

Kinetics and mechanism of oxidation of aliphatic alcohols by tetrabutylammonium tribromide

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MS received 20 May 2000; revised 3 January 2001

Abstract. Oxidation of nine primary aliphatic alcohols by tetrabutylammonium tribromide (TBATB) in aqueous acetic acid leads to the formation of the corresponding aldehydes. The reaction is first order with respect to TBATB. Michaelis–Menten type kinetics is observed with respect to alcohols. The reaction failed to induce the polymerization of acrylonitrile. Tetrabutylammonium chloride has no effect on the reaction rate. The proposed reactive oxidizing species is the tribromide ion. The oxidation of [1,1-²H₂]ethanol exhibits a substantial kinetic isotope effect. The effect of solvent composition indicates that the rate increases with increase in the polarity of the solvent. The reaction is susceptible to both polar and steric effects of substituents. A mechanism involving transfer of a hydride ion in the rate-determining step has been proposed.

Keywords. Aliphatic alcohols; hydride ion transfer; tetrabutylammonium tribromide.

1. Introduction

Tetraalkylammonium polyhalides are widely used as halogenating reagents in synthetic organic chemistry^{1–3}. Recently, tetrabutylammonium tribromide (TBATB) has been used for bromination of some selected organic substrates⁴. There are, however, only a few reports regarding their use as oxidizing and brominating agents in synthetic chemistry^{5–7}. These compounds are more suitable than molecular halogens because they are solids and hence easy to handle, and owing to their stability, selectivity and excellent product yields. We have been interested in the kinetic and mechanistic studies of the reactions of polyhalides and have already reported some of them^{8–10}. We discuss here the kinetics of oxidation of nine aliphatic alcohols by TBATB in aqueous acetic acid solution. Attempts have been made to correlate rate and structure in this reaction. A suitable mechanism has also been proposed.

2. Experimental

2.1 Materials

All the alcohols used were of commercial grade. Methanol, ethanol, and 1-propanol were purified by the magnesium alkoxide method¹¹. Other alcohols were dried over anhydrous

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potassium carbonate and fractionated. TBATB was prepared by the reported method¹ and its purity checked by the iodometric method. [1,1-²H₂]Ethanol was prepared by reported methods¹². Its isotopic purity, ascertained by its ¹H NMR spectrum, was 94 ± 4%. Acetic acid was refluxed with chromic oxide and acetic anhydride for 6 h and then fractionally distilled. All other reagents were commercial products and were purified by the usual methods¹³.

2.2 Product analysis

Product analysis was carried out under kinetic conditions. In a typical experiment, ethanol (4.6 g, 0.1 mol), KBr (0.2 mol) and TBATB (4.82 g, 0.01 mol) were made up to 50 ml in 1:1 (v/v) aqueous acetic acid and kept in the dark for ≈ 10 h to ensure completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ HCl and kept overnight under refrigeration. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. Yields of DNP before and after recrystallization were 4.31 g (94%) and 3.72 g (81%) respectively, based on the consumption of TBATB. The DNP was found to be identical (m.p. and mixed m.p.) with the DNP of acetaldehyde. In similar experiments with other alcohols, yields of the DNPs were in the range of 77–87% after recrystallization.

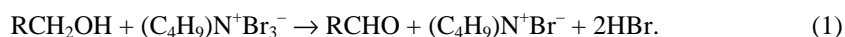
2.3 Kinetic measurements

The reactions were studied under pseudo-first-order conditions by using an excess (× 15 or greater) of the substrate over TBATB. The solvent was 1:1 (v/v) acetic acid–water, unless mentioned otherwise. Tribromide ion is known to dissociate to a large extent with bromine and bromide ion. The value¹⁴ of the dissociation constant in 1:1 (v/v) acetic acid–water is ≈ 0.02 mol dm⁻³. To suppress the dissociation, all kinetic runs were carried out in the presence of an excess (0.2 mol dm⁻³) of potassium bromide. The reactions were studied at constant temperature (± 0.1 K) and were followed by monitoring the decrease in the concentration of TBATB at 394 nm for up to 80% reaction. Pseudo-first-order rate constants, *k*_{obs}, were evaluated from linear plots (*r* > 0.995) of log[TBATB] against time. Duplicate kinetic runs showed that the rate constants are reproducible to within ± 3%. Simple and multivariate regression analyses were carried out by the least-squares method.

