Kinetics of Oxidation of Substituted Benzyl Alcohols by Quinolinium Chlorochromate

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The oxidation of substituted benzyl alcohols by quinolinium chlorochromate involves decomposition of an initially formed chromate ester *via* a concerted symmetrical transition state.

Quinolinium chlorochromate (QCC) is a mild and selective oxidant.[1] Not many reports on the kinetics of oxidation by QCC are available. Here we report the kinetics and mechanism of the oxidation of benzyl alcohol and nine monosubstituted benzyl alcohols by QCC in dimethyl sulfoxide (DMSO) as solvent.

QCC was prepared by a reported method[1] and its purity was checked by an iodometric method. Pseudo-first-order conditions were attained by keeping a large excess (10-fold or greater) of the alcohol over QCC. The reactions were followed by monitoring the decrease in [QCC] spectrophotometrically at 440 nm. The pseudo-first-order rate constant, k_1, was evaluated from linear plots of ln [QCC] *vs.* time.

The oxidation of the alcohols by QCC led to the formation of the corresponding aldehydes. The product analysis indicated a 1:1 stoichiometry with the following equation:

$$\mathrm{PhCH_2OH + CrO_2ClOQH \rightarrow PhCHO + CrOClOQH} \quad (1)$$

The oxidation of the alcohol by QCC was found to be first-order with respect to the alcohol and QCC. The reaction was catalysed by toluene-*p*-sulfonic acid, and showed a first-order dependence on acidity.

To ascertain the importance of the cleavage of the α-C—H bond in the rate-determining step, the oxidation of α,α-dideuteriobenzyl alcohol was studied. The presence of a substantial primary kinetic isotope effect of the order $k_H/k_D = 5.94$ (at 298 K) confirms the cleavage of the α-C—H bond in the rate-determining step. The k_H/k_D values at 303, 308 and 313 K were 5.63, 5.43 and 5.32 respectively.

The effect of temperature was studied for all the substituted benzyl alcohols. Activation parameters were calculated at temperatures between 298 and 313 K.

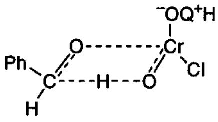
The reaction failed to induce polymerization of acrylonitrile. Furthermore the added acrylonitrile had no effect on the reaction rate. Thus a one-electron oxidation, giving rise to free radicals, is unlikely.

The acid catalysed oxidation of benzyl alcohol was studied in solutions containing varying proportions of dimethyl sulfoxide and dichloromethane. A linear relationship between log k_1 and $1/D$ (D = dielectric constant; $r = 0.998$) with a positive slope indicated the reaction to be an ion-dipole type.

The rate constants of the nine monosubstituted benzyl alcohols showed a good correlation (0.987) with Hammett's σ values.[14] From the Hammett plots the reaction constants (ρ) were negative, indicating the development of a positive charge in the rate-limiting step. The ρ values were -1.13 at 298 K, -1.19 at 303 K, -1.20 at 308 K and -1.19 at 313 K.

Correlation Analysis of Reactivity.—From the Hammett plots, the observed negative values of the reaction constant suggest that the rate-determining step involves transfer of a hydride ion. However, such a transfer may take place either by a cyclic process *via* an ester intermediate[15] or by an acyclic one-step bimolecular process.[16] The data for protio- and deuterio-benzyl alcohols, when fitted to the familiar expression $k_H/k_D = A_H/A_D\, e^{(-\Delta H^*/RT)}$ show a direct correspondence with the properties of a symmetrical transition state in which the activation-energy difference for the protio- and deuterio-compounds is equal to the difference in the zero-point energy for the respective C—H and C—D bonds (*ca.* 4.5 kJ mol^{-1}) and the entropies of activation of the respective reactions are almost equal.[17,18] It is thus clear that in the present reaction hydrogen transfer does not take place by an acyclic bimolecular process.

It is well established that intrinsically concerted sigmatropic reactions characterized by transfer of hydrogen in a cyclic transition state are the the only truly symmetrical processes involving linear hydrogen transfer.[20] Furthermore, a cyclic hydride-ion transfer in the oxidation of alcohols by Cr^{VI} is well known. As the transfer involves six electrons and is a Hückel-type system, it is an allowed process.[21] Thus a transition state having a planar, cyclic symmetrical structure can be envisaged for the decomposition of the ester intermediate (Fig. 1).



Technique used: UV–VIS spectrophotometry

References: 21

Table 1: Rate constants for the oxidation of benzyl alcohol

Table 2: Dependence of reaction rate on acidity

Table 3: Temperature dependence and the activation parameters

Table 4: Effect of solvent composition on the rate

Table 5: Reaction constants for the oxidation

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