KINETICS AND MECHANISM OF OXIDATION OF SECONDARY ALCOHOLS BY POTASSIUM BROMATE

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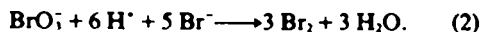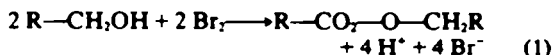Department of Chemistry, Vivekananda College, Madras 600004, India

Abstract—The oxidation by Br(V) of propan-2-ol follows the rate law $(-d[Br(V)]/dt) = k_r$ [alcohol][Br(V)][H$^+$]^2. The initial reaction is complicated by the presence of the product bromide ion. The reaction is composed of two second order reactions—the first, a comparatively slow one and the second stage, a faster reaction which is mainly bromine oxidation. The pure bromate oxidation can be followed by the initial addition of mercuric acetate which prevents the accumulation of bromine in the system under these conditions. The reaction rate does not depend on the nature and structure of the alcohol. A mechanism involving a slow rate-determining formation of an alkyl-bromate ester followed by a fast decomposition to the products is in accord with the observed results.

INTRODUCTION

Potassium bromate [Br(V)] is known to be a powerful oxidising agent with a redox potential of 1·44 volts.[1] Although several reactions involving Br(V) as an oxidising agent are known, kinetic aspects of these reactions have received very little attention. The oxidation of hydrogen peroxide by bromate in an acid medium was carried out by Bray and Davis.[2] Kinetic salt effects is the bromate-bromide reaction in presence of hydrogen peroxide were examined by Bray and Liefbhofsky[3] and by Sclar and Riesch[4] in the presence of allyl alcohol. Thompson[5] has shown the oxidation of hydrazoic acid by bromate in perchloric acid to be a two electron oxidation. Several weak one-electron reducing agents are oxidised by acid bromate at a rate that is second order in bromate and independent of both the concentration and chemical nature of the reducing agent. This was observed with Np(V), Mn(II) and Ce(III) in sulphuric acid.[6,7]

Most of the early investigations of the oxidation of organic substrates by bromate are essentially oxidation by bromine liberated by a reaction between Br(V) and the product bromide ion. Farkas and Schachter[8] studied the oxidation of primary aliphatic alcohols by bromate in the presence of bromine and proposed the following mechanism for this reaction.

$$2\text{ R}-\text{CH}_2\text{OH} + 2\text{ Br}_2 \longrightarrow \text{R}-\text{CO}_2-\text{O}-\text{CH}_2\text{R}$$
$$+ 4\text{ H}^+ + 4\text{ Br}^- \quad (1)$$

$$\text{BrO}_3^- + 6\text{ H}^+ + 5\text{ Br}^- \longrightarrow 3\text{ Br}_2 + 3\text{ H}_2\text{O}. \quad (2)$$

In a later kinetic investigation of the oxidation of ethyl alcohol in the presence of bromate and

bromine, Farkas[9] showed that the ratio of aldehyde to acetate in the reaction product was identical with the ratio found with oxidation by bromine alone. The reaction in the presence of bromate had the same rate law as the reaction with bromine. This established that the two reactions were essentially the same, the bromate supplying the free bromine necessary for the reaction to proceed.

Our interest in these oxidations stemmed from a desire to study the 'pure' oxidation of organic substrate by Br(V) in acid medium unmixed by any competing or faster oxidation by any generated molecular bromine. This could be achieved by suitably complexing the product bromide ions as they were formed.[10] We report in this communication the results of such an investigation with aliphatic secondary alcohols as the substrates.