3. Results

3.1 Stoichiometry

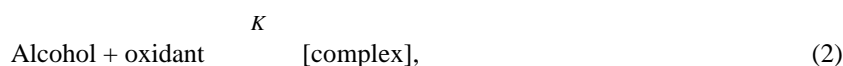
The oxidation of alcohols by TBATB results in the formation of corresponding aldehydes. The overall reaction may be represented as,



3.2 Rate laws

The reactions are of first order with respect to TBATB. Further, the pseudo-first-order rate constant, *k*_{obs}, are independent of the initial concentration of TBATB. The reaction

rate increases with an increase in the concentration of the alcohol but not linearly (table 1). A plot of $1/k_{\text{obs}}$ against $1/[\text{alcohol}]$ is linear ($r > 0.995$) with an intercept on the rate-ordinate. Thus, Michaelis–Menten type kinetics is observed with respect to the alcohols. This leads to the postulation of the following overall mechanism ((2) and (3)) and rate law, (4)



$$\text{Rate} = k_2 K [\text{alcohol}] [\text{oxidant}] / (1 + K [\text{alcohol}]). \quad (4)$$

Dependence of reaction rate on reductant concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. Thermodynamic parameters of complex formation and activation parameters of decomposition of the complexes were calculated from the values of K and k_2 respectively at different temperatures (tables 2 and 3).

3.3 Induced polymerization of acrylonitrile

Oxidation of ethanol, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation (table 1).

3.4 Kinetic isotope effect

To ascertain the importance of the cleavage of the $\alpha\text{-C-H}$ bond in the rate-determining step, the oxidation of $[1,1\text{-}^2\text{H}_2]\text{ethanol}$ was studied. Results showed the presence of a primary kinetic isotope effect (table 3). The rate of oxidation of the deuteriated alcohol was corrected for the protio alcohol present.

Table 1. Rate constants for the oxidation of ethanol by TBATB at 288 K.

$10^3 [\text{TBATB}] (\text{mol dm}^{-3})$	$[\text{Alcohol}] (\text{mol dm}^{-3})$	$10^5 k_{\text{obs}} (\text{s}^{-1})$
1.0	0.10	20.5
1.0	0.20	31.2
1.0	0.40	42.3
1.0	0.60	48.0
1.0	0.80	51.5
1.0	1.00	53.8
1.0	1.50	57.3
1.0	3.00	61.2
2.0	0.20	31.0
4.0	0.20	31.8
6.0	0.20	32.1
8.0	0.20	31.5
1.0	0.20	31.6*

*Contained $0.005 \text{ mol dm}^{-3}$ acrylonitrile

Table 2. Formation constants of the TBATB-RCH₂OH complexes and thermodynamic parameters.

Alcohol	K (dm ³ mol ⁻¹) at				ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
H	4.81	4.14	3.40	2.72	-16.9 ± 0.8	-37 ± 3	-5.93 ± 0.6
Me	4.52	3.80	3.32	2.63	-16.0 ± 0.8	-34 ± 3	-5.82 ± 0.7
Et	5.15	4.46	3.82	3.11	-15.5 ± 0.7	-31 ± 2	-6.16 ± 0.5
<i>n</i> -Pr	4.50	3.61	2.89	2.41	-18.5 ± 0.1	-43 ± 1	-5.67 ± 0.1
<i>n</i> -Bu	5.10	4.51	3.72	3.02	-15.9 ± 0.9	-33 ± 3	-6.14 ± 0.7
<i>i</i> -Pr	5.33	4.60	3.80	3.00	-17.0 ± 0.9	-37 ± 3	-6.21 ± 0.7
ClCH ₂	4.88	4.23	3.55	2.85	-16.1 ± 0.8	-34 ± 3	-6.01 ± 0.6
MeOCH ₂	5.63	4.92	4.25	3.41	-15.0 ± 0.9	-29 ± 3	-6.40 ± 0.7
<i>t</i> -Bu	5.25	4.55	3.83	3.06	-16.1 ± 0.8	-34 ± 3	-6.19 ± 0.7
MeCD ₂	4.60	3.82	3.10	2.50	-17.9 ± 0.5	-41 ± 2	-5.78 ± 0.7

