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Kinetics and Mechanism of Oxidation of Cyclopentanone by N-bromosuccinimide

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With 2 Figures

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N-bromosuccinimide oxidation of cyclopentanone in acidic media in presence of mercuric acetate has been made. A zero order dependance to N-bromosuccinimide and a first order dependence to cyclopentanone and hydrogen ion concentration has been observed. Ionic strength, mercuric acetate and succinimide has negligible effect while methanol addition has a positive effect. Various rate parameters have been computed and 1,2-cyclopentanedione identified as the end product. A suitable mechanism in confirmity with the above observations has been proposed.

The use of N-bromosuccinimide (*NBS*) as a potent oxidising agent has chiefly been restricted to the oxidimetric determination of several compounds[1] and the literature lacks with a detailed step by step mechanism of oxidation by *NBS*. This prompted us to report our kinetic results and to suggest a suitable mechanism in accord with the kinetic data, on the oxidation of cyclopentanone by *NBS*.

Experimental

NBS (G. R. S. Merck) was prepared always fresh and stored in black Japan coated bottles and its strength checked by iodometric method[2]. A Fluka AG sample of cyclopentanone was used. Mercuric acetate and succinimide used were of E. Merck (Germany) and H & W (England) grade resp. All other reagents viz. $NaClO_4$, methanol, perchloric acid were of analaR grade. Triple distilled water was used throughout the course of investigations and reaction stills blackened from outside.

Rate studies were carried out at constant temperature (± 0.1°). All reactants except cyclopentanone were allowed to mix and the reaction initiated by adding appropriate amounts of cyclopentanone. The kinetics was followed by estimating unconsumed *NBS* iodometrically.

A blank set was also made simultaneously.

The product 1,2-cyclopentanedione was detected by phenylhydrazine-hydrochloric acid test[3].

Results

Experiments showed that one mole of cyclopentanone consumes two moles of *NBS*.

Table 1. *Effect of Reactants Concentration on the Reaction Rate*
$[HClO_4] = 5.0 \times 10^{-2} M$, $[Hg(OAc)_2] = 2.0 \times 10^{-3} M$

10^3 [*NBS*], *M*	10^2 [Cyclopentanone], *M*	$k_0 \cdot 10^7$ mol $l^{-1} \cdot sec^{-1}$ 35°	40°
0.8	1.0	5.10	8.56
1.0	1.0	5.43	9.10
1.2	1.0	5.48	8.93
1.4	1.0	5.33	8.80
1.6	1.0	5.50	8.60
1.0	0.5	2.74	4.50
1.0	1.5	8.04	13.6
1.0	2.0	10.8	18.7
1.0	2.5	13.9	23.0

Table 2. *Effect of Hydrogen Ion Concentration on the Reaction Rate.*
$[NBS] = 1.0 \cdot 10^{-3} M$, $[Cyclopentanone] = 1.0 \cdot 10^{-2} M$,
$[Hg(OAc)_2] = 2.0 \cdot 10^{-3} M$

10^2 [$HClO_4$], *M*	$k_0 \cdot 10^7$ mol $\cdot l^{-1} \cdot sec^{-1}$ 35°	40°
2.5	2.67	4.72
5.0	5.43	9.10
7.5	8.22	13.9
10.0	10.4	18.5
12.5	14.1	23.7

It may be pointed out that neither mercuric acetate interferes with the liberated iodine nor the oxidation of cyclopentanone by mercuric acetate or iodine takes place under the experimental conditions. Further, there is no change in pH value of the reaction mixture for any particular kinetic run.

The oxidation of cyclopentanone by *NBS* was studied over a wide range of concentrations of the reactants (Table 1 and Table 2). A zero order rate constant in *NBS* was observed at all initial concentrations of the reactants. A linear increase in the zero order rate constant was observed with increase in initial concentrations of cyclopentanone (Fig. 1) and hydrogen ion. (Exactly the same figure.)

The average values of the first order rate constants calculated as $k_1' = k_0/[\text{Cyclopentanone}]$ and $k_1' = k_0/[\text{HClO}_4]$ were 5.45, $9.14 \times 10^{-5}\ \text{sec}^{-1}$ and 1.08, $1.86 \times 10^{-5}\ \text{sec}^{-1}$ at 35°, 40°, resp.

