Selective oxidation of benzyl alcohol with monochromate in non-polar solvents

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Kinetics of the oxidation of benzyl alcohol in non-polar media has been carried out using potassium dichromate under phase transfer catalysis (PTC) using tetrabutylphosphonium bromide (TBPB) and tetrabutylammonium bromide (TBAB) as phase transfer catalysts (PT catalysts). The reaction is first order each in [benzyl alcohol] and [chromate ions]. The oxidation is selective in the product formation. Benzaldehyde is formed in quantitative yield and no traces of benzoic acid has been detected. The reaction mixture fails to induce the polymerization of added acrylonitrile which rules out involvement of any radical intermediate. The energy of activation is significantly low in the range 29-31 kJ mol⁻¹.

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Potassium dichromate is a powerful oxidising agent both for organic as well as inorganic oxidations in polar media. Chromate ions also have been found to be very effective and selective in the oxidation of benzyl alcohol in non-polar solvents giving good yields of benzaldehyde under phase transfer catalysis.¹⁻³ There are reports on the use of alkylammonium salts in the oxidation of benzyl alcohol in polar media.⁴⁻⁵ Tait et al. have conveniently established the stoichiometry of the reaction under phase transfer catalysis as three moles of carbinols to one mole of dichromate. Kinetic studies on chromate oxidation in non-polar media under phase transfer catalysis is scanty and hence the present work. The phase transfer catalyts (PT catalysts) used in the present investigation are tetrabutylphosphonium bromide (TBPB) and tetrabutylammonium bromide (TBAB). The extraction of dichromate into the organic solvents occurs in the absence of acid. According to the present study the dichromate anion Cr₂O₇²⁻ is difficult to be transferred into the organic medium. The same has been the observation made elsewhere. This is due to the difficulty in transferring a bivalent ion. Kinetics of oxidation were carried out in non-polar solvents such as benzene, toluene and chloroform.

Experimental

Analar grade potassium dichromate was used. Benzyl alcohol used was 99.7% pure and further purified by vacuum distillation. The solvents benzene, toluene, and chloroform were purified by reported methods and doubly distilled water was used throughout this study. The extraction of dichromate into the organic solvents occur in the presence of 2 M mineral acids. The phase transferring of dichromate takes place only in the presence of 1-3 M mineral acid.¹ The dominant species, HCrO₄⁻ in the pH range 6-8 was used in the current work.

The phase transferring has been effected by equilibrating aqueous potassium dichromate (0.05 M) with pure benzene, toluene or chloroform containing TBPB or TBAB (0.1 M) in the presence of 2 M H₂SO₄. The organic layer containing the oxidant was separated and dried over anhydrous sodium sulphate. Concentration of the oxidant was estimated by spectrophotometric method. Oxidant solution remained stable for about five hours enabling convenient kinetic study.

The stoichiometry was established by equilibrating known excess concentration of the phase transferred oxidant with known amount of benzyl alcohol. It was found that one molecule of dichromate is equivalent to three molecules of benzyl alcohol. This is in accordance with the earlier observation.¹ The product, benzaldehyde was identified as its 2,4-dinitrophenylhydrazone (DNP). The yield of the product was above 90%.

The kinetic measurements were carried out under conditions where [PhCH₂OH] > [Q⁺HCrO₄⁻], where Q⁺ is quaternaryphosphonium cation or quaternary-ammonium cation. The progress of the reaction was followed spectrophotometrically using a Shimadzu 1601 UV-VIS spectrophotometer by measuring the
absorbance of $\text{HCrO}_4^-$ ions at 365 nm. The experiments were repeated and the pseudo-first order rate constants, $k_{\text{obs}}$, were computed from the linear ($r>0.996$) least squares plots of $\log [Q^+\text{HCrO}_4^-]$ versus time.

**Results and discussion**

The absorption spectra of the reaction system at various time intervals were obtained. The isosbestic points obtained at 321 nm and 394 nm clearly show the formation of a single product. It also shows the absence of any complex events in the process. The rate measurements were held at definite time intervals by measuring the absorbance at $\lambda_{\text{max}} = 365$ nm.

The oxidation of benzyl alcohol by phase transferred chromate in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile and this rules out the involvement of any radical intermediate.

The rate data in benzene with various concentrations of the oxidant and the substrate are presented in Table 1. Under the conditions when $[\text{PhCH}_2\text{OH}] >> [\text{oxidant}]$, the plots of $\log [\text{oxidant}]$ versus time were found to be linear indicating first order dependence in the [oxidant]. This was further confirmed from the constancy of the values of the specific rates ($k_{\text{obs}}$) for the different concentrations of the oxidant for a given [substrate]. This is given in the set of $k_{\text{obs}}$ values in the first and second rows in Table 1 for two different catalysts. The observed rate constants with different [substrate] and the same oxidant concentration with both the catalysts (set of $k_{\text{obs}}$ values given in third and fourth rows of Table 1) increase linearly with increase in [substrate]. Plots of $\log k_{\text{obs}}$ versus $\log [\text{substrate}]$ were linear with a slope of unity showing that the reaction is first order in [substrate].

