

MECHANISM OF OXIDATION OF SOME ALIPHATIC KETONES BY N-BROMOSUCCINIMIDE IN ACIDIC MEDIA

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Abstract—Kinetics of the oxidation of methyl n-propyl ketone and methyl isobutyl ketone by N-bromosuccinimide (NBS) have been studied in perchloric acid media in presence of mercuric acetate. A zero order dependence to N-bromosuccinimide and a first order dependence to both ketones and hydrogen ion concentrations have been observed. Sodium perchlorate, mercuric acetate and succinimide additions have negligible effect while methanol addition has a positive effect on the reaction rate. A solvent isotope effect ($k_0D_2O/k_0H_2O = 2.3-2.7$ and $2.4-2.8$ for MeCO_n.pr and MeCo_i-Bu, respectively) has been observed at 35°. Kinetic investigations have revealed that the order of reactivity is methyl n-propyl ketone > methyl isobutyl ketone. Various thermodynamic parameters have been computed and corresponding 1,2-diketones were found to be the products. A suitable mechanism in conformity with the above observations has been proposed.

Kinetic investigations involving aliphatic, cyclic, aromatic ketones and various oxidising agents have been reported by many workers.¹⁻⁵ N-bromosuccinimide is a potent oxidising agent and has been used in the determination of several organic compounds.^{6,7} Some investigations involving NBS oxidation of esters,⁸ alcohols^{9,10} and ketones^{11,12} are reported. The present work constitutes an investigation on the kinetics and mechanism of the oxidation of methyl n-propyl ketone and methyl isobutyl ketone by NBS in acidic media.

Materials and methods. All the reagents used were of highest purity available. E. Merck (Germany) sample of methyl isobutyl ketone, Riedel sample of methyl n-propyl ketone and G.R.S. Merck sample of NBS were used. Succinimide and mercuric acetate used were of H & W (England) and E. Merck grade, respectively. Sodium perchlorate and perchloric acid were of analar grade. NBS solution was always prepared fresh and its strength was checked by iodometric method. The solns of methyl n-propyl ketone and methyl isobutyl ketone were prepared in 50% A.R., B.D.H. methanol. Triple distilled water was used throughout the course of investigations and reaction stills were blackened from outside.

All reactants except ketone were allowed to mix and the reaction was initiated by adding subsequently appropriate amount of ketone. The progress of the reaction was monitored by estimating unconsumed NBS iodometrically using starch as indicator. All the rate studies were carried out at constant temperature ($\pm 0.1^\circ$).

Stoichiometry and product analysis. Various sets of experiments were carried out with varying NBS ketone ratios. The excess of NBS left in each set was estimated. These studies showed that one mole of ketone consumed two moles of NBS and accordingly the following stoichiometric equation could be formulated, where R represents n-C₃H₇ and i-C₄H₉ groups in the

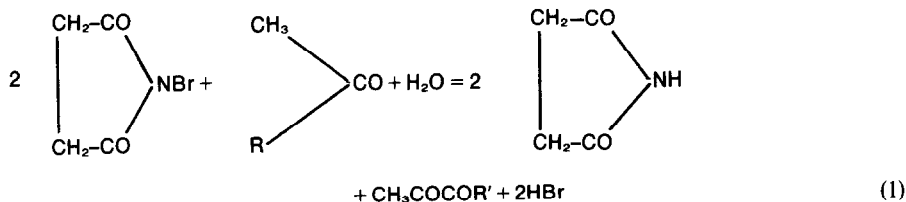
substrate molecule whilst R' represents Et and i-C₃H₇ groups in the respective diketone products. The end product, 1,2-diketones were identified by adopting tlc followed by conventional spot test analysis¹³ and also through dinitrophenylhydrazine (DNP) derivative.¹⁴

RESULTS AND DISCUSSION

The oxidation of ketones by NBS were studied over a wide range of concentrations of the reactions, i.e. substrate (ketones), NBS and hydrogen ion (Table 1). The order in NBS was found to follow the zero order law and the rate of the reaction was found to be independent of initial oxidant (NBS) concentration. Zero order in NBS was further supported through the plots of "(a-x)" and "t" for varying concentration of oxidant (NBS) where a set of parallel lines were obtained. A proportional increase in the zero order rate constant in NBS was observed with the increase in initial concentrations of ketone (Fig. 1) (for methyl n-propyl ketone). The average values of the first order rate constants calculated as $k_1 = k_0/[\text{ketone}]$ were found as 4.27, 5.56, 3.51, $5.74 \times 10^{-5} \text{ sec}^{-1}$ at 35° and 40° for methyl n-propyl ketone and methyl isobutyl ketone respectively.

