

Correlation Analysis of Reactivity in the Oxidation of Substituted Benzyl Alcohols by Benzyltrimethylammonium Tribromide

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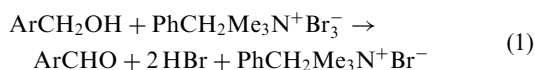
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The oxidation of benzyl alcohol by benzyltrimethylammonium tribromide involves an almost synchronous cleavage of the α -C–H and O–H bond.

Benzyltrimethylammonium tribromide (BTMAB) has been used as an effective halogenating and oxidizing agent in synthetic organic chemistry.^{1–3} The kinetics of the oxidation of primary aliphatic alcohols⁴ by BTMAB have been reported earlier from our laboratory. We now report here, the kinetics and effect of substituents on the oxidation of substituent benzyl alcohols by BTMAB in aqueous acetic acid.

BTMAB was prepared by the reported method¹ and its purity checked by an iodometric method. The reactions were studied under pseudo-first-order conditions by keeping an excess ($\times 15$ or greater) of the substrate over BTMAB. The solvent was acetic acid–water (1:1, v/v) unless stated otherwise. The reactions were followed by monitoring the decrease in the concentration of BTMAB at 354 nm for up to 80% of the reaction. Pseudo-first-order rate constants, k_{obs} , were evaluated from linear plots ($r > 0.990$) of $\log[\text{BTMAB}]$ vs. time.

The oxidation of benzyl alcohols results in the formation of corresponding benzaldehydes. The overall reaction is represented by eqn. (1).



The reactions are first order with respect to BTMAB and the alcohol. The oxidation of benzyl alcohol 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. Thus a one-electron oxidation, giving rise to free radicals, is unlikely. The rates of oxidation were studied at different temperatures and the activation parameters were calculated.

The oxidation of α, α -dideuteriobenzyl alcohol showed the presence of a substantial primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 3.17$ at 303 K). This confirms the cleavage of an α -C–H bond in the rate-determining step.

Addition of benzyltrimethylammonium chloride or potassium bromide had no effect on the rate of oxidation. These results are reminiscent of the results obtained in the oxidation of alcohols.⁴ This coupled with the results of conductivity measurements reported earlier,⁴ led us to propose that in the present reaction also, the reactive oxidizing species is tribromide ion.

The rates of oxidation of benzyl alcohol were determined in solvents containing different amounts of water and acetic acid. The rate increases as the water content of the solvent is increased. An analysis of the effect of solvent composition using the Grunwald–Winstein¹³ equation yielded a value of $m = 0.54 \pm 0.01$ ($r^2 = 0.9997$). The value of m indicates that the transition state is more polar than the reactants and a moderate degree of charge separation takes place in the transition state.

Correlation Analyses of Reactivity.—The rates of the *ortho*-, *para*- and *meta*-compounds failed to exhibit a significant correlation in terms of any single substituent-parameter equation.

The rates of *para*- and *meta*-substituted benzyl alcohols were subjected to analyses in terms of dual substituent parameter (DSP) equations of Taft¹⁶ and Swain *et al.*¹⁷ The rates of oxidation of the *para*-substituted benzyl alcohols show excellent correlation with Taft's σ_1 and $\sigma_{\text{R}}^{\text{B}}$ values while those of the *meta*-compounds correlate best with σ_1 and σ_{R}^0 .

The value of $\lambda^{\text{P}}(1.3)$ showed that the oxidation of *para*-substituted benzyl alcohols is more susceptible to the resonance effect than to the field effect. In the reaction of the *meta*-substituted compounds, however, the value of λ^{m} is *ca.* 0.75, indicating a greater importance of the field effect. In both cases, the magnitude of the reaction constants decreases with an increase in the temperature. This indicates a decrease in selectivity with an increase in the temperature.

Rates of the oxidation of the *ortho*-substituted alcohols were analysed by using Charton's²² eqns. (10) and (11), where σ_1 , σ_{R} , and V are field, resonance and steric substituent constants. No significant correlation was obtained using eqn. (10).

$$\log k_{\text{ortho}} = \rho_1\sigma_1 + \rho_{\text{R}}\sigma_{\text{R}} + h \quad (10)$$

$$\log k_{\text{ortho}} = \rho_1\sigma_1 + \rho_{\text{R}}\sigma_{\text{R}} + \Phi V + h \quad (11)$$

The rates showed an excellent correlation in terms of eqn. (11), the reaction constants being negative.