Table 3. Rate constants for the decomposition of TBATB-RCH₂OH complexes and the activation parameters.

Alcohol	$10^5 k_2$ (dm ³ mol ⁻¹ s ⁻¹) at				ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
H	1.31	3.81	11.2	31.3	78.1 ± 0.8	-68 ± 3	98.1 ± 0.6
Me	65.7	138	288	612	57.4 ± 0.6	-108 ± 2	89.4 ± 0.5
Et	108	220	430	880	50.5 ± 0.8	-127 ± 3	88.2 ± 0.7
<i>n</i> -Pr	178	350	672	1310	48.0 ± 0.6	-131 ± 3	87.0 ± 0.5
<i>n</i> -Bu	207	397	735	1390	46.2 ± 0.4	-136 ± 1	86.7 ± 0.3
<i>i</i> -Pr	280	555	1020	1810	44.7 ± 0.2	-139 ± 1	86.0 ± 0.2
ClCH ₂	1.91	5.04	13.1	33.2	69.9 ± 0.7	-93 ± 2	97.5 ± 0.5
MeOCH ₂	12.8	29.9	68.7	154	60.6 ± 0.6	-109 ± 2	93.1 ± 0.4
<i>t</i> -Bu	2650	4100	6010	8940	28.2 ± 0.3	-178 ± 1	81.0 ± 0.2
MeCD ₂	20.9	44.8	92.3	197	54.2 ± 0.8	-128 ± 3	92.1 ± 0.6
k_H/k_D	3.14	3.08	3.12	3.10			

3.5 Effect of tetrabutylammonium chloride

Addition of tetrabutylammonium chloride (TBACl) had no effect on the rates of oxidation (table 4).

3.6 Effect of solvent composition

Rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that rates increase with increase in the amount of water in the solvent mixture. To determine whether the solvent composition affects the formation constant, K , and/or rate constant, k_2 , the variation of rate with concentration of ethanol was studied in solutions of different compositions. The results (table 5) showed that the

Table 4. Effect of tetrabutylammonium chloride on the rate of oxidation of ethanol by TBATB.

[TBATB] = 0.001 mol dm⁻³ [ethanol] = 1.0 mol dm⁻³ Temp. = 288 K

10 ³ [TBACl] (mol dm ⁻³)	0.0	0.5	1.0	2.0	2.0	4.0
10 ⁵ <i>k</i> _{obs} (s ⁻¹)	53.8	52.8	53.1	52.6	53.3	52.0

Table 5. Dependence of rates for alcohol oxidation by TBATB on substrate concentration in solvents of different solvent compositions.

[TBATB] = 0.001 mol dm⁻³ Temp. = 288 K

Ethanol (mol dm ⁻³)	10 ⁴ <i>k</i> _{obs} (s ⁻¹) [at % AcOH (v/v)]				
	25	40	50	60	72
0.1	9.72	4.45	2.05	1.09	0.40
0.2	15.0	6.60	3.12	1.63	0.59
0.4	20.7	8.71	4.23	2.18	0.79
0.6	23.6	9.75	4.80	2.45	0.88
0.8	25.5	10.4	5.15	2.62	0.94
1.0	26.7	10.8	5.38	2.73	0.98
1.5	28.5	11.4	5.73	2.89	1.04
3.0	30.6	12.0	6.12	3.07	1.10
<i>K</i> (dm ³ mol ⁻³)	4.16	5.33	4.52	4.95	5.15
10 ⁴ <i>k</i> ₂ (s ⁻¹)	33.1	12.8	6.57	3.28	1.17

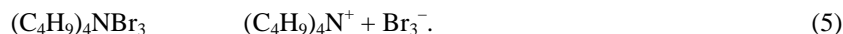
rate constants, *k*₂, vary considerably while the formation constant, *K*, remains practically independent of solvent composition.