RESULTS AND DISCUSSION

The Br(V) oxidation of propan-2-ol was carried out as a typical example. In a reaction to determine the order of the reaction with respect to Br(V), certain pecularities were observed. While the reaction data could be fitted into a first order plot, the plot shows that the reaction is indeed composed of two first order reactions. The first, a comparatively slow one, being superseded after a particular stage by a faster reaction (Fig 1). During the oxidation (after about 20% of the reaction) the solution also becomes yellow, presumably due to the liberation of bromine by an interaction between the unreacted bromate and the product bromide. That the faster, viz, the second step is mainly composed of molecular bromine oxidation with a much slower competing reaction by Br(V) and that the slower reaction is
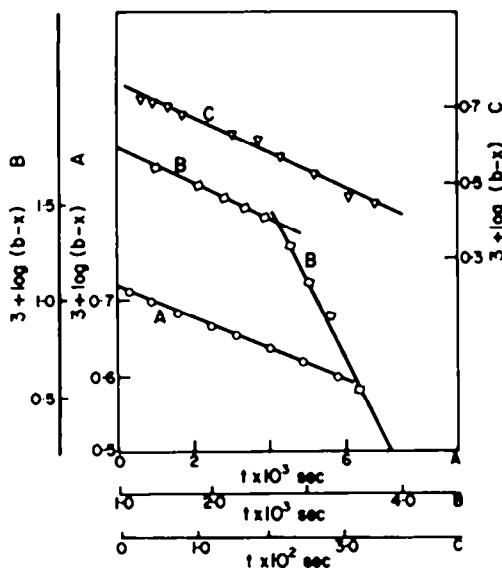
Fig 1. First order plots Propan-2-ol (55°C) HOAc-50%-H₂O-50%; H₂SO₄: 0·005M. (A) In the presence of Hg(OAc)₂; (B) In the absence of Hg(OAc)₂; (C) In the absence of Hg(OAc)₂ and the presence of added Br⁻.

made up of an oxidation by Br(V) could be demonstrated as follows.

The second order rate constant for bromine oxidation of these alcohols are close to the rate constants for the second part of the bromate oxidation (Table 1). Initial addition of KBr completely suppresses the first part of the reaction, and the reaction now follows simple first order kinetics from the beginning (Fig 1, Plot C). The rate constants again are nearly the same as those obtained for the second stage of the reaction or for the bromine oxidation under identical conditions.

A total suppression of the second stage of the reaction with only the slower first part being observed from the beginning to over two half lives can be achieved in another way. It is known that Hg²⁺ can fix up Br⁻ as unionised HgBr₂ or HgBr₄²⁻.[10] This is exactly what is observed on the addition of Hg²⁺ to the reaction mixture at the start when the evolution of molecular bromine *in situ* is totally

prevented–a single slow first order reaction (Fig 1, Plot A) being obtained. We attribute this slow reaction to an oxidation by Br(V) exclusively.

Different concentrations of added mercuric acetate over a four-fold range give the same value for the rate constant (Table 2). Concentrations of Hg²⁺ lower than 0·005 M are not sufficiently high to keep back all the Br⁻ produced, with the result that bromine evolution sets in slowly. The experiments with other substrate alcohols have been carried out in the presence of 0·01 M of mercuric acetate in binary solvent mixtures of acetic acid-water. The reported rate constants, therefore, can be taken for pure bromate oxidations.

Table 2. Effect of added mercuric acetate on bromate oxidation

[Propan-2-ol] = 0·05 M [H₂SO₄] = 0·1 M	solvent: 50% HOAc	[BrO₃⁻] = 0·005 M Temp. = 40°C
[Hg(OAc)₂]M	$k_1 \times 10^5$ sec⁻¹	$k_2 \times 10^3$ lit. mol⁻¹ sec⁻¹
0·005066	5·94	1·14
0·01062	5·46	1·10
0·02115	5·83	1·12

Effect of acidity on the reaction rate. The reaction between Br(V) and propan-2-ol is subject to considerable acid catalysis. The reaction rate increases with increasing acidity both with sulphuric acid and perchloric acid (Table 3). There is a second order dependence on the stoichiometric acid concentration in both the acid media. The complete rate law for the oxidation of propan-2-ol by Br(V) is thus

$$\frac{-d[Br(V)]}{dt} = k_4 [Br(V)] [alc.] [H^+]^2 \quad (1)$$

or under constant acidity conditions

$$\frac{[Br(V)]}{dt} = k_4' [Br(V)][alc.] \quad (2)$$

$$\text{where } k_4' = k_4 [H^+]^2. \quad (3)$$

Table 3. Effect of acidity on bromate oxidation

[Propan-2-ol] = 0·1 M [Hg(OAc)₂] = 0·01 M	solvent: 20% HOAc	[BrO₃⁻] = 0·005 M Temp. = 30°C
[H⁺] M	H₂SO₄ $k_2 \times 10^4$ lit. mol⁻¹ sec⁻¹	HClO₄
0·5	7·59	2
0·75	18·1	2·88
1·00	35·3	6·39
1·25	72·7	8·25
1·50	123	11·5
1·75	163	17·1
2·00	251	25·2
2·50		56·3

