# Kinetics and Mechanism of Oxidation of Methyl Ethyl Ketone by N-Bromophthalimide in Acid Medium

A. Ramesh*, B. Syamasundar† and P.S. Radhakrishna Murti†
*Department of Chemistry, SRR Engineering College*
*Padur, Chennai-603 103, India*

The kinetics of oxidation of methyl ethyl ketone by N-bromophthalimide in acetic acid-perchloric acid mixture has been studied. The reaction is first order in methyl ethyl ketone, first order in $H^+$ and zero order in N-bromophthalimide, indicating the acid catalyzed enolization of ketone as the rate determining step and the reaction between enol and N-bromophthalimide as the fast step. Arrhenius parameters have been computed. Addition of sodium perchlorate has no effect in the reaction rate indicates the absence of ionic salt effect. Addition of added $Br^-$, there is no acceleration in the reaction rate indicating the molecular bromine is not formed during the course of the reaction.

**Key Words: N-Bromophthalimide, Methyl Ethyl Ketone, Kinetics.**

## INTRODUCTION

N-halo compounds are versatile oxidizing agents. The kinetics of oxidation of ketones with a variety of oxidizing agents in acid medium has been well documented[1-4]. A survey of literature indicates that the kinetics of reaction of methyl ethyl ketone (MEK) with N-bromophthalimide (NBP) has not been studied. The present study proposes the mechanistic generalization of oxidation of MEK by NBP with a view to study structure and reactivity.

## EXPERIMENTAL

N-Bromophthalimide (NBP) of Fluka (purum) grade was used. Methyl ethyl ketone (MEK) and other chemicals of BDH (AR) grade were used. The reaction rate was followed by titrating the unreacted NBP iodometrically.

**Kinetic method:** Aliquots in reaction mixture were analyzed by iodometric method. 5 mL of the reaction mixture containing NBP was pipetted out at various intervals of time into a mixture of iodate free KI solution containing dilute sulphuric acid. The liberated iodine was titrated

†Department of Chemistry, Nagarjuna University, Nagarjuna Nagar-522 510, India.

against standard thiosulphate solution to the disappearance of the blue starch-iodine end point. Some kinetic runs were followed by analysis with a spectrophotometer. Rate constants obtained by both the methods agreed to an accuracy of ± 2 %.

In stoichiometric experiments employing $[NBP]_0 > [MEK]$, the disappearance of oxidant was monitored until a constancy in the value of left over oxidant was noticed. The stoichiometry and product identification points to the formation of mixture of acids.

## RESULTS AND DISCUSSION

**Effect of varying [NBP] on the reaction rate:** The values of rate constants $k_0$ for different initial concentrations of NBP are constant confirming the zero-order dependence on NBP (Table-1).

TABLE-1
$[MEK] = 0.011$ M; $[H^+] = 0.11$ M; AcOH = 20 %; T = 35 ºC

| $[NBP] \times 10^4$ M | $k_0 \times 10^6$ (mol min$^{-1}$) |
|---|---|
| 4.58 | 6.0 |
| 7.00 | 5.0 |
| 10.00 | 6.4 |
| 20.70 | 5.9 |

**Effect of varying [MEK] on the reaction rate:** The increase in [MEK] enhances the reaction rate. The plot of log $k_0$ *vs.* log [MEK] for different initial concentrations of substrate is linear with unit slope indicating the first order dependence on substrate (Table-2).

TABLE-2
$[NBP] = 7.0 \times 10^{-4}$ M; $[H^+] = 0.11$ M; AcOH = 20 %; T = 35 ºC

| $[MEK] \times 10^3$ M | $k_0 \times 10^6$ (mol min$^{-1}$) |
|---|---|
| 5.5 | 3.2 |
| 11.0 | 5.0 |
| 22.0 | 12.5 |
| 55.0 | 36.2 |

**Effect of varying [H⁺] on the reaction rate:** With the increase in [H⁺] the rate of reaction increases indicating a direct participation of H⁺ in the rate determining step. The plot of log $k_0$ *vs.* log [H⁺] is linear with unit slope shows the first order dependence on acidity (Table-3).

