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Kinetics and mechanism of the oxidation of substituted benzyl alcohols by butyltriphenylphosphonium dichromate

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The oxidation of substituted benzyl alcohols by butyltriphenylphosphonium dichromate proceeds by a hydride-ion transfer *via* a diester intermediate.

Keywords: oxidation of benzyl alcohols, butyltriphenylphosphonium dichromate

In 1997, Baltroke *et al.*[3] reported a new Cr(VI) derivative, butyltriphenylphosphonium dichromate (BTPPD). BTPPD is reported to convert alcohols to corresponding carbonyl compounds in yields ranging from 80 into 100%. We have been interested in the kinetics and mechanisms of the oxidations by BTPPD and a couple of reports have emanated from our laboratory.[4,5] In this paper, we report the kinetics of the oxidation of some monosubstituted benzyl alcohols by BTPPD in dimethyl sulfoxide (DMSO) as the solvent. The mechanistic aspects are discussed.

BTPPD was prepared by the reported method.[3] Pseudo-first order conditions were attained by keeping a large excess (× 10 or greater) of the alcohols over the oxidant. The reactions were carried out in the presence of toluene *p*-sulfonic acid. The reactions were followed by monitoring the decrease in the concentration of BTPPD at 364 nm for up to 80% of the reaction. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear ($r^2 > 0.995$) plots of log [BTPPD] *versus* time. The specific rate constant, k, was evaluated from the relation: $k = k_{obs} / [\text{alcohol}]^2 [H^+]^2$

The oxidation of benzyl alcohols resulted in the formation of the corresponding benzaldehydes. The overall reaction may be represented as follows:

$$3\,PhCH_2OH + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,PhCHO + 7\,H_2O + 2\,Cr^{3+} \quad (1)$$

The oxidation of benzyl alcohol by BTPPD, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. The addition of acrylonitrile had no effect on the rate of oxidation . 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 highly unlikely.

The reaction is of first order with respect to BTPPD. The reaction showed a second order dependence on the concentration of alcohol. The rate of oxidation of the alcohols increases with an increase in the concentration of hydrogen ions. The reaction is second order with respect to the acid. The oxidation of [1,1-$^2H_2$]benzyl alcohol ($PhCD_2OH$) by BTPPD exhibited a substantial kinetic isotope effect ($k_H / k_D = 6.31$ at 298 K). The rates of oxidation the alcohols by BTPPD were determined at different temperatures and the activation parameters were calculated

The oxidation of benzyl alcohol by BTPPD was studied in 19 organic solvents. The kinetics were similar in all the solvents. The values of the rate constant, k, in 18 solvents (CS_2 was not considered as the complete range of the solvent parameters are not available), did not show significant correlation in terms of linear solvation energy relationship (LSER) of Kamlet *et al.*[12]

The data on solvent effect were analysed in terms of Swain's equation[13] also, 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.

$$\log k = aA + bB + C \quad (7)$$

The results of the correlation analyses in terms of eqn (7), individually with A and B, and with (A + B) are given below. In correlation analyses, we have used coefficient of determination (R^2 or r^2), standard deviation (sd) and Exner's parameter,[10] ψ, as the measures of the goodness of fit.

$$\log k = 0.46 \pm 0.01\,A + 1.71 \pm 0.01\,B - 4.45 \quad (8)$$
$R^2 = 0.9996$, sd = 0.01, $n = 19, \psi = 0.02$

$$\log k = 0.21 \pm 0.56\,A - 3.28 \quad (9)$$
$r^2 = 0.0078$, sd = 0.46, $n = 19, \psi = 1.02$

$$\log k = 1.68 \pm 0.08\,B - 4.30 \quad (10)$$
$r^2 = 0.9629$, sd = 0.09, $n = 19, \psi = 0.20$

$$\log k = 1.29 \pm 0.16\,(A + B) - 4.41 \quad (11)$$
$r^2 = 0.7906$, sd = 0.21, $n = 19, \psi = 0.47$

The data on solvent effect showed an excellent correlation in terms of Swain's equation[13] 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* 96% of the data. The solvent polarity, represented by (A + B) accounted for *ca* 79% of the data.

The rates of the *para*- and *meta*-compounds, at 298 K, failed to exhibit a significant correlation in terms of Hammett[14] or Brown's[15] substituent constants. The rates of *para*- and *meta*-substituted benzyl alcohols were subjected to analyses in terms of dual substituent parameter (DSP) equations of Taft[16] and Swain *et al.*[17] The rates of oxidation of the *para*-substituted benzyl alcohols show an excellent correlation with Taft's σ_I and σ_R^+ values. Comparison showed that ψ is smaller for the σ_R^+ scale than for the other scales by factors of *ca* 9 to 47. The rates for the *meta*-substituted benzyl alcohols show an excellent correlation with σ_I and σ_R^{BA}, though the discriminating factor for the precision of fit with the other σ_R scales or with Swain's equation is not very sharp. The reaction constants are negative.