The anionic species ($\text{HCrO}_4^-$) which is formed in the given acidic aqueous medium gets phase transferred to organic medium as an ion pair ($Q^+\text{HCrO}_4^-$) in the presence of phase transfer catalysts. In earlier investigation it has been established that the reaction progresses through formation of a chromate ester by the interaction of $\text{HCrO}_4^-$ and the carbinol according to the following sequence:

$$\text{HCrO}_4^- + \text{PhCH}_2\text{OH} \rightarrow \text{PhCH}_2\text{OCrO}_4^- + \text{H}_2\text{O}$$

The chromate ester has greater stability in organic solvents than in water.
Table 2—Activation parameters for the oxidation of benzy l alcohol

\[ \text{[PhCH}_2\text{OH]} \times 10^3 = 2.0 \text{ mol dm}^{-3} \quad [\text{Q}^+\text{HCrO}_4^-] \times 10^3 = 5.0 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Medium: Benzene</th>
<th>k [x 10^4 (dm^3 mol^-1 s^-1)] at temp (K)</th>
<th>Ea (kJ mol^-1)</th>
<th>(\Delta H^\circ) (kJ mol^-1)</th>
<th>(\Delta S^\circ) (J K^-1 mol^-1)</th>
<th>(\Delta G^\circ) (kJ mol^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT Catalyst</td>
<td>303</td>
<td>308</td>
<td>313</td>
<td>318</td>
<td></td>
</tr>
<tr>
<td>TBAB</td>
<td>3.0707</td>
<td>3.8959</td>
<td>4.6444</td>
<td>5.4312</td>
<td>30.28</td>
</tr>
</tbody>
</table>

Table 3—Effect of solvent on the rate of oxidation of benzyl alcohol

\[ \text{[PhCH}_2\text{OH]} \times 10^3 = 2.0 \text{ mol dm}^{-3} \quad [\text{Q}^+\text{HCrO}_4^-] \times 10^3 = 5.0 \text{ mol dm}^{-3}; \text{Temp.}=308 \text{ K} \]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Intrinsic dielectric constant</th>
<th>k_{obs} [x 10^5 (s^-1)]</th>
<th>k_2 [x 10^4 (dm^3 mol^-1 s^-1)]</th>
<th>k_{obs} [x 10^5 (s^-1)]</th>
<th>k_2 [x 10^4 (dm^3 mol^-1 s^-1)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.27</td>
<td>8.5979</td>
<td>4.2989</td>
<td>7.7919</td>
<td>3.8959</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.40</td>
<td>9.5191</td>
<td>4.7595</td>
<td>8.7514</td>
<td>4.3757</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.70</td>
<td>11.6302</td>
<td>5.8151</td>
<td>10.7857</td>
<td>5.3929</td>
</tr>
</tbody>
</table>

The mechanism can be proposed as

\[ \text{[Q}^+\text{HCrO}_4^-] \text{H}_2\text{O} \rightleftharpoons [\text{Q}^+\text{HCrO}_4^-]_{\text{org}} \]
\[ [\text{Q}^+\text{HCrO}_4^-]_{\text{org}} + \text{PhCH}_2\text{OH} \rightarrow [\text{PhCH}_2\text{OCrO}_3^\text{Q}^+]_{\text{org}} + \text{H}_2\text{O} \]
\[ [\text{PhCH}_2\text{OCrO}_3^\text{Q}^+]_{\text{org}} \rightarrow \text{PhCHO} + \text{Cr (IV)} + \text{Q}^+ + \text{H}^+ \]

Chromium (V) and chromium(IV) are possible intermediates in these type of oxidations. The temperature coefficient studies indicate that the activation energy is quite low and is of the order of 29-31kJ mol^-1 and is quite significant. The negative \(\Delta S^\circ\) values are in agreement with the formation of the chromate ester with a high degree of orderedness due to structural modification and solvation. These data are given in Table 2. The effect of toluene and chloroform are presented in Table 3. It has been observed that the rate of the oxidation increased with increase in polarity of the medium. This is in agreement with the possible interaction between a negative ion (HCrO_4^-) and a dipole (benzyl alcohol) as evidenced by the linear correlation of log k_2 versus 1/D (correlation coefficient, r=0.995) where D is the dielectric constant of the medium.

Thus, the oxidation of benzyl alcohol to benzaldehyde by phase transferred chromate occurs smoothly and selectively in benzene and other non-polar organic solvents with appreciable rate. The reaction practically does not occur in the organic media without the presence of phase transfer catalysts. This method offers a convenient route to study the kinetics and mechanism of the oxidation of these organic compounds in non-polar organic solvents.

References