A strong dependence on hydrogen ion concentration was observed and the average values of first order rate constants in hydrogen ion calculated as $k'_1 = k_0/[\text{HClO}_4]$ were found as 3.55, 5.48; 2.93, $4.86 \times 10^{-6} \text{ sec}^{-1}$ at 35°, 40° for methyl n-propyl ketone and methyl iso-butyl ketone respectively.

The overall second order rate constants k_2 calculated as $k_2 = k_0/[\text{HClO}_4][\text{ketone}]$ were found to be 3.54, $2.92 \times 10^{-4} \text{ mol}^{-1} \text{ sec}^{-1}$ at 35° for methyl n-propyl ketone and methyl isobutyl ketone respectively.



The reactivity order methyl n-propyl ketone > methyl isobutyl ketone is explained on the basis of the steric factors¹⁵ operative in the neighbourhood of the ketonic group. The larger the alkyl group in a particular substrate the slower is the rate of its oxidation.

Sodium perchlorate, mercuric acetate and succinimide variations had negligible effect on the rate of reaction while methanol addition had a positive effect (Table 2),

i.e. negative dielectric effect. Solvent isotope effect studied in different D₂O-H₂O mixture at 35° showed an increase of the rate constants values (Table 3).

The rate study measurements carried out at five different temperatures (30°-50°) led to compute the energy of activation (ΔE^\ddagger), frequency factor (A), entropy of activation (ΔS^\ddagger), heat of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) as 16.9, 20.2 K cal mol⁻¹,

Table 1. Effect of concentration of reactants and [H⁺] on the rate. [H_g(OAc)₂] = 2.0 × 10⁻³ M

10 ³ [NBS]	10 ² [Ketone]	[HClO ₄]	k _o × 10 ⁷ mol l ⁻¹ sec ⁻¹			
			MeCon-pr		MeCoI-Bu	
			35°	40°	35°	40°
0.8	1.0	0.12	4.17	6.50	3.33	5.67
1.0	1.0	0.12	4.25	6.58	3.50	5.83
1.2	1.0	0.12	4.37	6.67	3.42	6.00
1.4	1.0	0.12	4.08	6.33	3.58	5.57
1.6	1.0	0.12	4.42	7.00	3.67	6.16
1.0	0.6	0.12	2.58	3.83	2.17	3.33
1.0	1.4	0.12	6.00	9.33	4.83	8.33
1.0	1.8	0.12	7.58	11.67	6.42	10.00
1.0	2.2	0.12	9.42	14.66	7.50	13.34
1.0	1.0	0.08	2.85	4.33	2.42	3.83
1.0	1.0	0.16	5.75	8.83	4.75	8.00
1.0	1.0	0.20	7.00	10.84	5.75	9.50
1.0	1.0	0.24	8.58	13.32	6.82	12.00

Table 2. Effect of methanol on the reaction rate at 35° [NBS] = 1.0 × 10⁻³ M, [Ketone] = 1.0 × 10⁻² M, [HClO₄] = 0.12 M, [Hg(OAc)₂] = 2.0 × 10⁻³ M

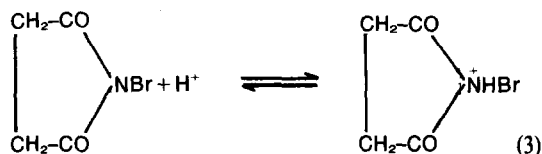
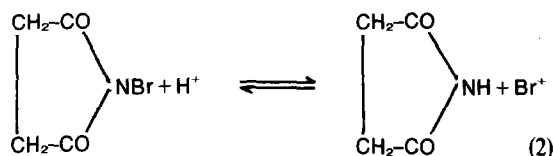
Methanol %	k _o × 10 ⁷ mol l ⁻¹ sec ⁻¹	
	MeCon-pr	MeCoI-Bu
0	4.25	3.50
10	4.67	3.75
20	5.02	4.17
30	5.66	4.52
40	6.42	4.84

Table 3. Solvent Isotope effect on the reaction rate at 35° [NBS] = 1.0 × 10⁻³ M, [Ketone] = 1.0 × 10⁻² M [HClO₄] = 0.12 M, [Hg(OAc)₂] = 2.0 × 10⁻³ M

D ₂ O - H ₂ O %	k _o × 10 ⁷ mol l ⁻¹ sec ⁻¹	
	MeCon-pr	MeCoI-Bu
40-60	9.8	7.5
60-40	10.6	8.6
80-20	11.4	9.8

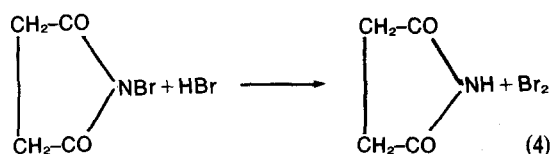
2.9×10^8 , $4.7 \times 10^{10} \text{ l mol}^{-1} \text{ sec}^{-1}$, -20.9 , -10.7 e.u. , 16.3 , $19.5 \text{ K cal mol}^{-1}$, 22.8 , $22.9 \text{ K cal mol}^{-1}$ for methyl n-propyl ketone and methyl isobutyl ketone respectively.

