

Chemistry

KINETIC STUDY OF OXIDATION OF CYCLOHEPTANONE BY
N-BROMOSUCCINIMIDE IN ACIDIC MEDIA

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Cycloheptanone in perchloric acid media is oxidised to 1,2 cycloheptanedione by N-bromosuccinimide (NBS). The oxidation process has been monitored in presence of mercuric acetate. A zero order dependence in NBS and a first order dependence in cycloheptanone and $[H^+]$ is observed. Addition of mercuric acetate, succinimide, and sodium perchlorate have negligible effect on the rate of oxidation. Methanol addition showed a positive effect. Solvent isotope effect ($k_{O_2D_2O}/k_{O_2H_2O}$) was found as 2.4 to 2.8 at 35°C. Various thermodynamic parameters have been computed. The oxidative kinetic parameters have been mechanistically interpreted. It is suggested that the enol form of cycloheptanone and NBS are the principal reactive species controlling the rate of oxidation and a rate law deduced as $-d/dt [NBS] = 2k_1 k_2 / (k_{-1} + k_2) [Cyclo-Hp] [H^+]$ explains the kinetic results.

INTRODUCTION

A survey of literature shows that the kinetics of oxidation of cycloheptanone by suitable oxidants has not been much studied. Some details on the kinetic studies of cycloheptanone oxidation by V(V) (Radhakrishnamurti & Devi, 1973), Hexacyanoferrate (III) (Radhakrishnamurti & Devi, 1976) and Chloramine-T (Kumar *et al.*, 1975) are available. Mhala *et al.* (1976) have reported the kinetics of enolisation of cycloheptanone catalysed by amino acids. Lamaty and Roque (1967) studied a series of ketones on the basis of conformational consideration. Reduction of ketones by secondary alcohols, catalysed by triphenylphosphine complexes of ruthenium and rhodium were reported by Sharaf *et al.* (1973). The Rh complex was found to be more active than its Ru analog. Thompson *et al.* (1965) have reported the base catalysed auto-oxidation of cycloheptanone. In the present paper are reported our results of the kinetics and mechanism of oxidation of cycloheptanone by a new redox titrant viz., N-bromosuccinimide.

EXPERIMENTAL

Aqueous solutions of cycloheptanone [Fluka AG (Buchs SG)] and N-bromosuccinimide (G. R. S. Merck) were prepared in triple distilled water. NBS solution was always prepared fresh and its strength was checked by iodometric method. Succinimide and mercuric acetate used were of H & W (England) and E. Merck (Germany) grade respectively. Sodium perchlorate, methanol and perchloric acid used were of analaR grade. The reaction stills were coated black from outside to prevent photo-

*For correspondence.

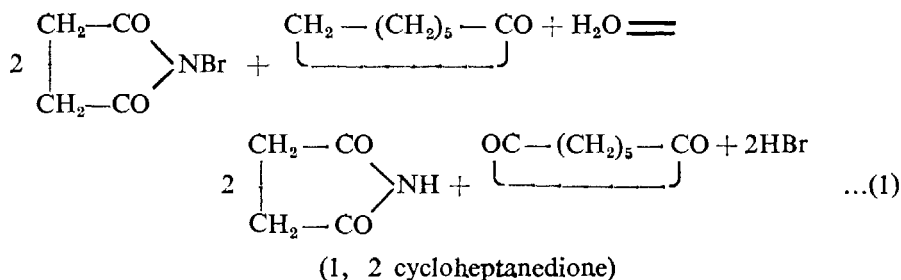
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chemical effect. Heavy water was obtained from BARC (India) and was 99.4 per cent pure.

Requisite amounts of mercuric acetate, perchloric acid and water were taken in reaction flasks containing 5 ml of NBS solution and kept in water bath at desired temperature for half-an-hour. Reaction was initiated by adding appropriate volume of cycloheptanone maintained at the same temperature and progress of the reaction was monitored by estimating unconsumed NBS iodometrically.