TABLE-3

$[NBP] = 7.0 \times 10^{-4} M'$ $[MEK] = 0.011$ M; AcOH = 20 %; T = 35 °C

| $[H^+]$ M | $k_0 \times 10^6$ (mol min$^{-1}$) |
|---|---|
| 0.11 | 5.00 |
| 0.22 | 8.85 |
| 0.33 | 14.00 |
| 0.44 | 18.50 |

**Effect of change in solvent composition:** The reaction was studied at different compositions of acetic acid-water mixtures. The rate of the reaction increases slightly with the increase in the percentage of acetic acid (Table-4).

TABLE-4

$[NBP] = 7.0 \times 10^{-4} M$; $[MEK] = 0.011$ M; $[H^+] = 0.11$ M; T = 35 °C

| AcOH (%) | $k_0 \times 10^6$ (mol min$^{-1}$) |
|---|---|
| 20 | 5.00 |
| 40 | 5.21 |
| 60 | 5.50 |

**Effect of added salt:** Addition of sodium perchlorate has no effect in the reaction rate indicates the absence of ionic salt effect.

Addition of added Br$^-$, there is no acceleration in the reaction rate indicating the molecular bromine is not formed during the course of the reaction (Table-5).

TABLE-5

$[NBP] = 7.0 \times 10^{-4} M$; $[MEK] = 0.011$ M; $[H^+] = 0.11$ M
AcOH = 20 %; T = 35 °C

| Salt | $k_0 \times 10^6$ (mol min$^{-1}$) |
|---|---|
| – | 5.00 |
| NaClO$_4$ (0.01 M) | 5.60 |
| Br$^-$ (0.01 M) | 5.47 |

**Effect of temperature:** The reaction was studied at different temperatures. The rate of the reaction increases with the increase in temperature (Table-6). Plot of log $k_0$ *vs.* 1/T is linear. Various thermodynamic parameters have been computed (Table-7).

TABLE-6

$[NBP] = 7.0 \times 10^{-4}$ M; $[MEK] = 0.011$ M; $[H^+] = 0.11$ M; AcOH = 20 %

| T (ºC) | $k_0 \times 10^6$ (mol min$^{-1}$) |
|--------|--------------------------------------|
| 35     | 5.00                                 |
| 40     | 7.88                                 |
| 45     | 14.90                                |

TABLE-7

| ΔE (KJ/mol) | ΔH (KJ/mol) | log PZ | $-\Delta S$ (JK$^{-1}$ mol$^{-1}$) |
|-------------|-------------|--------|-------------------------------------|
| 18.5        | 15.95       | 8.4    | 70.5                                |

**Mechanism:** The first order dependence of reaction rate on the MEK, the zero-order dependence with respect to NBP and the first order dependence with respect to acid reveal the general rate expression as

$$ -\frac{d[NBP]}{dt} = k_0 [NBP]^0 [MEK][H^+] $$

The detailed mechanism can be envisaged as the protonation of MEK in the presence of $H^+$ and the enolization of the protonated MEK in a rate determining slow step which finally combines with NBP in a fast step to give the brominated ketone[5].
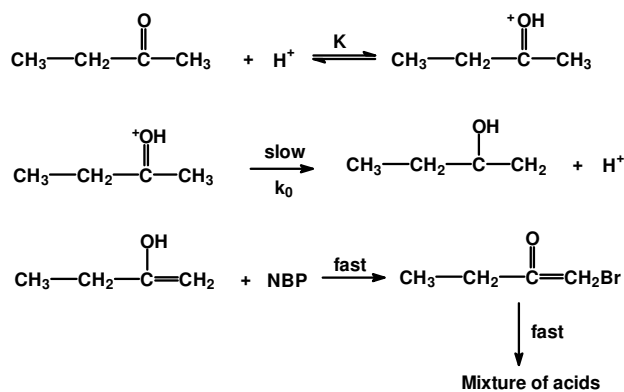


## REFERENCES

1.  J.S. Littler, *J. Chem. Soc.*, 827 (1962).
2.  P.S. Radhakrishnamurti and S.N. Pati, *Indian J. Chem.*, **16A**, 319 (1978).
3.  P.S. Radhakrishnamurti and S.N. Pati, *Indian J. Chem.*, **17A**, 97 (1979).
4.  P.S. Radhakrishnamurti and D.K. Mahapatro, *Indian J. Chem.*, **18A**, 53 (1979).
5.  P.S. Radhakrishnamurti and D.K. Mahapatro, *Indian J. Chem.*, **19A**, 207 (1980).