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A KINETIC STUDY OF THE OXIDATION OF ISOPROPYL ALCOHOL BY N-BROMO SUCCINIMIDE

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While the use of N-bromo succinimide as a versatile oxidising agent is well known, the kinetics and mechanism of these oxidation reactions have not been clearly established, although several interpretations have been advanced[1]. It has been suggested that oxidations of alcohols by this reagent in polar media take place via molecular bromine or by a 'positive' halogen and that the reaction proceeds either by a rate-determining formation of a hypo bromite which readily loses hydrogen bromide to form the carbonyl product[2], or by a rate-determining formation of a α-halo intermediate followed by a fast dehydrobromination[3]. As the mechanisms of oxidation of alcohols by bromine have been placed on surer grounds[4,5] and this involves an attacking species of the above type we have now investigated the kinetics of the oxidation of a typical secondary alcohol, isopropyl alcohol, by NBS in solvent mixtures of acetic acid and water (v/v). We report, in this communication, certain peculiarities noted in the kinetics for the first time.

The kinetics was investigated by following the rate of disappearance of NBS by iodometric estimation, and the data reveal a second order kinetics - first with respect to both NBS and the alcohol. But a second order plot (Fig.) for the oxidation shows that the reaction is indeed composed of two second order reactions -- the first, a comparatively slow one being superseded after a particular stage by a faster second order reaction.

Our interpretation of this behaviour is based on the following arguments. During the oxidation, after about 20% of the reaction the solution

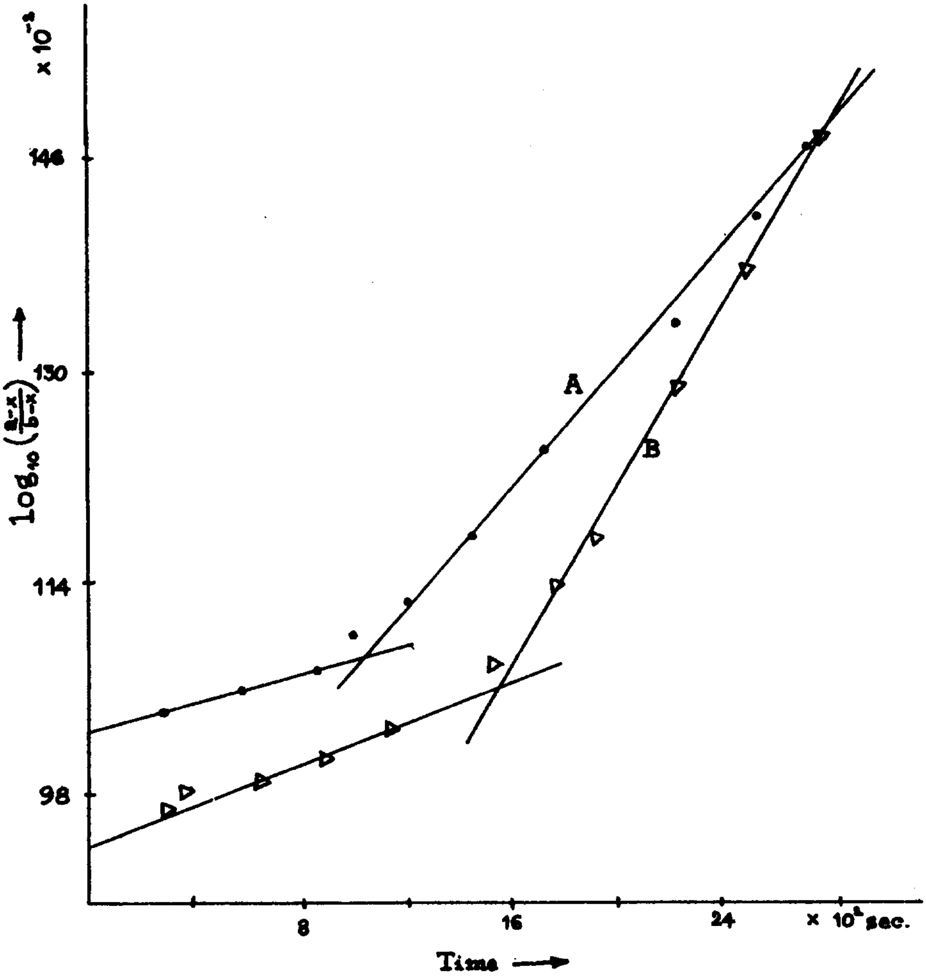

Fig. Second order plot for the oxidation of Isopropyl alcohol by NBS at 35°C.

A —— 30% acetic acid.

B —— 50% acetic acid.

becomes distinctly yellow in colour — obviously due to the liberation of bromine by an interaction between the unreacted NBS and Br^-, one of the products of reduction. That the second and faster part of the reaction is due to the oxidation of the alcohol by molecular bromine (presumably with a little competing oxidation by NBS also*) has been proved by two independent routes. We have followed the oxidation of isopropyl alcohol by bromine under the same conditions and the second order rate constant of the reaction is very nearly the same as for the second part of the reaction. Further initial addition of potassium bromide completely suppresses the first part of the reaction, the reaction now being of a simple second order right from the beginning and the rate constant is nearly the same as that obtained either for the second stage of the reaction or for the bromine oxidation under identical conditions (Table II)

TABLE I

Oxidation of Isopropyl alcohol by NBS.