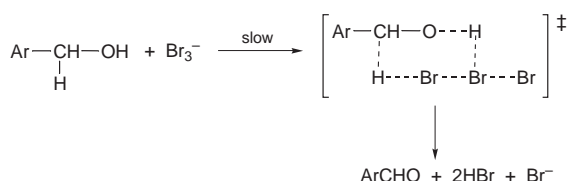
It is of interest to compare the values of reaction constants of the three series of compounds. The values of ρ_1 of the *ortho*-, *meta*- and *para*-substituted compounds, at 303 K, are -1.49 , -1.20 and -1.07 , respectively, *i.e.* the magnitude of the reaction constant decreases as the substituent moves away from the reaction centre. On the other hand the values of ρ_{R} are -1.37 , -0.89 and -1.36 respectively. This showed that ρ_{R} is essentially identical at *para*- and *ortho*-positions but is reduced at *meta*-position. Both the trends are in the expected direction.

Mechanism.—The negative polar reaction constant points to an electron-deficient carbon centre in the transition state of the rate-determining step. However, the low magnitudes of ρ_1 and ρ_{R} indicates a less pronounced charge separation in the transition state. 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 temperature invariance of the primary kinetic isotope effect can be interpreted in terms of a mechanism in which two bonds are cleaved more or less synchronously.

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Therefore, a rate-determining step involving cleavage of both the C–H and O–H bonds can be envisaged (Scheme 1). The low magnitude of the polar reaction constants also supports the occurrence of a synchronous mechanism. However, the 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 ahead of 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 non-linear transition state, implied in the synchronous mechanism, is supported by the relatively low magnitude of the kinetic isotope effect ($k_H/k_D \approx 3.2$).



Scheme 1

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Techniques used: Spectrophotometry, correlation analysis

References: 26

Equations: 16

Table 1: Rate constants for the oxidation of benzyl alcohol by BTMAB at 303 K

Table 2: Rate constants for the oxidation of substituted benzyl alcohols by BTMAB and the activation parameters

Table 3: Effect of benzyltrimethylammonium chloride (BTMC) on the oxidation of benzyl alcohol

Table 4: Effect of bromide ion on the oxidation of benzyl alcohol

Table 5: Effect of solvent composition on the rate of oxidation of benzyl alcohol

Table 6: Correlation of rate constants of the oxidation of *para*- and *meta*-substituted benzyl alcohols with dual substituent-parameters

Table 7: Temperature dependence of the reaction constants for the oxidation of *para*- and *meta*-substituted benzyl alcohols by BTMAB

Table 8: Temperature dependence of the reaction constants of the oxidation of *ortho*-substituted benzyl alcohols by BTMAB

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References cited in this synopsis

- 1 S. Kajigaeshi, T. Kakinami, H. Tokiyama, T. Hirakawa and T. Okamoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 2667.
- 2 S. Kajigaeshi, M. Moriuaai, T. Tanaka, S. Fujisaki, T. Kakinami and T. Okamoto, *J. Chem. Soc., Perkin Trans. 1*, 1990, 897; S. Kajigaeshi, K. Murakawa, S. Fujisaki and T. Kakinami, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 3376.
- 3 S. Kajigaeshi, Y. Shinmasu, S. Fujisaki and T. Kakinami, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 941; S. Kajigaeshi, H. Kawamukai and S. Fujisaki, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2585.
- 4 S. Goel, S. Kothari and K. K. Banerji, *J. Chem. Res.*, 1996, (S) 230; (M) 1318.
- 13 A. H. Falnberg and S. Winstein, *J. Am. Chem. Soc.*, 1956, **78**, 2770.
- 16 S. K. Dayal, S. Ehrensens and R. W. Taft, *J. Am. Chem. Soc.*, 1974, **94**, 9113.
- 17 C. S. Swain, S. H. Unger, N. R. Rosenquest and M. S. Swain, *J. Am. Chem. Soc.*, 1983, **105**, 492.
- 22 M. Charton, *J. Org. Chem.*, 1975, **40**, 407.