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A Kinetic Study of Oxidation of Aliphatic Ketone with N-Bromobenzamide in Acidic Medium

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The kinetics of oxidation of ethyl methyl ketone by N-bromobenzamide (NBB) in aquoacetic acid media has been done. The reaction has a zero order dependency on [NBB] and a first order dependency with respect to substrate [ethyl methyl ketone]. The reaction is catalysing by H^+. The effect of ionic strength, mercuric acetate and product [benzamide] variations has been studied. Various thermodynamic parameters have been computed and a probable reaction mechanism consistent with the kinetic results has been suggested.

INTRODUCTION

The work on the oxidation and halogenation by N-halo compounds has received considerable attention of number of workers[1–4]. But a very limited work on the kinetics of oxidation of ketones by different N-halo compounds has been done.[5–9] In the present work we report the kinetics of oxidation of ethyl methyl ketone by N-bromo benzamide (NBB) in acidic medium.

EXPERIMENTAL

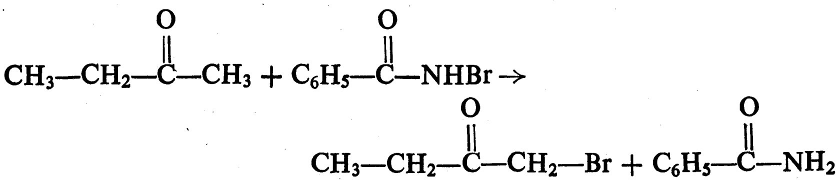
Benzamide used obtained from Fluka. Ethyl methyl ketone, bromine, perchloric acid (60 %) and acetic acid used were of GR grade. Potassium chloride, potassium bromide, mercuric acetate and other salts and acids were of BDH Analar grade.

NBB used was prepared by the method given by Charles[10]. Its purity was checked by the M. pt. determination (129°–131°) and was identified by IR spectra also. The estimation was done iodometrically. Stock solutions of NBB were always prepared directly by taking the known amount of it and dissolving in 50% (v/v) acetic acid-water solution and was kept in dark to protect from photodecomposition.

All reactants except ketone were mixed in a reaction bottle painted black from outside and was kept in a thermostat maintained at constant temperature (± 0.1°C). The reactions were initiated by adding appropriate amount of the thermally equilibriated ketone in the above reaction mixture. The kinetics were followed by estimating unconsumed NBB, iodometrically using starch as an indicator.

RESULTS AND DISCUSSION

Several sets of experiments with varying ratios of NBB over ethyl methyl ketones were carried out. The excess of NBB left in each set was estimated. Experiments showed that one mole of ethyl methyl ketone consumes one mole of NBB and has been found to follow the following stoichiometry of the reaction.



$$CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_3 + C_6H_5—\overset{\overset{O}{\|}}{C}—NHBr \rightarrow CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_2—Br + C_6H_5—\overset{\overset{O}{\|}}{C}—NH_2$$

The end product, bromo ethyl methyl ketones was identified by usual spot test analysis[11].

The experiments were carried out at several concentrations of NBB and ethyl methyl ketones at constant hydrogen ion concentration (Table 1). A zero order rate constant with respect to [NBB] was observed and the rate of the reaction was found to be independent of initial NBB concen-

TABLE 1

EFFECT OF REACTANTS CONCENTRATION ON REACTION RATE

S. No.	10^3[NBB] mol. dm^{-3}	10^2[EM ketone] mol. dm^{-3}	[$HClO_4$] Mol. dm^{-3}	10^3K_0 mol dm^{-3} sec^{-1}	k_1 sec^{-1}
1.	0.1	2.0	1.25	2.40	—
2.	0.2	2.0	1.25	2.42	—
3.	0.3	2.0	1.25	2.43	—
4.	0.4	2.0	1.25	2.45	—
5.	0.5	2.0	1.25	2.44	—
6.	0.8	2.0	1.25	2.45	—
7.	1.0	2.0	1.25	2.41	—
8.	2.0	0.5	1.25	0.63	0.13
9.	2.0	1.0	1.25	1.21	0.12
10.	2.0	2.0	1.25	2.42	0.12
11.	2.0	3.0	1.25	3.40	0.11
12.	2.0	4.0	1.25	4.91	0.12
13.	2.0	5.0	1.25	6.02	0.12
14.	2.0	6.0	1.25	6.91	0.12
15.	2.0	2.0	0.50	0.80	1.60
16.	2.0	2.0	1.00	1.62	1.62
17.	2.0	2.0	2.00	3.30	1.65
18.	2.0	2.0	3.0	4.90	1.63
19.	2.0	2.0	4.0	6.40	1.60

tration. A proportional increase in the zero order rate constant with increase in the initial concentrations of ethyl methyl ketone was observed (Fig. 1). The average values of the first order rate constant were calculated, $k_1 = k_0/[\text{ethyl methyl ketone}]\ \text{sec}^{-1}$ and found equal to 12.0×10^{-2} sec^{-1} at 313 *K*.