In acidic media NBS is known to exist in the following equilibria:



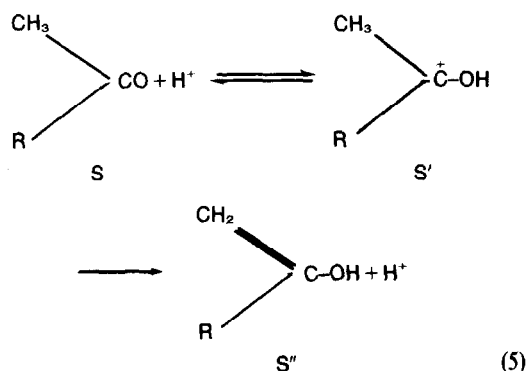
Thus, NBS itself or Br^+ or the protonated NBS viz NBSH^+ are the possible oxidising species¹⁶⁻¹⁸.

It may be pointed out that all kinetic studies have been made in presence of $\text{Hg}(\text{OAc})_2$ in order to avoid any possible bromine oxidation which may be produced as:



Mercuric acetate acts as a capture agent for any Br^- formed in the reaction and exists as HgBr_4^{2-} or unionised HgBr_2 and ensures that oxidation takes place purely through NBS.¹⁹

Ketones are known to enolise in acidic media as follows:



where S represents the ketone, S' the conjugate acid and S'' its enolic form.

It has been established through kinetic investigation that the order in NBS is zero and taking into consideration Littler and Water²⁰'s contention that in such cases enolisation step will be slow and rate determining, following mechanistic scheme is formulated in which NBS itself acts as an oxidising species:

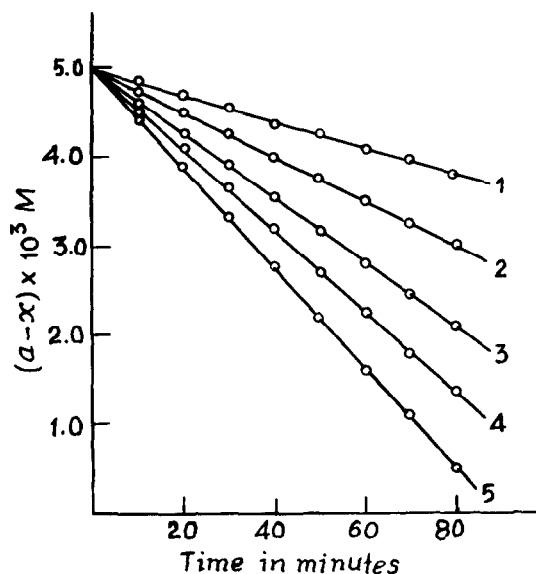
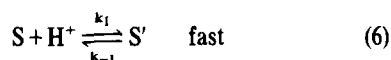
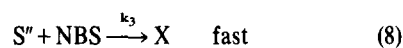


Fig. 1. Zero order rate plots at 35° . $[\text{NBS}] = 1.0 \times 10^{-3} \text{ M}$, $[\text{HClO}_4] = 0.12 \text{ M}$, $[\text{Hg}(\text{OAc})_2] = 2.0 \times 10^{-3} \text{ M}$, $[\text{MeCon-pr}] = 0.6$, 1.0 , 1.4 , 1.5 and $2.2 \times 10^{-2} \text{ M}$ in 1, 2, 3, 4 and 5, respectively.



slow and rate determining step



(Intermediate species)



Application of steady state treatment to S', S'' and X gives the rate law as:

$$-\frac{d}{dt} [\text{NBS}] = \frac{2k_1k_2}{k_{-1} + k_2} [\text{S}][\text{H}^+] \quad (10)$$

The above mechanism is supported by the following experimental observations:

(1) The experimental stoichiometry is in good agreement with the mechanism proposed.

(2) The rate law derived above, is in accordance with the experimental observations.

(3) A negative dielectric effect is supported by the above mechanism.

(4) The magnitude of the solvent isotope effect also supports the proposed mechanism. The higher rate value in D_2O indicates a pre-equilibrium fast proton transfer with specific acid catalysed reaction. It is reported in the literature that for any proton catalysed reaction one should expect a solvent isotope effect ($k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$) of about 2.0 to 2.5.²¹ A value of $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.1$ has been found for the rate of acid catalysed enolization of acetone.²² In the present investigation a solvent isotope effect corresponding to $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.3-2.7$ and $2.4-2.8$ for MeCon-pr and MeCO₂-Bu, respectively, has been obtained in 40%-80% D_2O . Thus the observed solvent isotope effect is in the close agreement with the reported values and further establishes that the oxidation proceeds through the enol and not through the keto form.

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