Kinetics and mechanism of the oxidation of diols by butyltriphenylphosphonium dichromate

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The oxidation of four vicinal, four non-vicinal diols and one of their monoethers by butyltriphenylphosphonium dichromate (BTPPD), in dimethylsulfoxide (DMSO), resulted in the formation of corresponding hydroxyaldehyde as a main product of the oxidation. The reactions are of first order with respect to BTPPD, however, second order dependence is obtained with respect to each the diol and hydrogen ion. The oxidation of [1,1,2,2-\textsuperscript{2}H\textsubscript{4}]ethanediol exhibited primary kinetic isotope effect (\(k_1/k_0 = 6.61\) at 298 K). The temperature dependence of the kinetic isotope effect suggested the symmetrical transition state in the rate-determining step. The rate constants of oxidation of four vicinal diols show excellent correlation with Taft’s \(\Sigma \sigma^*\) values with negative reaction constant, \(\rho^*\). The rate of oxidation of ethanediol has been determined in nineteen different solvents. An analysis of the solvent effect indicates the importance of the cation-solvating power of the solvents. A suitable mechanism has been postulated involving the formation of chromate ester in a pre-equilibrium.

Keywords: Diol, butyltriphenylphosphonium dichromate, kinetics, mechanism, oxidation, kinetic isotope effect, hydroxyaldehyde

Materials and Methods

BTPPD was prepared by the reported method\textsuperscript{3} and its purity was checked iodometrically. The diols and the monoethers (BDH or Fluka) were distilled under reduced pressure before use. [1,1,2,2-\textsuperscript{2}H\textsubscript{4}]Ethanediol (DED) was prepared by reducing diethyl oxalate with lithium aluminium deuteride\textsuperscript{14}. Its isotopic purity, determined by its NMR spectrum, was 91±5%. The solvents (amongst the solvents, CS\textsubscript{2} is a toxic, inflammable liquid) were purified by the reported methods\textsuperscript{15}. Toluene \(p\)-sulphonic acid (TsOH) was used as a source of hydrogen ions.

Product analysis

Product analysis was carried out under kinetic conditions. In a typical experiment, the diol (0.1 mole) and BTPPD (0.01 mole) were taken in DMSO (100 mL) in the presence of 1.0 mol dm\textsuperscript{-3} TsOH and the mixture was allowed to stand in the dark for ca. 10 hr to ensure completion of the reaction. It was then treated overnight with an excess (250 mL) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm\textsuperscript{-3} HCl. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, recrystallized from ethanol and weighed. The DNP derivatives
were found to be homogeneous by TLC. The identity of the products was established by comparing the m.p. of the DNP derivatives with the literature values\(^\text{16}\). The melting points were obtained in open capillaries and are uncorrected. The melting points and their yields are summarized in Table I.

### Kinetic measurements

Pseudo-first order conditions were attained by keeping a large excess (10-fold or greater) of diol over the oxidant. The reactions were carried out at constant temperature (±0.1 K). The solvent was DMSO, unless stated otherwise. The reactions were followed by monitoring the decrease in the concentration of BTPPD at 364 nm for up to nearly 85% of the reaction. The pseudo-first order rate constant, \(k_{\text{obs}}\), was evaluated from the linear (\(r^2 > 0.995\)) plots of log [BTPPD] versus time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. In correlation analyses, we have used coefficient of determination (\(R^2\) or \(r^2\)), standard deviation (sd) and Exner’s parameter\(^\text{17}\), \(\psi\), as the measures of the goodness-of-fit.

### Results and Discussion

The rate and other experimental data were obtained for all the diols. Since the results are similar, only representative data are reproduced here.

The oxidation of diols by BTPPD resulted in the formation of corresponding hydroxycarbonyl compound. To determine the stoichiometry, BTPPD (0.005 mole) and diol (0.001 mole) were made up to 100 mL in DMSO in the presence of 1.0 mol dm\(^{-3}\) TsOH. The reaction was allowed to stand for ca. 10 hr to ensure completion of the reaction. The residual BTPPD was determined spectrophotometrically at 364 nm. Several determinations, with different diols, showed that the stoichiometry is 3:1 i.e. three moles of diol are consumed by 1 mole of oxidant. BTPPD thus acts as a 6-electron oxidant and is reduced to Cr(III). The product analysis and the stoichiometry determination suggested the following overall reaction:

\[
3 \text{ HOCH}_2\text{CH}_2\text{OH} + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \rightarrow \\
3 \text{ HOCH}_2\text{CHO} + 2 \text{ Cr}^{3+} + 7\text{H}_2\text{O} \quad \ldots \quad (1)
\]

