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Kinetics and mechanism of the oxidation of aliphatic alcohols by benzyltrimethyl-ammonium chlorobromate

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The oxidation of alcohols by benzyltrimethylammonium chlorobromate, to the carbonyl compounds, proceeds by a hydride transfer from the alcohol to chlorobromate ion.

Benzyltrimethylammonium chlorobromate (BTMACB) has been used as a halogenating and oxidizing agent in synthetic organic chemistry.[1] There seems to be no report on the kinetics of oxidation by BTMACB, except that of aldehydes.[9] We are interested in the kinetic and mechanistic studies of the newer oxidizing agents and report here the kinetics of the oxidation of 14 aliphatic alcohols by BTMACB in aqueous acetic acid solution.

BTMACB was prepared by the reported method[1] and its purity checked by an iodometric method. [1,1-$^2H_2$]ethanol and [2-^2H]propan-2-ol were prepared by reported methods.[11,12] The reactions were studied under pseudo-first-order conditions by keeping an excess of the substrate over BTMACB. The solvent was 1:1(v/v) acetic acid–water, unless mentioned otherwise. The reactions were followed by monitoring the decrease in the concentration of BTMACB 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[BTMACB] against time. The second order rate constant, k_2, was determined from the relation: $k_2 = k_{obs}/$ [alcohol].

The oxidation of alcohols by BTMACB results in the formation of corresponding carbonyl compounds. The overall reaction may be represented as eqn (1).

$$R_2CHOH + [PhCH_2Me_3N]^+Br_2Cl^- \rightarrow R_2CO + [PhCH_2Me_3N]^+ + Cl^- + 2H^+ + 2Br^- \quad (1)$$

The reactions are of first order with respect to both the alcohol and the BTMACB. Addition of benzyltrimethylammonium chloride (BTMACl) or potassium bromide had no effect on the rates of oxidation. The rates of oxidation of alcohols were obtained at different temperatures and the activation parameters were calculated.

To ascertain the importance of the cleavage of the α-C–H bond in the rate-determining step, the oxidation of [1,1-$^2H_2$]ethanol and [2-^2H]propan-2-ol was studied. Results showed the presence of a substantial primary kinetic isotope effect ($k_H/k_D = 5.22$ and 5.18, at 298 K, for ethanol and 2-propanol respectively). This confirmed the cleavage of the α-C–H bond in the rate-determining step.

Conductivity measurements showed that addition of BTMACB increases the conductivity of glacial acetic acid.[9] Conductivity measurements of BTMACB in solvents containing different proportions of acetic acid (100–30%) and water showed that the conductivity increases sharply as the water content is initially increased but reaches a limiting value in a mixture of about 60% acetic acid–water. Therefore, BTMACB can be considered as an ionic compound, which exists under our reaction conditions as benzyltrimethylammonium and chlorobromate ions [eqn (2)]. No effect of added benzyltrimethylammonium ion also indicates that the equilibrium (2) lies far towards the right. The absence of any effect of bromide or chloride ion led us to propose that the reactive oxidizing species is chlorobromate ion.

$$PhCH_2Me_3NBr_2Cl \rightleftharpoons PhCH_2Me_3N^+ + Br_2Cl^- \quad (2)$$

Solvent composition effect: The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that the rate of reaction increased with an increase in the amount of water in the solvent mixtures. This suggests that the transition state is more polar than the reactants. The solvent effect was analysed using the Grunwald-Winstein equation.[15]

$$\log k_2 = \log k_0 + mY \quad (5)$$

The plot of log k_2 *versus* Y is linear ($r = 0.9992$) with $m = 0.79 \pm 0.01$. The value of m suggests a transition state that is more polar than the reactants. Thus considerable charge separation takes place in the transition state of the reaction.

The rate of oxidation of alcohols failed to yield any significant correlation separately with Taft's[16] σ^* and E_s. The rates were, therefore, correlated in terms of Pavelich-Taft's[17] dual substituent -parameter eqn (8).

$$\log k_2 = \rho^* \Sigma\sigma^* + \delta\, \Sigma E_s + \log k_o \quad (8)$$

The correlations are excellent; reaction constants being negative (Table 6). The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The negative steric reaction constant shows a 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.

The oxidation of ethanol and 2-propanol, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation. Therefore, a hydrogen abstraction mechanism leading to the formation of free radicals is unlikely. The presence of a substantial kinetic isotope effect confirms the cleavage of an α-C–H bond in the rate-determining step. The large negative values of the polar reaction constant together with a deuterium isotope effect indicate that the transition state approaches a carbocation in character. Hence, transfer of a hydride ion from the alcohol to the oxidant is suggested.

$$R-CH_2-OH + Br_2Cl^- \xrightarrow{\text{slow}} R-\overset{+}{C}H-O-H + H^+ + 2Br^- + Cl^-$$

$$R-\overset{+}{C}H-O-H \xrightarrow{\text{fast}} R-CHO + H^+$$

Scheme 1

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Table 6 Temperature dependence of the reaction constants

Temp (K)	ρ^*	δ	R^2	SD	ψ^a
288	–1.71±0.01	–0.69±0.01	0.9998	0.02	0.008
298	–1.61±0.02	–0.60±0.01	0.9998	0.02	0.011
308	–1.50±0.01	–0.56±0.01	0.9999	0.01	0.008
318	–1.38±0.02	–0.51±0.01	0.9994	0.02	0.016

[a]Ref. 19

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Techniques used: spectrophotometry, correlation analysis

Equations: 8

References: 19

Table 1: Rate constants for the oxidation of ethanol and 2-propanol by BTMACB at 288 K

Table 2: Rate constants and the activation parameters of the oxidation of alcohols by BTMACB

Table 3: Kinetic isotope effect in the oxidation of ethanol and propanol-2 by BTMACB

Table 4: Effect of benzyltrimethylammonium chloride or potassium bromide on the rate of oxidation of ethanol by BTMACB

Table 5: Effect of solvent composition on the oxidation of ethanol by BTMACB

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