RESULTS

Stoichiometry of the reaction was established as 2 : 1 (two moles of NBS being consumed by one mole of cycloheptanone) by carrying out several sets of experiments with varying ratios of NBS over cycloheptanone in 0.2M perchloric acid at 50° for 48 hours. The stoichiometric equation may thus be formulated as :



The reaction product was identified by conventional spot test (Feigl, 1966) methods.

Pseudo zero order rate constants (k'_1) in NBS were obtained at each initial concentration of reactants (Table I). A proportional increase in the rate constant was observed with increase in cycloheptanone concentration and the values of the first

TABLE I

Effect of reactants concentration on the reaction rate
 $[\text{HClO}_4] = 1.6 \times 10^{-1}\text{M}$ and $[\text{Hg}(\text{OAc})_2] = 2.0 \times 10^{-3}\text{M}$

$10^2[\text{NBS}]\text{M}$	$10^2[\text{Cyclo-Hp}]\text{M}$	$k_0 \times 10^7 \text{ mol l}^{-1} \text{ sec}^{-1}$	
		30°	35°
0.8	1.0	3.98	6.16
1.0	1.0	4.02	6.02
1.2	1.0	3.96	5.96
1.4	1.0	3.98	5.90
1.6	1.0	4.02	6.05
1.0	0.7	2.86	4.31
1.0	0.8	3.32	4.86
1.0	0.9	3.69	5.55
1.0	1.1	4.48	6.67

order rate constants calculated as $k'_1 = k_0 / [\text{Cyclo-Hp}]$ were found to be 4.09 and $6.10 \times 10^{-5} \text{ sec}^{-1}$ at 30° and 35° respectively and thus established a first order dependence in cycloheptanone concentration.

A strong dependence of the reaction rate with respect to $[\text{H}^+]$ has been observed (Table II) and the rate constants increase linearly with an increase in $[\text{H}^+]$. The values of the first order rate constants $k'_1 = k_0 / [\text{HClO}_4]$ calculated as 2.51 and $3.81 \times 10^{-6} \text{ sec}^{-1}$ at 30° and 35° clearly establishes a first order with respect to hydrogen ion concentration.

TABLE II

Effect of hydrogen ion concentration on the reaction rate

$[\text{NBS}] = 1.0 \times 10^{-3} \text{M}$, $[\text{Cyclo-Hp}] = 1.0 \times 10^{-2} \text{M}$, $[\text{HClO}_4] = 1.6 \times 10^{-1} \text{M}$ and $[\text{Hg}(\text{OAc})_2] = 2.0 \times 10^{-3} \text{M}$

$10[\text{HClO}_4] \text{M}$	$k_0 \times 10^7 \text{ mol l}^{-1} \text{ sec}^{-1}$	
	30°	35°
1.2	2.94	4.67
1.4	3.49	5.40
1.6	4.02	6.02
1.8	4.67	6.86
2.0	5.69	7.55

TABLE III

Effect of methanol on the reaction rate

$[\text{NBS}] = 1.0 \times 10^{-3} \text{M}$, $[\text{Cyclo-Hp}] = 1.0 \times 10^{-2} \text{M}$, $[\text{HClO}_4] = 1.6 \times 10^{-1} \text{M}$, and $[\text{Hg}(\text{OAc})_2] = 2.0 \times 10^{-3} \text{M}$ Temp. = 30°

Methanol (%)	$k_0 \times 10^7 \text{ mol l}^{-1} \text{ sec}^{-1}$
0	4.02
10	4.45
20	5.00
30	5.67
40	6.24

Ionic strength, mercuric acetate and succinimide variations have an insignificant effect on the values of the rate constants while methanol addition showed a positive effect (Table III) pointing to a negative dielectric effect. Solvent isotope effect studied in different $\text{D}_2\text{O-H}_2\text{O}$ mixture at 35° showed an increase of the rate constants values (Table IV).

Values of the various activation parameters have been computed and are compiled in Table V.