The reactions were found to be of first order with respect to BTPPD as evidenced by the individual kinetic runs. The plot of log [BTPPD] versus time was found to be linear (\(r^2 > 0.995\)). Further, the pseudo-first order rate constants do not depend on the initial concentration of BTPPD (Table I). The reactions showed a second order dependence on the concentration of diol, as observed by either the nearly constant values of \(k_{\text{obs}}/[\text{diol}]^2\) (Table II) or by slope, equal to two, using Van’t Hoff differential method of determining order (Figure 1). The rate of oxidation increases with an increase in acidity. The dependence on hydrogen ion concentration is of the form: Rate = \(k_{1}[\text{H}^+]^2\), as observed by the nearly constant values of \(k_{\text{obs}}/[\text{H}^+]^2\) (Table III). Further, the magnitude of slope of a plot of log \(k_{\text{obs}}\ vs. \log [\text{H}^+]\) is found to be two (Figure 2). It indicates that a diprotonated species is involved in the rate-determining step.

The experimental rate law can be written as-

\[
\text{Rate} = k [\text{BTPPD}][\text{diol}]^2[\text{H}^+]^2 \quad \ldots \quad (2)
\]
Test for free radicals

The oxidation of diols by BTPPD, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. In blank experiments, i.e., in absence of the substrate, no noticeable consumption of BTPPD was observed. The addition of acrylonitrile had no

\[
\text{Rate}/[\text{BTPPD}] = k_{\text{obs}} = k \ [\text{diol}]^2 \ [\text{H}^+]^2 \quad \cdots (3)
\]

or, Rate/[BTPPD] = k_{\text{obs}} = k \ [\text{diol}]^2 \ [\text{H}^+]^2 \quad \cdots (3)

Table II — Rate constants for the oxidation of diols by BTPPD at 328 K

<table>
<thead>
<tr>
<th>[Diol] (mol dm(^{-3}))</th>
<th>(10^3[\text{BTPPD}]) (mol dm(^{-3}))</th>
<th>(10^3[\text{H}^+]) (mol dm(^{-3}))</th>
<th>Ethanediol</th>
<th>Propane-1,3-diol</th>
<th>(10^4k_{\text{obs}}/\text{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.90</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>1.0</td>
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<td>3.48</td>
<td>5.50</td>
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</tr>
<tr>
<td>0.3</td>
<td>1.0</td>
<td>1.0</td>
<td>7.77</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
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<td>1.0</td>
<td>23.1</td>
<td>34.7</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>1.0</td>
<td>55.2</td>
<td>88.9</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>85.8</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.5</td>
<td>1.0</td>
<td>56.5</td>
<td>86.9</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.8</td>
<td>1.0</td>
<td>54.7</td>
<td>89.0</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
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<td>1.0</td>
<td>55.0</td>
<td>88.3</td>
<td></td>
</tr>
<tr>
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<td>1.0</td>
<td>55.1</td>
<td>87.7</td>
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</tr>
<tr>
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<td>1.0</td>
<td>57.0</td>
<td>88.0</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>86.3*</td>
<td>138*</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>85.2**</td>
<td>144**</td>
<td></td>
</tr>
</tbody>
</table>

* & ** Contained 0.001 and 0.005 mol dm\(^{-3}\) acrylonitrile

Table III — Effect of acidity on the oxidation of diols by BTPPD

\[
[\text{Diol}] = 1.0 \text{ mol dm}^{-3}, \ [\text{BTPPD}] = 0.001 \text{ mol dm}^{-3}, T = 328 \text{ K}
\]

<table>
<thead>
<tr>
<th>[H(^+)] (mol dm(^{-3}))</th>
<th>Ethanediol</th>
<th>Propane-1,3-diol</th>
<th>(10^4k_{\text{obs}}/\text{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.83</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>0.8</td>
<td>54.9</td>
<td>88.7</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>85.8</td>
<td>141</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 — A plot of log [BTPPD] vs. time for ethanediol at 328 K

Figure 2 — A plot of log \(k_{\text{obs}}\) vs. log [diol]
effect on the rate of oxidation (Table II). 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. Thus, a one-electron oxidation, giving rise to free radicals, is unlikely in view of the failure to induce polymerization of acrylonitrile. BHT is an excellent trap for free radicals\(^1\). The fact that BHT was recovered unchanged also goes against the occurrence of a one-electron oxidation.

**Effect of temperature**

The rates of oxidation of four vicinal, four non-vicinal diols and one of their monoethers were determined at different temperatures and the activation parameters were calculated (Table IV).

