of $\log k_{323K}$ *vs.* $\log k_{303\,K}$, which was linear with isokinetic temperature $\beta = 263$ K ($r = 0.98$) which is below the experimental range (303–323 K) this result suggests the existence of isokinetic relationship and that the reaction is enthalpy controlled. The constancy of $\Delta G^{\neq}$ values indicates that the same mechanism prevails in all acetophenones studied.

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