Table 1

Propan-2-ol: 0·05 M [H₂SO₄]: 0·005 M	solvent: 50% HOAc Temp.: 55°C
	$k_2 \times 10^4$ lit. mol⁻¹ sec⁻¹
Oxidation by bromate [0·005 M] in the presence of added Br⁻ [0·001 M]	105
Oxidation by bromine [0·005 M]	309
Oxidation by pure bromate [0·005 M]	3·84

$$R\underset{R'}{\overset{R}{\diagdown}}C\underset{OH}{\overset{H}{\diagup}} + H_2\overset{\cdot}{B}rO_3 \xrightarrow{\textit{slow}} \underset{R'}{\overset{R}{\diagdown}}C\underset{O-\overset{\cdot}{B}rO_2H}{\overset{H}{\diagup}} + H_2O \qquad (4)$$

$$\underset{R'}{\overset{R}{\diagdown}}\overset{:B}{C}\underset{O-\overset{\cdot}{B}r-O_2H}{\overset{H}{\diagup}} \xrightarrow{\textit{fast}} \underset{R'}{\overset{R}{\diagdown}}C{=}O + H\overset{\oplus}{B}rO_2 + BH^- \qquad (5)$$
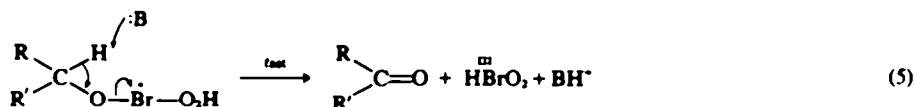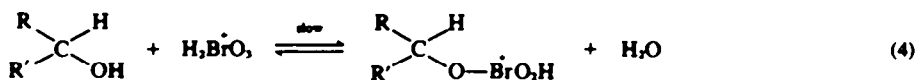
Thus when reactions are carried out at a definite acid concentration (particularly for comparison of reactivities of substrates) the k_2' values could be used for direct comparison.

Effect of solvent polarity. The effect of solvent polarity on the rate of oxidation has been studied in binary solvent mixtures of acetic acid–water of compositions ranging from 10% acetic acid–90% water to 80% acetic acid–20% water in the temperature range of 30°–50°C (Table 4).

Isotopic effect on reaction rate. An interesting observation of the present study is that propan-2-ol α-d is oxidised at almost the same rate as the protic compound (Table 5), indicating that the α—CH bond was not involved in any cleavage in the rate determining step.

Structural effects in the bromate oxidation of alcohols. The effect of structural variations in the alcohol moiety R.CH$_2$. CHOH. CH$_3$ on the rate of oxidation was brought out (Table 6). It is interesting to note that the reaction rate is totally insensitive to these variations and it is only in the case of 1:3

dichloro propan-2-ol that a significant lowering of the oxidation rate is observed.

On the basis of the above experimental findings a mechanism for this oxidation reaction can be proposed (equations 4 and 5).

The above proposal has a formal analogy to the chromic acid oxidation of alcohols[11,12] from which, of course, it differs in a number of respects.

The second order dependence on acidity indicates that the reaction is between ROH and H$_2$BrO$_3$ or between $R\overset{+}{O}H_2$ and HBrO$_3$. In the latter case the reaction will be mechanistically similar to a bimolecular nucleophilic substitution reaction and one would expect considerable change in reactivity dependant on the structure of the alcohol. The insensitivity of the reaction rate to the structure of the alcohol therefore rules out any important protonation of the alcoholic hydroxyl group.

While the rate-law shows that a molecule of the alcohol and H$_2$BrO$_3$ are involved in the transition state, the lack of dependence of the rate on structure of the substrate and the absence of a kinetic

Table 4. Acetic acid variation

[Propan-2-ol] = 0·05 M [Hg(OAc)$_2$] = 0·01 M	[H$_2$SO$_4$] = 0·1 M	[BrO$_3^-$] = 0·005 M Temp. = 30°C
solvent (% v/v) HOAc–H$_2$O	$k_2 \times 10^5$ lit. mol^{-1} sec^{-1}	
10–90	2·46	
20–80	4·90	
30–70	10·4	
40–60	20·3	
50–50	49·9	
60–40	100	
70–30	330	
80–20	1250	

