Kinetics and mechanism of oxidation of alcohols by butyltriphenylphosphonium dichromate

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Butyltriphenylphosphonium dichromate (BTPPD) oxidizes aliphatic alcohols to the corresponding carbonyl compounds. The reaction is first order in BTPPD. The reaction exhibits a second order dependence each on the alcohol and hydrogen ions. The oxidation of deuterated ethanol and 2-propanol indicates the presence of a substantial primary kinetic isotope effect. The reaction has been studied in nineteen organic solvents and the solvent effect was analyzed using multiparametric equations. It is observed that the cation-solvating power plays a major role in the reaction. The rate of oxidation shows excellent correlation with the polar and steric substituent constants. Suitable mechanisms have been proposed.

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Selective oxidation of organic compounds under non-aqueous conditions is important in synthetic organic chemistry. For this, a number of different chromium (VI) derivatives have been reported. In 1997, Baltroke et al. reported a new Cr(VI) derivative, butyltriphenylphosphonium dichromate (BTPPD), for the oxidation of alcohols to the corresponding carbonyl compounds in high yields. We have been interested in the kinetics and mechanism of oxidation by BTPPD and a number of reports have emanated from our laboratory. There seems to be no report on the mechanistic aspects of the oxidation of aliphatic alcohols by BTPPD. In this note, we report the kinetics of oxidation of some aliphatic primary and secondary alcohols by BTPPD in DMSO as the solvent. The mechanistic aspects are discussed.

Experimental

BTPPD was prepared by the reported method and its purity checked iodometrically. The alcohols and solvents were commercial products and were purified by the usual methods. [1,1-²H₂]Ethanol and [2-²H]propan-2-ol were prepared by the reported methods. Their isotopic purity, as ascertained by their PMR spectra, was 92±4% and 90±5% respectively. Toluene p-sulphonic acid (TsOH) was used as a source of hydrogen ions.

Product analysis

The product analyses were performed under kinetic conditions, i.e., with an excess of the alcohol over BTPPD. In a typical experiment, 2-propanol (0.3 mol), TsOH (0.05 mol), and BTPPD (0.02 mol) were made up to 100 ml in DMSO and allowed to stand in the dark for ca. 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 in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yield of DNP, before and after recrystallization, was 1.41 g (91%) and 1.32 g (85%) respectively. The DNP was identical (m.pt. and mixed m.pt.) to the DNP of acetone. In similar experiments, with other alcohols, the yields of DNP were in the range of 80-92%, after recrystallization. Cr(VI) was reduced to Cr(III).

Kinetic measurements

The reactions were studied under pseudo-first-order conditions by keeping an excess (×10 or greater) of the alcohol over BTPPD. The solvent was DMSO, unless mentioned otherwise. The reactions were studied at constant temperature (±0.1 K) and were followed by monitoring the decrease in [BTPPD] spectrophotometrically at 364 nm for up to 80% reaction. Beer's law was valid for BTPPD within the concentration range used in our experiments. The pseudo-first-order rate constants, kₐ₀, were evaluated from the linear plots (r>0.9990) of log [BTPPD] against time. Duplicate kinetic runs showed that the rates were reproducible to within ±5%. The specific rate constant, k, was evaluated from the relation: k = kₐ₀ [alcohol]² [H⁺]².
Results and discussion

The oxidation of alcohols by BTPPD yields the corresponding carbonyl compounds as the main products. The overall reaction can be represented as follows:

$$3R_2\text{CHOH} + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \rightarrow 3R_2\text{C}=\text{O} + 7\text{H}_2\text{O} + 2\text{Cr}^{3+} \quad \ldots \quad (1)$$

The oxidation of alcohols, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the rate of oxidation was not affected by the addition of acrylonitrile (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm$^{-3}$ of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

The reaction is first order in BTPPD. Further, the pseudo-first order rate constant, $k_{\text{obs}}$, does not depend on the initial concentration of BTPPD. The reaction showed a second order dependence on the concentration of alcohol (Table 1). The rate of oxidation exhibited a second order dependence on hydrogen-ion concentration. The values of rate constant, $10^4 k_{\text{obs}}$ (s$^{-1}$), for oxidation of ethanol, at $[\text{H}^+] = 0.05, 0.10, 0.20, 0.30, 0.50, 0.75$ and 1.00 mol dm$^{-3}$ are 0.43, 1.73, 6.87, 15.8, 29.7 and 176 respectively, with $[\text{EtOH}] = 1.0$ mol dm$^{-3}$ and temp.$=318$ K. The corresponding values for oxidation of 2-propanol are 0.41, 1.65, 6.64, 14.6, 41.3, 93.2 and 164 with $[2\text{-PrOH}] = 0.20$ mol dm$^{-3}$ and temp.$=288$ K. The rates of oxidation of fifteen primary and secondary aliphatic alcohols were determined at different temperatures and the activation parameters were calculated (Table 2).

