

## Effect of Cyclodextrin on the Oxidation of Acetophenone and Substituted Acetophenones by N-Bromophthalimide in Aqueous Acetic Acid Medium

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The kinetics of oxidation of acetophenone and substituted acetophenones by N-bromophthalimide (NBP) has been investigated in aqueous acetic acid medium in the presence of mercuric acetate for a temperature range of 308–323 K. The reaction is zero order in oxidant and first order in substrate. Increase in  $[H^+]$  increases the rate with a fractional order dependence. No primary salt effect was observed whereas added phthalimide shows retarding effect. The thermodynamic parameters were evaluated. Catalytic effect was observed with cyclodextrins, with larger magnitude for the  $\alpha$ -cyclodextrins.

### INTRODUCTION

N-halocompounds have been used widely as oxidising and halogenating reagents in organic compounds<sup>1-9</sup>. However, such studies on aromatic ketones are very few and hence the present study also deals with the oxidation of acetophenone and a few substituted acetophenones in aq. acetic acid medium (20–80% v/v) by N-bromophthalimide (NBP) in the presence of mercuric acetate at 308 K. The effects of added  $\alpha$ - and  $\beta$ -cyclodextrins were studied at the same temperature for the oxidation of acetophenone, *m*-nitro, *p*-nitro, *p*-bromo, *p*-chloro, and *p*-methyl acetophenones. The effect of cyclodextrins on hypohalite oxidation of acetophenone in alkaline medium has already been reported<sup>10</sup>.

### EXPERIMENTAL

NBP was synthesised<sup>11</sup> and its purity was ascertained by standard methods. Its solution was prepared in glacial acetic acid distilled afresh by the standard procedures. Acetophenone (AcP) used was of Merck grade and was further purified by distillation under reduced pressure. The substituted acetophenones were used as such and were of AnalaR quality. All other chemicals used were of AnalaR grade. The kinetics of the reaction in aqueous acetic acid medium was followed iodometrically. The cyclodextrins used were supplied by Aldrich (USA). Kinetic measurements were made in thermostat whose temperature was controlled to within  $\pm 0.1^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The stoichiometry of the reaction was carried out by equilibrating the mixture consisting of oxidant, substrate, mercuric acetate and acid for sufficient length of time and estimating the unreacted NBP, showing equivalence of one mole of acetophenone to three moles of NBP. Under the experimental conditions, the final product of oxidation was identified as benzoic acid.

Kinetic studies were conducted under the conditions where concentration of acetophenone and  $\text{Hg}(\text{OAc})_2 \gg \text{NBP}$ . All the investigations were made in the presence of mercuric acetate to avoid any possible bromine oxidation<sup>12</sup>. The plots of concentration of oxidant vs. time showed linear relations and hence the reaction is zero order with respect to the oxidant. The rate of oxidant increased with increase in substrate concentration. The plot of  $\ln k_{\text{obs}}$  vs.  $\ln [S]$  was linear with unit slope indicating first order dependence on the substrate. The reaction rate did not vary with variation in ionic strength. The values of the specific rates for various concentrations of NBP and acetophenone are given in Table-1.

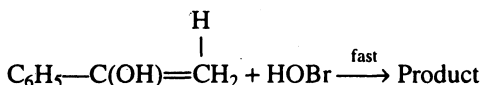
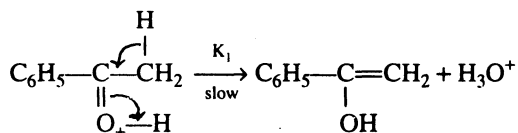
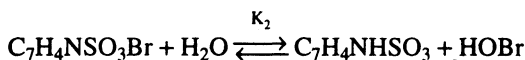
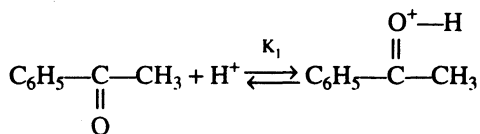
TABLE-1  
EFFECT OF CONCENTRATION OF NBP AND ACETOPHENONE ON OBSERVED RATE CONSTANT IN THE OXIDATION OF ACETOPHENONE BY NBP

$[\text{NBP}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$	$[\text{H}^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$
$[\text{AcP}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$	$[\text{MA}] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$
$[\text{Solvent}] = 20\% \text{ aq. HOAc (v/v)}$	$T = 308 \text{ K.}$