Second order rate constants ($k_2 \times 10^3$ litre-mol^{-1} sec^{-1}) for the first and second stage at 35°C.

Solvent % $H\overline{OAC}-H_2O$ v/v	First Stage	Second Stage
30	1.651	6.006
50	1.923	8.414
70	2.507	6.564

We have further achieved in another way, a total suppression of the second stage of the reaction with only the slower first part being observed from the beginning to over 70% of the reaction. If the incursion of the second stage is due to the accumulation of Br^- in the system, the addition of $Hg(O\overline{AC})_2$ should fix it up both as unionised $HgBr_2$ or more likely as $HgBr_4^{--}$

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* Fortunately the iodometric estimation of unreacted NBS would give the amount of unreacted oxidant and/or bromine and these two are equivalent quantities.

TABLE II

Second order rate constants ($k_2 \times 10^3$ litre-mol^{-1} sec^{-1}) for the oxidation of Isopropyl alcohol by NBS in the presence of 0.009456M KBr at 35°C.

Solvent % HOAc-H_2O v/v	In presence of Br^-	Br_2 oxidation
30	8.330	...
50	6.482	7.660
70	5.129	7.508

so that the evolution of molecular bromine would be totally prevented[6]. This is exactly what is observed in our investigations. (Table III) The rate constants observed in the presence of added mercuric acetate are thus possibly the pure NBS oxidation rates and the slightly higher rates obtained from the slopes of the first part of the reaction between the alcohol and NBS in the absence of added mercuric acetate are likely to be a mixture of NBS and bromine oxidations.

TABLE III

Second order rate constants for the oxidation of Isopropyl alcohol by NBS in the presence of 0.01416M mercuric acetate at 35°C.

Solvent % HOAc-H_2O v/v	$k_2 \times 10^5$ litre-mol^{-1} sec^{-1}
30	5.205
50	4.615
70	7.150

That the role of mercuric acetate is essentially that of effectively combining with the Br^- formed during the course of the reaction is also well illustrated by another method. Changes in concentration of added mercuric acetate over a nearly fourfold range still give the same value for the rate constant while at concentrations below 0.004M, the concentration of the mercuric salt is not sufficiently high to keep all the Br^- produced back, with the result that bromine evolution sets in slowly. (Table IV)

TABLE IV

Effect of mercuric acetate concentration on the oxidation of Isopropyl alcohol by NBS at 45°C in 70% $H\overline{OAC}$.

Concn. of $Hg(O\overline{AC})_2$	$k_2 \times 10^5$ litre-mol^{-1} sec^{-1}
0.003956M	17.04
0.005000M	17.28
0.010500M	16.68
0.014160M	17.26

It should also be pointed out that the NBS oxidations (in presence of $Hg(O\overline{AC})_2$) are between 70 and 100 times slower than the corresponding bromine oxidations. This should be surprising because both seem to oxidise via the same 'positive' end. One reason for the slower rate with NBS, we feel, is the cyclic nature of the mechanism and the entropy factor might outweigh the energy factor in the case of NBS leading to a considerable reduction in the rate.

We also notice that an initial addition of 0.101M succinimide reduces the second order rate constant to 4.771×10^{-4} and 2.672×10^{-2} for the first and second stages of the oxidation in 70% $H\overline{OAC}$ at 35°C. This reduction in rate is certainly a mass-law effect, as added succinimide will reduce the concentration of the active oxidising species Br^+ in the equilibrium

We further notice that the incursion of the bromine oxidation (i.e. the second limb) is solvent dependent and occurs at different stages of the total reaction. Thus for the oxidation of isopropyl alcohol at 35°C it occurs at 16%, 19%, and 25% in 30, 50 and 70% acetic acid. This is quite in accordance with the dielectric constants of three solvent systems--for the concentration of Br^-, which has to react with NBS to form molecular bromine, will be largest in 30% $\overline{HOAc}$ and least in 70% at any specified interval of time since the reaction between the alcohol and NBS is essentially a dipole-dipole reaction.

REFERENCES

1. Filler, R.Chem.Reviews.(1963),63,21.
2. Kruse,Jr.,P.F.,Grist,K.L.,and Mccoy,T.A., Anal.Chem.(1954),26,139.
3. Lecomte,J., and Gault,H. Compt.rend.(1954),238,2538.
4. Swain,C.G., Wiles,R.A. and Bader,R.F.W., J.Amer.Chem.Soc.(1961),83,1945.
5. Barker,I.R.L., Overend,W.G., and Rees,C.W., J.Chem.Soc.(1964).
6. J.C.Bailar. The Chemistry of the coordination Compounds, Reinhold publishing corporation, N.Y.(1956). pages 4 to 16.