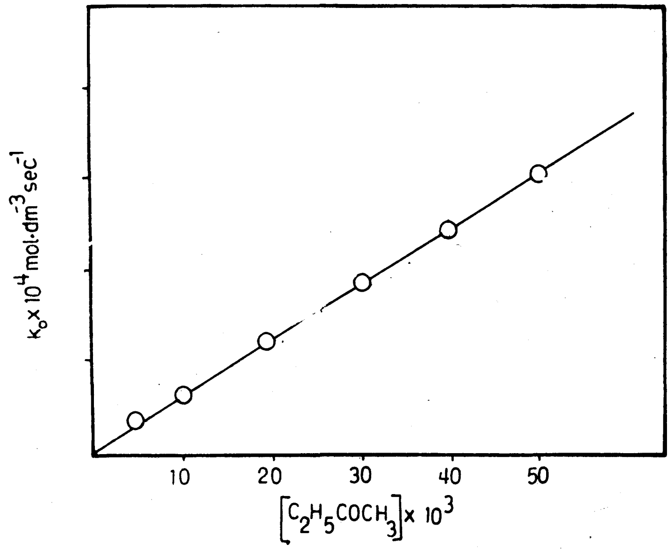


Fig. 1. Plot of K_0 vs. Substrate Concentration.

The zero order rate constant was found to increase with increase in the initial concentration of hydrogen ion (Table 1). Hence, the zero order rate constant has direct dependency with the initial concentration of H^+ ion (Fig. 2).

The average value of first order rate constant calculated as $k_1 = k_0/[HClO_4]$ was found as 1.62×10^{-3} sec $^{-1}$ at 313 *K*.

The effect of variation of acetic acid concentrations was investigated and found that the reaction rate increases with the increase of acetic acid concentration. This indicates that the reaction is sensitive with the change of dielectric constant of the medium.

Sodium perchlorate, mercuric acetate and benzamide variations have negligible effect on the reaction velocity.

Various kinetic and activation parameters viz. energy of activation (ΔE_a) : frequency factor (A), entropy of activation (ΔS^*) and Heat of activation (ΔH^*) were computed using five different temperatures and average values were found as 19.81 kcal mol^{-1}, 1.64×10^{11} mol dm^{-3} min^{-1}, -8.17 kcal mol. cm^{-3} and 19.19 kcal mol^{-1} respectively.

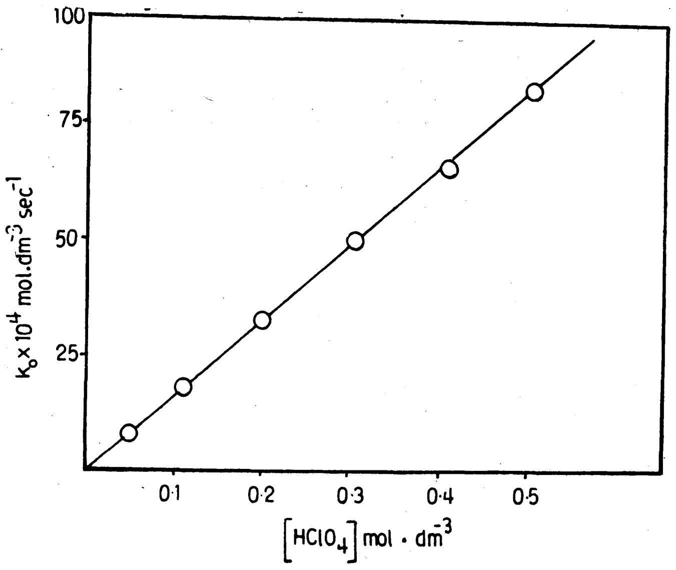
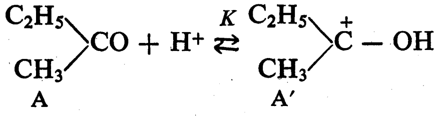


Fig. 2. Plot of K_o vs [$HClO_4$].

In the acidic solution the rate of enolisation is directly proportional to H^+ ion concentration. The possibility of formation of H_2OBR^+ in the acid solution does also exist but in comparison to the rate of enolisation the above possibility is more or less negligible.

On the basis of the above information, the reaction seems to follow the following probable reaction mechanism;



$$\underset{A}{(C_2H_5)(CH_3)CO} + H^+ \overset{K}{\rightleftarrows} \underset{A'}{(C_2H_5)(CH_3)\overset{+}{C}-OH} \quad \text{fast} \tag{2}$$

As the reaction is zero order dependent on NBB concentration. Littler and Walters[12] contention can be taken into account. Enolisation will therefore be the slow and rate determining step.

$$A' \xrightarrow[\text{(enol)}]{k_1} A'' + H^+ \text{ slow and rate determining} \tag{3}$$

where A represents ketone, A′ the conjugate acid and A″ its enolic form.

$$A'' + NBB \xrightarrow{k_2} \underset{\text{(inter species)}}{X} \quad \text{fast} \tag{4}$$

$$X \xrightarrow{k_3} \text{Products fast} \tag{5}$$

Now the rate of disappearance of NBB is given by;

$$-\frac{d[NBB]}{dt} = k_2[A''][NBB]^\circ \tag{6}$$

From equation (3), (4) and (5) we have

$$-\frac{d\,[\mathrm{NBB}]}{dt} = \frac{k_1K[\mathrm{KETONE}][\mathrm{H}^+][\mathrm{NBB}]^\circ}{1 + K[\mathrm{H}^+]} \tag{7}$$

which is consistent with the kinetic parameters.

In the light of above rate expression the possibility of Br^+ or NBB^+H as the oxidising species may be ruled out.

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