4. Discussion

There is no significant isokinetic relationship between activation entropy and enthalpy of the oxidation of nine primary alcohols (*r*² = 0.5568). Correlation between the calculated values of enthalpies and entropies of activation is often vitiated by the experimental errors associated with them. Exner¹⁵ has suggested an alternative method of testing the validity of the isokinetic relationship. An Exner plot between log *k*₂ at 288 and 318 K was linear (*r*² = 0.9982; slope 0.7675 ± 0.0122). The value of isokinetic temperature evaluated from this plot is 485 ± 17 K. The linear isokinetic correlation suggests that all the alcohols are oxidized by the same mechanism and changes in the rates are governed by changes in both the enthalpy and entropy of activation.

We have carried out some conductivity measurements to determine the nature of TBATB in aqueous acetic acid solutions. It is observed that acetic acid has very low conductivity. Addition of TBATB increases the conductivity of acetic acid. We measured the conductivity of TBATB in solvents containing different proportions of acetic acid (100–30%) and water. We found that conductivity increases sharply as the water content is initially increased but reaches a limiting value in about 60% acetic acid–water mixture.

Therefore, TBATB can be considered an ionic compound, which exists under our reaction conditions as tetrabutylammonium and tribromide ions, (5) below. Absence of any effect due to added tetrabutylammonium ion also indicates that the equilibrium (5) lies far towards the right,



Tribromide ion is known to dissociate to bromine and bromide ion and dissociation constant values have been reported¹⁴. However, in the presence of large excess of bromide ion, the following reaction is suppressed. Thus in the present reaction the reactive oxidising species is the tribromide ion,



The oxidation of alcohols by bromine is reported to be much faster¹⁶ as compared to this reaction. This also supports the view that bromine is not the reactive species in this oxidation.

4.1 Solvent composition effect

Increase in the rate constant of disproportionation of the intermediate complex with an increase in the polarity of the medium suggests that the transition state is more polar than the reactants. The plot of $\log k_2$ against the inverse of the dielectric constant is nonlinear. The solvent effect was analysed using Grunwald–Winstein equation¹⁷,

$$\log k_2 = \log k_0 + mY \quad (7)$$

The plot of $\log k_2$ versus Y is linear ($r = 0.9997$) with $m = 0.78 \pm 0.01$. The value of m suggests a transition state which is more polar than the reactants. Thus considerable charge separation takes place in the transition state of the reaction.

4.2 Correlation analysis of reactivity

The data in table 2 show that the formation constants of alcohol-TBATB complexes are not sensitive to the nature of the substituent in the alcohol molecule. The rate constants, k_2 of disproportionation of the complexes (table 3), however, showed considerable variation.

The rate constants, k_2 , of oxidation of alcohols failed to yield any significant correlation separately with Taft's¹⁸ σ^* and E_s . The correlation with \mathbf{s}^* accounts for $\approx 82\%$ of the data but correlation is not acceptable by Exner's criterion¹⁹,

$$\log k_2 = -2.16 (\pm 0.39) \Sigma \mathbf{s}^* - 2.95, \quad (8)$$

$$r^2 = 0.8167, \text{ sd} = 0.49, n = 9, \mathbf{y} = 0.33, T = 288 \text{ K},$$

$$\log k_2 = -1.20 (\pm 0.34) \Sigma E_s - 3.51 \quad (9)$$

$$r^2 = 0.6357, \text{ sd} = 0.69, n = 9, \mathbf{y} = 0.48, T = 288 \text{ K}.$$

Here n is the number of data points and \mathbf{y} is Exner's statistical parameter¹⁹. The rate constants were, therefore, correlated in terms of Pavelich–Taft's²⁰ dual substituent-parameter as below,

$$\log k = \mathbf{r}^* \Sigma \mathbf{s}^* + \mathbf{d} \Sigma E_s + \log k_0. \quad (10)$$

The values of the substituent constants were obtained from the compilation by Wiberg¹⁸. The correlations are excellent, reaction constants being negative (table 6). There is no significant collinearity ($r^2 = 0.2322$) between \mathbf{s}^* and E_s of the nine substituents.