Table 5. Isotopic effect on Propan-2-ol oxidation

[Propan-2-ol] = 0·08 M [Hg(OAc)$_2$] = 0·01 M	[H$_2$SO$_4$] = 0·005 M solvent: 50% HOAc	[BrO$_3^-$] = 0·005 M Temp. = 55°C
[alcohol]	$k_2 \times 10^4$ lit. mol^{-1} sec^{-1}	
Propan-2-ol	3·84	
Propan-2-ol α – d	3·62	

Table 6. Structural effect on the rate of bromate oxidation

[H$_2$SO$_4$] = 0·1 M		[BrO$_3$] = 0·005 M
[Hg(OAc)$_2$] = 0·01 M	solvent: 50% HOAc	Temp. = 55°C

[alcohol]	$k_2 \times 10^4$ lit. mol⁻¹ sec⁻¹
Propan-2-ol	36·8
1,3 dichloropropan-2-ol	13·5
1,Methoxy propan-2-ol	35·6
Butan-2-ol	34·0
Pentan-2-ol	34·4
Octan-2-ol	34·8

isotope effect in the reaction show that the second step in the above mechanism can not be the rate determining step. This step involves the breakage of a strong C—H bond and is bound to be influenced by structural changes in the substrate alcohol, as was observed in chromic acid oxidations, where a negative rho has consistently been obtained. If on the other hand, the first step involving the formation of bromate ester is assumed to be the slow step, this will be in accord with the observed insensitivity to structural variations. Inorganic esterification reactions of this type are known to be not influenced by structural alterations in the alcohol moiety.[12-15] There is evidence for the formation of the alkyl bromate ester and its decomposition is known to yield in addition to hydroxylic products, oxidation products too.[16] In the case of alcohol with a highly electronegative substituent(s) as in the case of 1,3-dichloro-propan-2-ol it is likely that the esterification step becomes dependent on the structure of the alcohol, because of the considerable depletion of electron density on the alcohol oxygen atom.

The first stage of the oxidation of alcohols by Br(V) depicted by equations 4 and 5 can be condensed to the form

$$R—CHOH—R' + Br(V) \longrightarrow R—CO—R' + Br(III). \quad (6)$$
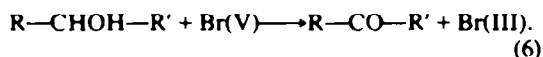
The subsequent stages of reduction of Br(III) to the final bromide ion can proceed by one of several pathways. One such pathway involving stepwise two-electron transfers can be

$$R—CHOH—R' + Br(III) \longrightarrow R—CO—R' + Br(I) \quad (7)$$

$$R—CHOH—R' + Br(I) \longrightarrow R—CO—R' + Br \quad (8)$$
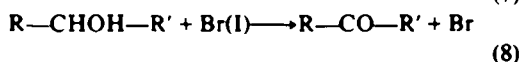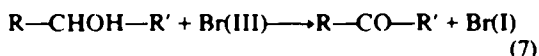
although intermediate species of the type Br(IV) can also be proposed. The elucidation of the inorganic aspects of the Br(V)—Br reaction are presently being undertaken.

EXPERIMENTAL

AnalaR potassium bromate was used in all the experiments. All liquid organic compounds were purified by dis-

tillation. Solid organic compounds (Fluka, K and K Laboratories, Koch-Light) were of extra pure quality. AR Grade acetic acid was used after fractional distillation. Propan-2-ol α-d (99% isotopic purity) was kindly provided by Prof. C. N. Pillai.

Solutions of the alcohol and bromate containing 0·01 M mercuric acetate in the appropriate solvent were thermostated for nearly two hours before each run and 50 ml of each of the solutions were mixed. 5 ml Aliquots were pipetted out at regular intervals and quenched in 4% potassium iodide. The liberated iodine was then titrated against standard sodium thiosulphate solution to a starch end point. Added mercuric acetate did not interfere with the kinetics of oxidation. The mercuric acetate oxidation of alcohols also does not take place under experimental conditions.

All the alcohols investigated in the present work are smoothly and quantitatively oxidised to the corresponding ketones. Typically propan-2-ol is oxidised to acetone (characterised as the DNP derivative), in over 90% yield. As the individual orders had been shown by prior investigations to be one each in Br(V) and alcohol, in subsequent reactions the ratio of alcohol to bromate was kept at 10:1 and the second order rate constants were calculated by dividing the pseudo first order rate constants by the respective alcohol concentrations. The results reported herein are those of duplicate or triplicate runs and the rate constants were reproducible with in ±3%.

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