TABLE IV

Solvent isotope effect on the reaction rate

[NBS] = 1.0×10^{-3} M, [Cyclo-Hp] = 1.0×10^{-2} M, [HClO₄] = 1.6×10^{-1} M and
 [Hg(OAc)₂] = 2.0×10^{-3} M Temp. = 35°

D ₂ O-H ₂ O (%)	$k_0 \times 10^7$ mol l ⁻¹ sec ⁻¹
40-60	9.64
60-40	10.4
80-20	11.3

TABLE V

Effect of temperature on reaction rate

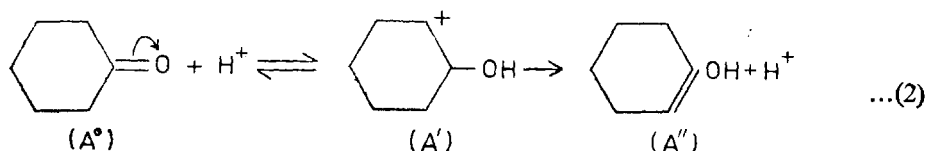
[NBS] = 1.0×10^{-3} M, [Cyclo-Hp] = 1.0×10^{-2} M,
 [HClO₄] = 1.6×10^{-1} M and [Hg (OAc)₂] = 2.0×10^{-3} M

Temp. °C	$k_0 \times 10^7$ mol l ⁻¹ sec ⁻¹	$k^* \times 10^4$ l mol ⁻¹ sec ⁻¹	$A \times 10^{-8}$ l mol ⁻¹ sec ⁻¹	ΔS^\ddagger e.u.	ΔH^\ddagger K. cal ^s mol ⁻¹	ΔF^\ddagger K. cal ^s mol ⁻¹
25	2.38	1.48	4.17	-20.2	16.5	22.5
30	4.02	2.51	4.56	-20.0	16.5	22.5
35	6.02	3.81	4.37	-20.1	16.5	22.6
40	9.80	6.13	4.44	-20.0	16.4	22.6
45	14.3	8.93	4.27	-20.1	16.4	22.7
50	22.2	13.8	4.26	-20.1	16.4	22.7

*Specific rate constant.

DISCUSSION

Ketones are compounds having the functional group $>C=O$ and the presence of such carbonyl group adjacent to methylene group gives rise to an interesting property viz. tautomerism or enolisation. Acid catalysed enolisation of ketones involve the removal of proton from the conjugate acid of ketone and cycloheptanone therefore is known to enolise as follows :

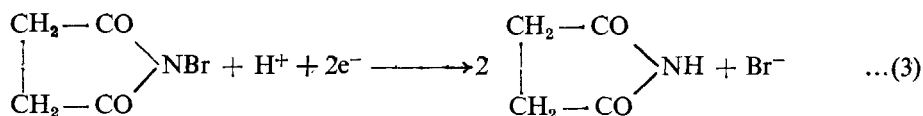


where A^o represents the cycloheptanone, A' its conjugate acid and A'' the enol form of the ketone.

As mentioned in our earlier papers(Mushran *et al.*, 1976; 1978; and Tiwari *et al.*, 1976)[NBS] may exist in three different forms in acid media and there exist the

possibility of either of the three oxidising species viz. NBS itself, bromonium ion Br^+ or protonated NBS i.e., $(^+\text{NBSH})$ interacting with cycloheptanone in the oxidation process.

In order to carry out pure NBS oxidation and to avoid any possible bromine oxidation the kinetic investigations have been made in presence of mercuric acetate which acts as a capture reagent for any bromide ion (Br^-) formed in the reaction as shown by eqn. (3) :



Thus NBS undergoes two electron reduction to produce succinimide and bromide ion.

The bromide ion thus formed in the reaction reacts with H^+ in the reaction mixture to give hydrogen bromide which would interact with NBS molecule to liberate free bromine as shown in eqs. (4) and (5).