$[\text{AcP}] \times 1.0 \times 10^{-2}$ $\text{mol dm}^{-3}$	$[\text{NBP}] \times 1.0 \times 10^{-3}$ $\text{mol dm}^{-3}$	$k_{\text{obs}} \times 10^8$ $\text{mol dm}^{-3} \text{ s}^{-1}$
1.0	1.0	2.40
1.5	1.0	3.62
2.0	1.0	4.87
2.5	1.0	6.19
3.0	1.0	7.40
1.0	0.5	2.42
1.0	1.0	2.40
1.0	1.5	2.42
1.0	2.0	2.43

The rate coefficients were found to increase with decrease in acetic acid concentration. Further, the plot of  $\ln k$  vs.  $\frac{D-1}{2D+1}$  is linear suggesting dipole-dipole type of interaction in the reaction path. No primary salt effect was observed on the addition of neutral salts. The reaction system did not induce polymerisation of added acrylonitrile, confirming the absence of free radicals in the system. Addition of phthalimide has a retarding effect on the rate.

The reactive oxidant species of NBP oxidation in aqueous acetic acid can be protonated NBP, Br radical, Br<sub>2</sub>, Br<sup>+</sup>, HOBr, etc. The fact that added acrylonitrile has no effect on rate rules out the reaction by Br radicals, Br<sub>2</sub> molecule, etc. Catalysis by H<sup>+</sup> has been shown by the increase in rate with increase in the concentration of H<sup>+</sup>. This favours the protonated NBP as well as HOBr as the reactive species. The retarding effect on the addition of phthalimide is indicative of either the protonated NBP or HOBr as the reactive species. However, rate retarding effect by added phthalimide rather rules out the oxidation by NBP itself and it supports reaction by HOBr. When Br<sup>+</sup> or HOBr are the reactive species the oxidation rate would diminish by added phthalimide. Hence HOBr may be the reactive species which attacks the enol form of acetophenone. The rate is accelerated by the addition of mineral acid which points out the formation of larger proportion of HOBr from NBP, on addition of acid. Hence, a plausible mechanism could be proposed as:



so that  $\frac{dx}{dt} = k_1[\text{C}_6\text{H}_5-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{CH}_2] = K_1 K_{\text{eqm}}[\text{C}_6\text{H}_5\text{COCH}_3][\text{H}^+]$  supports reaction

by HOBr.

The activation parameters were calculated from Arrhenius plots and the values are given in Table-2.

### Effect of cyclodextrin

Cyclodextrins are reported to be of amazing catalytic activity towards many organic reactions. In the oxidation of acetophenone itself under alkaline conditions using hypohalite, it was earlier observed that the cyclodextrin catalyses the reaction. These molecules are capable of encapsulating reactants of appropriate size and thereby catalyse the reaction.

TABLE-2  
 SUBSTITUENT EFFECTS AND ACTIVATION PARAMETERS FOR THE  
 OXIDATION OF ACETOPHENONES BY NBP IN THE PRESENCE AND  
 ABSENCE OF CYCLODEXTRIN

$$[\text{NBP}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{Substrate}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{MA}] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{Solvent}] = 20\% \text{ Aq. HOAc (v/v)}$$

Substrate	$k \times 10^8 \text{ dm}^{-3} \text{ S}^{-1}$		$E_a$ kJ mol <sup>-1</sup>	$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ JK <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>
	Normal	Catalysed AC <sub>y</sub> D				
AcP	2.40	3.33	62.35 *51.96	60.04	193.38	119.60
MNA	1.76	2.33	59.38	57.15	207.85	121.17
PNA	1.88	3.50	60.46	59.38	200.27	121.06
PBA	2.09	3.41	62.35	57.16	206.01	120.76
PCA	2.55	3.41	66.57	62.35	188.09	120.28
PMA	4.44	9.41	51.96	46.18	235.96	118.86
PM <sub>y</sub> A	17.60	—	—	—	—	—

\* when AC<sub>y</sub>D was used.

It is of interest to note that the added cyclodextrins have positive catalytic effect. Compared to β-form, the α-form of the cyclodextrin showed pronounced catalytic effect on the rate of oxidation of acetophenons by NBP.

The oxidation of acetophenone and a few substituted acetophenones using NBP as oxidant was carried out in the presence of α and β cyclodextrins.

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