5. Mechanism

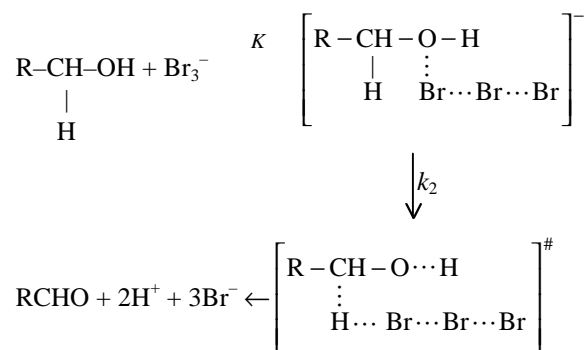
Negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. Negative steric reaction constants point to steric acceleration of the reaction. This may be explained on the basis of the high ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the product aldehyde as well as in the transition state leading to it, the transition state energy of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore, results.

From the rate law, it is apparent that an intermediate complex is formed in a rapid pre-equilibrium. However, with the present data, it is not possible to conclude definitely about the nature of the complex. A complex may be formed by interaction between the non-bonded pairs of electrons of the alcohol-oxygen and tribromide ion. The formation of a similar complex has been postulated in the oxidation of the alcohols²¹ by pyridinium hydrobromide perbromide (PHPB) also. Formation of moderately stable complexes is also supported by the values of the thermodynamic parameters. Complex formation is favoured by the enthalpy term but there is loss of entropy indicating the formation of a rigid structure.

Temperature invariance of the primary kinetic isotope effect (cf. table 3) can be interpreted in terms of a mechanism in which two bonds are cleaved more or less synchronously. Therefore, a rate-determining step involving cleavage of both the C-H and O-H bonds can be envisaged. The low magnitude of the polar reaction constants also supports the occurrence of a synchronous mechanism. However, correlation analysis of the substituent effect indicated the presence of an electron-deficient carbon centre in the transition state. It seems, therefore, that in the transition state the cleavage of the C-H bond, yielding an electron-deficient carbon centre, is before the cleavage of the O-H bond. The transition state remains polar in this mechanism and is consistent with the observed solvent effect. The solvent effect is similar to that found for synchronous homopolar reactions. A nonlinear transition state, implied in the synchronous mechanism, is supported by the relatively low magnitude of the kinetic isotope effect ($k_H/k_D \approx 3.1$). The oxidation of benzyl alcohol by PHPB²¹ also was reported to involve a nonlinear transition state and the kinetic isotope effect was found to be ≈ 3.5 . The mechanism depicted in scheme 1 accounts for all the observed results.

Table 6. Temperature dependence of the reaction constants.

Temp. (K)	\mathbf{r}^*	\mathbf{d}	R^2	sd	\mathbf{y}
288	-1.62 ± 0.008	-0.73 ± 0.005	0.9999	0.009	0.008
298	-1.52 ± 0.004	-0.66 ± 0.003	0.9998	0.005	0.011
308	-1.41 ± 0.004	-0.58 ± 0.003	0.9999	0.005	0.008
318	-1.31 ± 0.006	-0.51 ± 0.004	0.9997	0.007	0.014



Scheme 1.

The observed negative entropy of activation also supports the mechanism. As the charge separation takes place, the charged ends become highly solvated. This results in immobilization of a large number of solvent molecules, reflected by the loss of entropy²².

Acknowledgements

Thanks are due to the Council of Scientific and Industrial Research, New Delhi for financial assistance and to Prof. Kalyan K Banerji for his valuable help and suggestions.

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