**Kinetic isotope effect**

To ascertain the importance of the cleavage of \(\alpha\)-C-H bond in the rate-determining step, the oxidation of \([1,1,2,2-^2\text{H}_4]\)ethanediol was studied. The results (Table IV) showed that the rate of oxidation exhibited a substantial kinetic isotope effect \((k_H/k_D = 6.61 \text{ at } 298 \text{ K})\). It indicates the cleavage of \(\alpha\)-C-H bond in the rate-determining step.

**Isokinetic relationship**

The values of \(\log k\) at 298 K and at 328 K, for the four vicinal, four non-vicinal and one of their monoethers are linearly related \((r^2 = 0.9977)\). The value of isokinetic temperature, determined by Exner’s method\(^1\), is \(1976 \pm 50 \text{ K}\). A linear isokinetic relationship is found to be a necessary condition for the validity of linear free energy relationships\(^1\). It also implies that all the reactions, so correlated, follow a similar mechanism. The linear correlation here, involves a typical monohydric alcohol, 3-methoxy-butan-1-ol. Thus, it seems likely that the behaviour of diols is similar to that of alcohols\(^5\) towards BTPPD. This is further supported by product analysis and the non-reactivity of pinacol towards BTPPD.

**Effect of solvent**

The oxidation of diols by BTPPD was studied in nineteen organic solvents. The solubility of the reactants and the reaction of BTPPD with primary and secondary alcohols limited the choice of solvents. There was no reaction with the chosen solvents. The kinetics were similar in all the solvents. The values of the rate constant, \(k\), are recorded in Table V.

The data on solvent effect were then analysed in terms of Swain’s equation\(^2\), where \(A\) represents the anion-solvating power of the solvent and \(B\) the cation-solvating power; \(C\) is the intercept term, and \((A + B)\) is postulated to represent the solvent polarity.

\[
\log k = aA + bB + C \quad \ldots \quad (4)
\]
The results of the correlation analyses in terms of Eqn. (4), individually with A and B, and with (A + B) are given below.

\[
\log k = 0.23 \pm 0.01 A + 1.82 \pm 0.01 B - 4.11 \quad \ldots (5)
\]
\[
R^2 = 0.9998, \text{ sd } = 0.01, n = 19, \psi = 0.02
\]

\[
\log k = 0.05 \pm 0.61 A - 2.86 \quad \ldots (6)
\]
\[
r^2 = 0.0001, \text{ sd } = 0.50, n = 19, \psi = 1.0
\]

\[
\log k = 1.80 \pm 0.04 B - 4.03 \quad \ldots (7)
\]
\[
r^2 = 0.9913, \text{ sd } = 0.05, n = 19, \psi = 0.10
\]

\[
\log k = 1.29 \pm 0.20 (A + B) - 4.06 \quad \ldots (8)
\]
\[
r^2 = 0.7042, \text{ sd } = 0.26, n = 19, \psi = 0.56
\]

The data on solvent effect showed an excellent correlation in terms of Swain’s equation\(^{21}\) with both anion- and cation-solvating powers contributing to the observed solvent effect. However, the role of anion-solvation is negligible in comparison to cation-solvation. The role of cation-solvation alone accounts for ca. 99% of the data. There is no significant collinearity between A and B for the nineteen solvents \((r^2 = 0.0108; \text{ sd } = 0.27)\). The solvent polarity, represented by \((A + B)\) accounted for ca. 70% of the data. In view of the fact that ca. 70% of the data is accounted for by \((A+B)\), an attempt was made to correlate the data with the relative permittivity of the solvents. A plot of \(\log k\) against the inverse of the relative permittivity, however, is not linear \((r^2 = 0.4414)\). In earlier studies also with BTPPD\(^\text{47}\), it was observed that the correlation analysis of the solvent effect did not exhibit a good correlation in terms of Kamlet’s equation. The correlations with Swain’s equation were excellent and major contribution towards the solvent effect was of cation solvating power of the solvent.

The solvent effect suggests that the transition state is more polar than the reactants and broadly it is cationic in nature. The increased polarity of the transition state implies the increase in rate with an increase in the polarity of the solvent. This is justified by observed rate data.

**Correlation analysis of reactivity**

The rates of oxidation of four vicinal diols exhibited an excellent correlation with Taft’s \(\Sigma \sigma^*\) values\(^\text{22}\), the reaction constants being negative (Table VI).

\[
\log k = \rho^* \Sigma \sigma^* + \log k_0 \quad \ldots (9)
\]

Here, \(\Sigma \sigma^*\) represents the sum of the substituent constant for the substituents present on the two alcoholic carbons of the vicinal diols. Though the number of compounds is small (four) for a correlation analysis but the results can be used qualitatively. The negative polar reaction constant confirms the generation of electron-deficient centre in the rate-determining step, resulting in an enhancement of the reaction rate with an increase in the electron-donating power of the alkyl group.