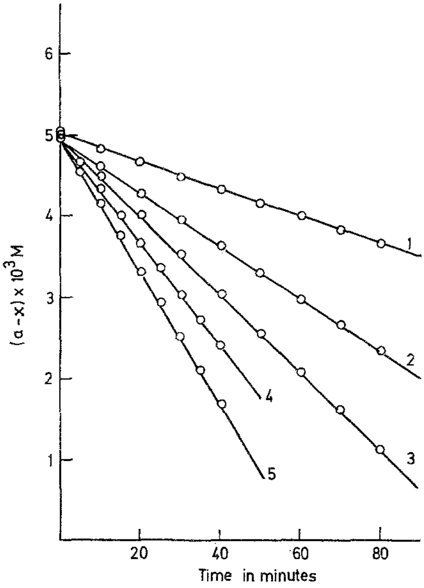


Fig. 1. Zero order rate plots at 35° $[NBS] = 1.0 \cdot 10^{-3} M$, $[\text{HClO}_4] = 5.0 \cdot 10^{-2} M$, $[\text{Hg}(OAc)_2] = 2.0 \cdot 10^{-3} M$, [Cyclopentanone] = 0.5, 1.0, 1.5, 2.0 and $2.5 \cdot 10^{-2} M$ in 1, 2, 3, 4 and 5 respectively. Exactly the same zero order rate plots at 35° were obtained with $[NBS] = 1.0 \cdot 10^{-3} M$, $[\text{Cyclopentanone}] = 1.0 \cdot 10^{-2} M$, $[\text{Hg}(OAc)_2] = 2.0 \cdot 10^{-3} M$, $[\text{HClO}_4]$ = 2.5, 5.0, 7.5, 10.0 and $12.5 \cdot 10^{-2} M$ in 1, 2, 3, 4 and 5 resp.

Ionic strength, mercuric acetate and succinimide variations had an insignificant effect while methanol addition (Table 3) had a positive effect pointing to a negative dielectric effect.

Average values of the rate parameters (Table 4) viz. energy of activation ($\Delta E^{\neq}$), frequency factor (A), entropy of activation ($\Delta S^{\neq}$), heat of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta F^{\neq}$) were computed as $22.0\ \text{kcal} \cdot \text{mol}^{-1}$, $3.37 \cdot 10^{12}\ \text{l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$, -2.18 e.u., $21.4\ \text{kcal} \cdot \text{mol}^{-1}$ and $22.1\ \text{kcal} \cdot \text{mol}^{-1}$ from the rate study measurements carried out at five temperatures (Fig. 2).

Table 3. *Effect of Methanol on the Reaction Rate.* $[NBS] = 1.0 \cdot 10^{-3} M$, [Cyclopentanone] $= 1.0 \cdot 10^{-2} M$, $[HClO_4] = 5.0 \cdot 10^{-2} M$, $[Hg(OAc)_2] = 2.0 \cdot 10^{-3} M$, Temp. = 35 °C

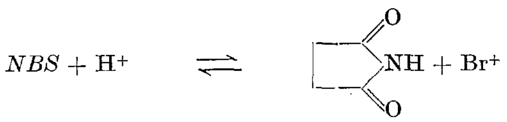
[Methanol], %	$k_0 \cdot 10^7$ mol · l^{-1} · sec^{-1}
0	5.43
10	5.94
20	6.67
30	7.25
40	8.25

Table 4. *Effect of Temperature on the Reaction Rate.* $[NBS] = 1.0 \cdot 10^{-3} M$, [Cyclopentanone] $= 1.0 \cdot 10^{-2} M$, $[HClO_4] = 5.0 \cdot 10^{-2} M$, $[Hg(OAc)_2] = 2.0 \cdot 10^{-3} M$

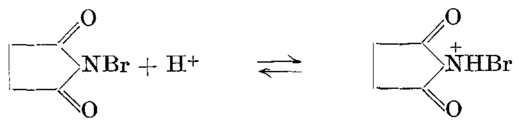
Temp., °C	$k_0 \cdot 10^7$ mol · l^{-1} · sec^{-1}	$k \cdot 10^4$ l · mol^{-1} · sec^{-1}	$A \cdot 10^{-12}$ l · mol^{-1} · sec^{-1}	$\Delta E^{\neq}$ kcal · mol^{-1}	$\Delta S^{\neq}$ e.u.	$\Delta H^{\neq}$ kcal · mol^{-1}	$\Delta F^{\neq}$ kcal · mol^{-1}
30	3.06	6.12	3.60	22.0	— 2.04	21.4	22.0
35	5.43	10.9	3.52	22.0	— 2.09	21.4	22.0
40	9.10	18.2	3.16	22.0	— 2.30	21.4	22.1
45	16.2	32.4	3.32	22.0	— 2.21	21.4	22.1
50	26.2	52.4	3.23	22.0	— 2.26	21.4	22.1

Discussion

NBS is known to exist in acidic media in the following equilibria.



(1)



(2)

Thus *NBS* itself[4] or Br^+[5, 6] or protonated *NBS*[7] are the possible oxidising species.

The presence of mercuric acetate (more than that of *NBS* concentration) simply means that Br_2 oxidation has been completely suppressed, which otherwise would have formed by the interaction of HBr and *NBS* as follows [*M* = succinimide]:

$$NBS + HBr \rightarrow M + Br_2 \qquad (3)$$

Mercuric acetate acts as scavenger[4, 8] for any Br^- formed in the reaction as $HgBr_4^{2-}$ or unionised $HgBr_2$ and thus ensuring that oxidation takes place purely through *NBS*.

In an acidic media, ketones are known to enolise.

It is seen that the order in *NBS* is zero and according to *Littler*[9] in such a case with two electron oxidants, the rates of oxidation are related to the rates of enolisation. Therefore, assuming the enolisation step to be the slow and rate determining the following schemes may be proposed. S represents cyclopentanone, SH^+ its enolic cation.

