

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

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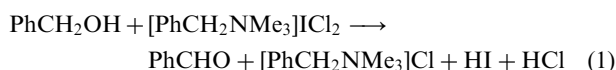
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The oxidation of benzyl alcohol involves transfer of a hydride ion to a benzyltrimethylammonium dichloroiodate–zinc dichloride complex in the rate-determining step.

Benzyltrimethylammonium polyhalides are widely used as halogenating reagents in synthetic organic chemistry.<sup>1,2</sup> We have recently reported the oxidation of phosphorus oxyacids by benzyltrimethylammonium dichloroiodate (BTMACI).<sup>7</sup> Here, we describe kinetics of oxidation of benzyl alcohol and thirty-two monosubstituted benzyl alcohols by BTMACI, in glacial acetic acid in the presence of zinc chloride. Mechanistic aspects are discussed.

BTMACI was prepared by the reported method<sup>1</sup> and its purity was checked by an iodometric method. BTMACI is only slightly soluble in acetic acid at room temperature. However, addition of zinc chloride renders it readily soluble in acetic acid. The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the alcohol over BTMACI. The solvent was glacial acetic acid. The reactions were carried out in the presence of zinc chloride and were followed by monitoring the decrease in [BTMACI] iodometrically. The pseudo-first-order rate constant,  $k_{\text{obs}}$ , was evaluated from the linear plots of  $\log[\text{BTMACI}]$  vs. time. The experimental third-order rate constant,  $k_3$ , was determined from the relationship:  $k_3 = k_{\text{obs}}/[\text{alcohol}][\text{ZnCl}_2]$ .

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

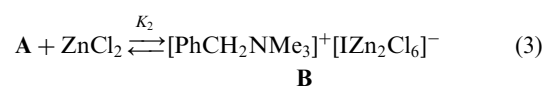
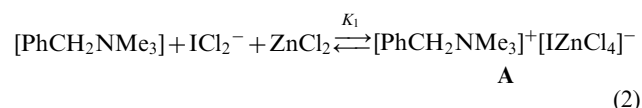


The reaction is first-order with respect to BTMACI, the alcohol and  $\text{ZnCl}_2$ . Addition of benzyltrimethylammonium chloride (BTMACI) enhances the reaction rate slightly. The oxidation of alcohols, under a nitrogen atmosphere, failed to induce polymerization of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate. Thus a one-electron oxidation, giving rise to free radicals, is unlikely. The rates of oxidation of the alcohols were determined at different temperatures and the activation parameters were calculated.

The oxidation of deuteriated benzyl alcohol showed the presence of a substantial primary kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 5.21$  at 318 K). This confirms the cleavage of the  $\alpha$ -C–H bond in the rate-determining step.

UV–VIS spectra of BTMACI alone and in the presence of varying amounts of  $\text{ZnCl}_2$  showed that the nature of the spectra is not much different in the presence and absence of zinc chloride. However, there is an initial sharp decrease in the absorbance followed by a regular but gradual decrease in the absorbance of BTMACI on further addition of increasing amounts of  $\text{ZnCl}_2$ . This clearly showed that a strong complex is formed initially which undergoes further complexation, whose concentration increases with an increase in the concentration of  $\text{ZnCl}_2$ .

From our data on the solubility of BTMACI in the absence and presence of  $\text{ZnCl}_2$ , the value of the equilibrium constant for complex formation,  $K_1$ , is estimated to be ca.  $2400 \text{ dm}^3 \text{ mol}^{-1}$ . This indicates that even at the lowest concentration of  $\text{ZnCl}_2$  used, almost all of the BTMACI will be in the form of complex **A** [eqn. (2)]. The linear increase in the rate with  $[\text{SnCl}_2]$  points to a further complexation [eqn. (3)]. This is also supported by the spectral studies.



Therefore, **B** is postulated as the reactive oxidizing species in the present reaction.

The rate constants of the oxidation of the substituted benzyl alcohols do not exhibit significant correlation with any single- or dual-substituent parameter equation. The rate constants,  $k_3$ , of *meta*-, *para*- and *ortho*-substituted benzyl alcohols, were, therefore, analysed in terms of LDR/LDRS eqns. (9) and (11) introduced by Charton<sup>22</sup> in the 1980s for the quantitative description of structural effects on chemical reactivities.

$$\log k_3 = L\sigma_1 + D\sigma_d + R\sigma_e + h \quad (9)$$

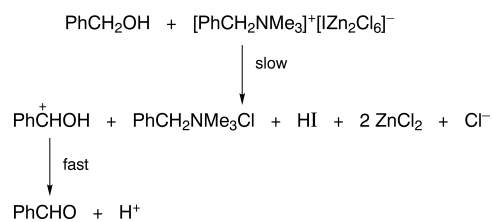
$$\log k_3 = L\sigma_1 + D\sigma_d + R\sigma_e + SV + h \quad (11)$$

The rates of oxidation of the *ortho*-, *meta*- and *para*-substituted compounds show excellent correlations with structure in terms of the LDR/LDRS equations. All the three polar regression coefficients,  $L$ ,  $D$  and  $R$ , are negative indicating an electron-deficient carbon centre in the transition state of the rate-determining step. The positive value of  $\eta$  adds a negative increment to  $\sigma_d$ , thereby increasing electron-donating power of the substituent and its capacity to stabilize a cationic species.

The positive value of  $S$  indicates that the reaction is subjected to a steric acceleration by the *ortho*-substituent. This may be explained on the basis of high ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the transition state as well as in the product formed, the transition state energy of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore, results.

The large negative reaction constants coupled with the large deuterium isotope effect suggest that the transition state approaches a carbocation in character. A hydride-ion transfer from the alcohol to the oxidant is, therefore, indicated. Hence, the following mechanism may be proposed for the oxidation (Scheme 1).

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**Scheme 1**

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Techniques used: Correlation analysis

Equations: 13

References: 23

Table 1: Rate constants for the oxidation of benzyl alcohol by BTMACI at 318 K

Table 2: Dependence of oxidation rate on zinc chloride

Table 3: Effect of benzyltrimethylammonium chloride on the oxidation

Table 4: Rate constants for the oxidation of substituted benzyl alcohols by BTMACI and the activation parameters

Table 5: Correlation of the rates of oxidation of *meta*- and *para*-substituted benzyl alcohols by BTMACI with Taft's dual substituent parameters at 298 K

Table 6: Temperature dependence of the reaction constants for the oxidation of substituted benzyl alcohols by BTMACI

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- 22 M. Charton and B. Charton, *Bull. Soc. Chim. Fr.*, 1988, 199 and references therein.