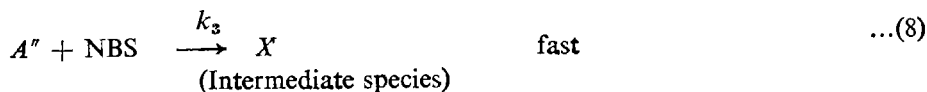


Thus, mercuric acetate acts as a scavenger for any Br^- formed and inhibits the formation of free bromine. According to Bailar (1956), the reagent mercuric acetate reacts with Br^- and exists as HgBr_2^{4-} or unionised HgBr_2 .

Since the reaction is independent of oxidant concentration, the observed rate of oxidation is undoubtedly dependent on the rate of enolisation. In order to ensure whether keto form or enol form of cycloheptanone is attacked in the oxidation process the rate study measurements were carried out in different $\text{D}_2\text{O}-\text{H}_2\text{O}$ mixtures. The higher rate values observed in D_2O excludes the possibility of keto form being the main reactive species oxidised. Further, the magnitude of the solvent isotope effect ($k_{\text{O}}\text{D}_2\text{O}/k_{\text{O}}\text{H}_2\text{O} = 2.4-2.8$) obtained in the oxidation of cycloheptanone is in conformity with the reported value of acid catalysed enolisation processes (Rule & Lamer, 1938) ($k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 2.0-2.5$) and confirms that the enol form of cycloheptanone is the main species oxidised. A solvent isotope effect of magnitude 2.1 reported for enolisation of acetone (Reilz, 1937) also supports the above contention.

Further, the observed negative dielectric effect and ionic strength effect which play a definite role in the oxidation process indicate that the rate determining step must involve the interaction between an ion and a dipole molecule. It has been confirmed from stoichiometry that two moles of NBS are consumed per mole of cycloheptanone. In such a case, Littler and Waters (1962) have suggested that in two electron abstracting processes, enolisation step will be slow and rate determining. Thus, assuming enolisation of cycloheptanone as the slow and rate determining step, three possible mechanistic routes involving (a) NBS itself, (b) $^+\text{NBSH}$ and (c) Br^+ may be proposed. Out of these, it can be shown that taking (b) and (c) as the oxidising species several complicated hypothetical steps are involved and one

is therefore led to conclude that in the mechanistic model the unprotonated form of NBS viz., (a) is undoubtedly the principal oxidant. The following mechanism is proposed :



The rate of disappearance of NBS is given by

$$-\frac{d}{dt} [\text{NBS}] = k_3 [A''] [\text{NBS}] + k_4 [X] [\text{NBS}] \quad \dots(10)$$

Application of steady state treatment to intermediate X gives :

$$k_3 [A''] [\text{NBS}] = k_4 [X] [\text{NBS}] \quad \dots(11)$$

From relations (10) and (11) we have,

$$-\frac{d}{dt} [\text{NBS}] = 2k_3 [A''] [\text{NBS}] \quad \dots(12)$$

On applying steady state treatment to A' and A'' we have relations (13) and (14)

$$k_1 [A^\circ] [H^+] = k_{-1} [A'] + k_2 [A'] \quad \dots(13)$$

$$k_2 [A'] = k_3 [A''] [\text{NBS}] \quad \dots(14)$$

Combining eqns. (12) and (14), we get,

$$-\frac{d}{dt} [\text{NBS}] = 2 k_2 [A'] \quad \dots(15)$$

From eqn. (13) $[A'] = \frac{k_1}{k_{-1} + k_2} [A^\circ] [H^+]$, substituting the value of $[A']$ in eqn. (15), the rate law thus obtained is

$$-\frac{d}{dt} [\text{NBS}] = \frac{2k_1 k_2}{k_{-1} + k_2} [A^\circ] [H^+] \quad \dots(16)$$

Rate law governed by eqn. (16), shows that the rate of disappearance of NBS follows a first order dependence in the substrate $[A^\circ]$ and hydrogen ion $[H^+]$ and is independent of the oxidant $[\text{NBS}]$ and this agrees very well with the kinetic results experimentally obtained. Further, stoichiometry and solvent isotope effect also strongly support the proposed mechanism.

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