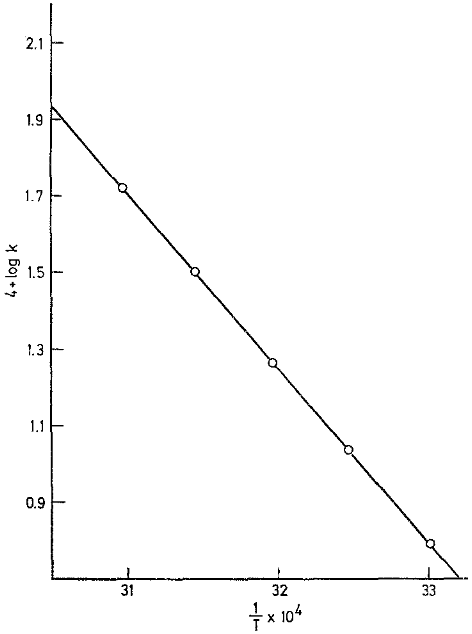


Fig. 2. *Arrhenius* plot

A. *NBS as the Oxidising Species*

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ \qquad \text{slow \& r.d.} \qquad (4)$$

$$SH^+ + NBS \xrightarrow{k_2} X^+ + M \qquad \text{fast} \qquad (5)$$

$$X^+ + NBS \xrightarrow{k_3} \text{Products} \qquad \text{fast} \qquad (6)$$

Application of steady state treatment with approximation $k_{-1} \ll k_2$, yields the rate law as

$$-\frac{d}{dt}[NBS] = 2\,k_1\,[S]\,[H^+] \qquad (7)$$

B. Br^+ *as the Oxidising Species*

$$S + \mathrm{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S\mathrm{H}^+ \qquad \text{slow \& r.d.} \qquad (8)$$

$$NBS + \mathrm{H}^+ \underset{k_{-2}'}{\overset{k_2'}{\rightleftharpoons}} M + \mathrm{Br}^+ \qquad \text{fast} \qquad (9)$$

$$S\mathrm{H}^+ + \mathrm{Br}^+ \xrightarrow{k_3'} X^{+2} \qquad \text{fast} \qquad (10)$$

$$X^{+2} + \mathrm{Br}^+ \xrightarrow{k_4} \text{Products} \qquad \text{fast} \qquad (11)$$

Application of steady state treatment with approximation $k_{-1} \ll k_3'$, yields the rate law as

$$-\frac{\mathrm{d}}{\mathrm{d}\,t}[NBS] = 2\,k_1\,[S]\,[\mathrm{H}^+] \qquad (12)$$

C. $\overset{+}{N}BSH$ *as the Oxidising Species*

A mechanism similar to **B** could be proposed with the exclusion of M term only in step (9) and replacing $\overset{+}{N}BS\mathrm{H}$ for Br^+ [refer eqn. (2)] and the rate law thus obtained is similar to equation (12) above with the same approximation $k_{-1} \ll k_3'$.

All the three schemes with the assumption that the enolisation step is the slow & rate determining lead to a rate law in accord with the experimental rate law and are in harmony with the negligible influence of ionic strength and succinimide effect and a positive methanol effect.

Despite the fact that all the three schemes are in perfect accord with the experimental observations, scheme **A** is more likely to occur for having an edge over schemes **B** and **C** in the sense that steps (10) and (11) involving interaction between two positively charged ions have been assumed to be fast steps compared to step (5) involving interaction between an ion and dipole which does not appear to be very reasonable. Thus schemes **B** and **C** can easily be ruled out and it is concluded that the reaction follows exclusively a path as shown in scheme **A**.

Thus it may be concluded that *NBS* oxidation of cyclopentanone in acidic media in presence of mercuric acetate involves the enolisation of cyclopentanone as the slow and rate determining step followed by rapid attack of *NBS* molecule on the enolic cation of cyclopentanone forming an intermediate which is subsequently destroyed by another molecule of *NBS* in a fast step, yielding products.

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References

[1] *R. Filler*, Chem. Rev. **63**, 21 (1963).

[2] *M. Z. Barakat* and *M. F. Abd-El Wahab*, Anal. Chem. **26**, 1973 (1954).

[3] *F. Feigl*, Spot Tests in Organic Analysis, p. 325. New York: Elsevier. 1966.

[4] *N. Venkatasubramanian* and *V. Thiagarajan*, Canad. J. Chem. **47**, 694 (1969).

[5] *P. F. Kruse*, Jr., *K. L. Grist*, and *T. A. McCoy*, Anal. Chem. **26**, 139 (1954).

[6] *J. Lecomte* and *H. Gault*, C. r. hebdomad. Sé. Acad. Sci **238**, 2538 (1954).

[7] *N. S. Srinivasan* and *N. Venkatasubramanian*, Indian J. Chem. **9**, 726 (1971).

[8] *J. C. Bailar*, The Chemistry of Coordination Compounds, p. 4. New York: Reinhold. 1956.

[9] *J. S. Littler*, J. Chem. Soc. **1961**, 827, 832.

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