**Mechanism**

Since the negative reaction constant indicates that the transition state is carboxication in character, a
transfer of hydride-ion from diol to BTPPD is postulated. The solvent effect analyses suggesting greater role of cation solvation also supports a hydride-ion transfer mechanism.

A hydride-ion transfer may take place either by an acyclic process or via a chromate ester. Kwart and Nickle have shown that a dependence of kinetic isotope effect on temperature 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 ethanediol and deuterated ethanediol fitted to the familiar expression:

\[ \frac{k_H}{k_D} = \frac{A_H}{A_D} \exp\left(\frac{-\Delta E_a}{RT}\right) \]

showed 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 bonds (ca. 4.5 kJ mol\(^{-1}\)) and the entropy of activation of the respective reactions are nearly equal\(^{24,25}\). Similar phenomenon were observed earlier in the oxidation of diols by quinolium fluorochromate\(^{11}\) (QFC) and pyridinium bromochromate (PBC)\(^{12}\). Bordwell\(^{26}\) has given cogent evidence against the occurrence of concerted one-step bimolecular processes of hydrogen transfer and it is clear that in the present reaction also, the hydrogen transfer does not occur by an acyclic bimolecular process. The only truly symmetrical process involving linear transfer of hydrogen are intrinsically concerted sigmatropic reactions characterized by transfer via a cyclic transition state\(^{27}\). Littler\(^{28}\) has also shown that a cyclic hydride-ion transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and being a Hückel type system, is an allowed process. Therefore, one can safely conclude that in the oxidation of diols by BTPPD, the hydride-ion transfer occurs via a chromate ester. Formation of ester intermediate in the oxidation of diols by Cr(VI) compounds is well documented\(^{29}\). The oxidation of alcohols by BTPPD\(^{5}\) is also reported to exhibit a similar mechanism. The observed acid-dependence of the reaction points to either a rapid reversible protonation of the ester intermediate prior to its disproportionation or protonation of BTPPD first, prior to its esterification with alcohol. The observed solvent effect supports the formation of reactive cationic species. Hence, the observed results can be explained on the basis of two alternative mechanisms. In Scheme I, BTPPD may
react as a neutral molecule with the diol to form a diester, which undergoes protonation followed by disproportionation in the rate-determining step to form the corresponding hydroxyaldehyde. Alternatively, BTPPD is first suggested to get protonated to give a doubly protonated Cr(VI) species which is a stronger oxidant and electrophile and undergoes esterification followed by disproportionation in the rate-determining step to give final product (Scheme II). The derived rate laws for the two mechanisms are as below:

\[
\begin{align*}
\text{k}_{\text{obs}} &= \frac{k_3 K_2 K_1 [S]^2 [H^+]^2}{1 + K_1 [S]} \\
\text{k}_{\text{obs}} &= \frac{k_3 K_2 K_1 [S]^2 [H^+]^2}{1 + K_1 [H^+]^2}
\end{align*}
\]

The observed second order dependence on each the diol and hydrogen-ion concentration is accounted by low magnitude of equilibrium constant either for the formation of chromate ester (Scheme I) or for the protonation of BTPPD (Scheme II). It may be mentioned that though the formation of complex and its diprotonation are shown as single steps, these must be taking place in two steps each. Similar type of mechanism was observed earlier in the oxidation of diols by other Cr(VI) complexes\(^{10,11}\).

Initially Cr(VI) is reduced to Cr(IV). It is likely to react with another Cr(VI) to generate Cr(V) which is then reduced in a fast step to the ultimate product Cr(III). Such a sequence of reactions in Cr(VI) oxidations is well known\(^{29}\).

It may be mentioned here that pinacol is oxidized by chromic acid but not by BTPPD. Chatterji and Mukherji\(^{30}\) reported an abrupt change from butane-2,3-diol to pinacol, the latter reacting very fast. As pointed by Littler\(^{28}\) a cyclic ester mechanism is forbidden in the diol-Cr(VI) reaction. Chromic acid oxidation of pinacol may therefore involve two one-electron steps. Chromic acid oxidations are known to induce polymerization of acrylamide under certain conditions\(^{31}\). No such observations has yet been recorded with BTPPD. Thus, the capability of chromic acid and the inability of BTPPD to act as a one-electron oxidant may explain the different behaviour of pinacol towards these two oxidants.

The observed negative entropy of activation supports the proposed mechanism. As the charge separation takes place, in the transition state of the
rate-determining step, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy.

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References