To ascertain the importance of the cleavage of the $\alpha$-C-H bond in the rate-determining step, the oxidation of deuteriated ethanol and 2-propanol was studied. The kinetic isotope effect, $k_{\text{H}}/k_{\text{D}}$, for ethanol, at 288 K, 298 K, 308 K and 318 K, is 6.28, 5.96, 5.69 and 5.38 respectively. The corresponding values for

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$10^4 k$ (mol$^{-1}$ dm$^3$ s$^{-1}$)</th>
<th>$\Delta H^o$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^o$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G^o$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>2-Chloroethanol</td>
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<td>0.039</td>
<td>0.146</td>
<td>0.570</td>
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<td>0.140</td>
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<td>1.74</td>
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<tr>
<td>Ethanol</td>
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<td>1.98</td>
<td>6.23</td>
<td>22.1</td>
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<tr>
<td>1-Chloropropan-2-ol</td>
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<td>58.7</td>
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<td>451</td>
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<td>15.5</td>
<td>41.0</td>
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<td>336</td>
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<tr>
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<td>267</td>
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<td>43.8</td>
<td>115</td>
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<td>51000</td>
<td>106000</td>
<td>235000</td>
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</table>
2-propanol are 5.23, 4.97, 4.75 and 4.48. The enthalpy and entropy of activation for the oxidation of deuteriated ethanol and 2-propanol are 84.2±1.3 kJ mol⁻¹, -29±2 J mol⁻¹ K⁻¹, 65.2±1.1 kJ mol⁻¹, and -41±2 J mol⁻¹ K⁻¹ respectively.

The oxidation of 2-propanol was studied in nineteen organic solvents. There was no reaction with the chosen solvents. The kinetics were similar in all the solvents. The value of rate constant at 298 K, the chosen solvents. The kinetics were similar in all the solvents. The value of rate constant at 298 K, 1 mol⁻¹, 10³±10² s⁻¹ was 242, 275, 282, 930, 263, 440, 204, 318, 110, 12.0, 82.7, 371, 133, 105, 138, 78.2, 43.2, 118, and 44.6 in chloroform, 1,2-dichloroethane, dichloromethane, DMSO, acetone, DMF, butanone, nitrobenzene, benzene, cyclohexane, toluene, acetonaphone, THF, t-BuOH, dioxane, 1,2-dimethoxyethane, acetic acid, ethyl acetate, and carbon disulphide respectively.

The values of the rate constants, k, in eighteen solvents (CS₂ was not considered as the complete range of solvent parameters are not available), did not exhibit significant correlation in terms of linear solvation energy relationship of Kamlet et al. The data on solvent effect were analyzed in terms of Swain’s equation with both anion- and cation-solvating powers contributing to the observed solvent effect. However, the role of cation-solvation is major. It alone accounts for ca. 95% of the data. There is no significant collinearity between A and B for the nineteen solvents (r²=0.0108, sd=0.27).

Preliminary computation showed that the rate constants, k, of the oxidation of the alcohols do not exhibit satisfactory correlation with either the polar or steric substituent constants separately. Therefore, the rates were analyzed in terms of dual substituent-parameter (DSP) equation of Pavelich and Taft.

\[ \log k = \rho^* \sum \sigma^* + \delta \sum E_s + \log k_0 \]  

Excellent correlations were obtained with the reaction constants being negative (Table 3). The negative steric reaction constant indicates a steric acceleration. This may be explained by relief of steric crowding as the reaction proceeds from an sp² hybridized carbon atom in the alcohol substrates towards an sp³ hybridized carbon in the product.

The presence of a substantial primary kinetic isotope effect confirms the cleavage of the α-C-H bond in the rate-determining step. A one-electron oxidation, giving rise to free radicals, is unlikely in view of the failure to induce polymerization of acrylonitrile and recovery of unchanged BHT. The analysis of solvent effect indicates the importance of cation-solvation. The negative polar reaction constants point towards the presence of an electron-deficient reaction centre in the transition state of the rate-determining step. Therefore, the transfer of a hydride-ion from the alcohol to the oxidant is indicated. A hydride transfer may take place either by an acyclic process or via a chromate ester. Kwast and Nickle have shown that temperature dependence of kinetic isotope effect can be gainfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic process. The data for protio- and deuterio-ethanols and 2-propanols fitted to the familiar expression:

\[ k_H/k_D = A_H/A_D \exp(-\Delta E_{\text{ACT}}/RT) \]

show a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference for k_H/k_D is equal to the zero-point energy difference for the respective C-H and C-D bond (ca. 4.5 kJ mol⁻¹) and the activation entropy of the respective reactions are almost equal. Therefore, one
can safely conclude that in the oxidation of alcohols by BTPPD, the hydride-ion transfer occurs via a chromate ester. The observed results can be explained on the basis of two alternative mechanisms. BTPPD may be ionized in DMSO to dichromate and butyltriphenylphosphonium ions (Scheme 1). The formation of a cation is supported by the analysis of the solvent effect. The dichromate ion undergoes protonation followed by esterification. Alternatively, BTPPD may react with the alcohol as a neutral molecule to form a diester, followed by protonation (Scheme 2). The rate-law for both the mechanisms has the following form (Eq. 8), in agreement with the experimental results.

\[
\text{Rate} = k [\text{BTPPD}] [\text{alcohol}]^2 [\text{H}^+]^2 \quad \ldots \quad (8)
\]

The disproportionation of the ester, in either case, involves a hydride-ion transfer via a cyclic transition state. It may be mentioned that though the formation of the diester and the diprotonation is shown as the single steps, they must be taking place in two steps each. Though both the mechanisms explain all the data available, on the basis of earlier work on other organic derivatives of Cr(VI), Scheme 2 seems to be more plausible.

**Acknowledgement**

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**References**