The value of λ^p (*ca* 1.4) showed that the oxidation of *para*-substituted benzyl alcohols is more susceptible to the resonance effect than to the field effect. In the reaction of the *meta*-substituted compounds, however, the value of λ^m is *ca* 0.8, indicating the greater importance of the field effect.

The presence of a substantial primary kinetic isotope effect confirms the cleavage of the α-C – H bond in the rate-determining step. The analysis of the solvent effect indicated the importance of the cation-solvating power of the solvent. The negative polar reaction constants indicate the presence of an

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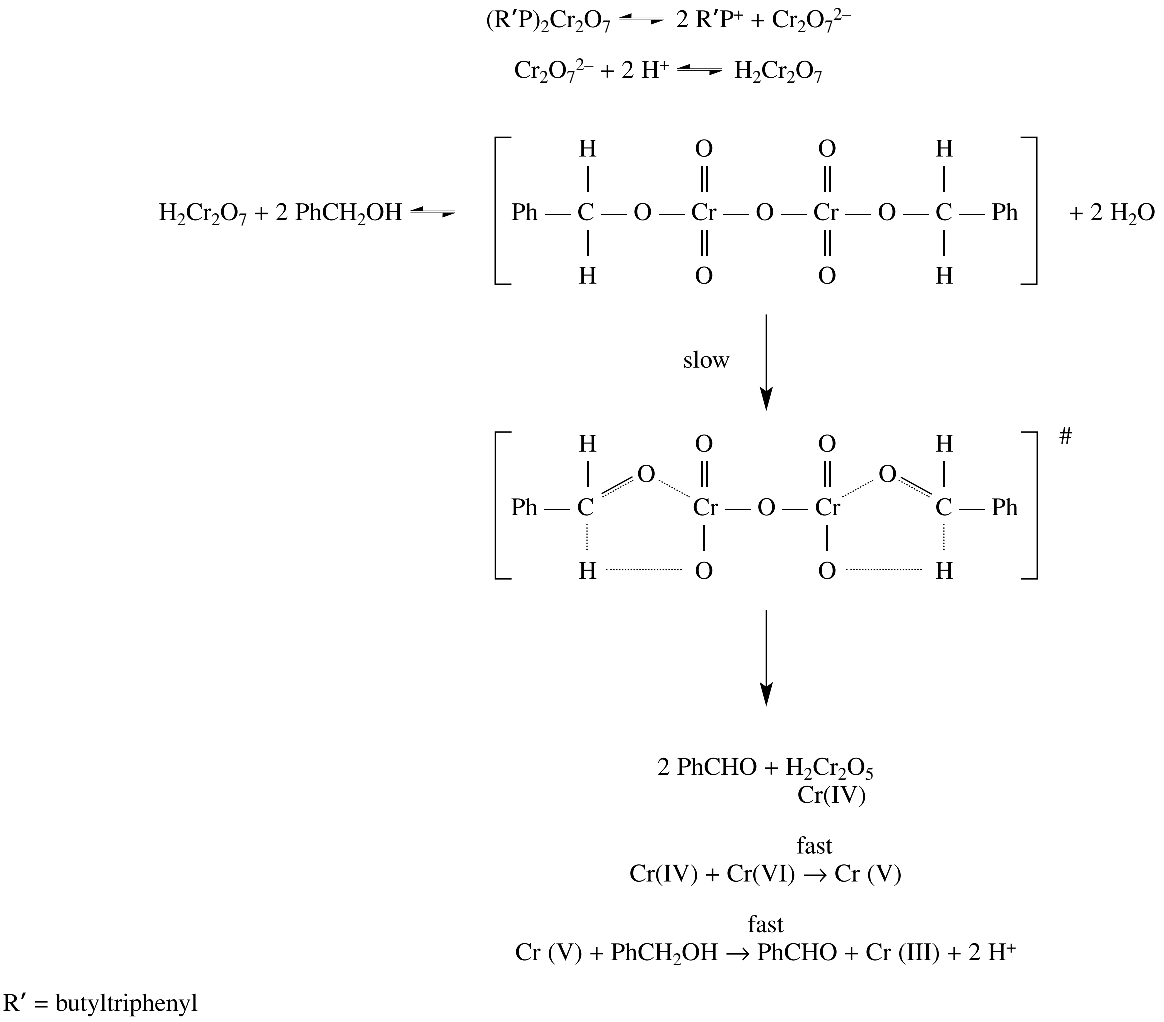
electron-deficient reaction centre in the transition state of the rate-determining step. Therefore, the transfer of a hydride ion from the alcohol to the oxidant is indicated. A hydride-ion transfer may take place either by an acyclic process or *via* a chromate ester. An analysis of the temperature dependence of the kinetic isotope effect, by the method of Kwart and Nickle,[21] shows that the reaction proceeds *via* a symmetrical cyclic transition state. The observed results can be explained on the basis of two alternative mechanisms. BTPPD may be ionised in DMSO to butyltriphenylphosphonium and dichromate ions. The formation of a cation is supported by the major role of the cation-solvating power of the solvent. The dichromate ion undergoes protonation followed by esterification. The chromate ester then disproportionates, in the rate-determining step, to the carbonyl products (Scheme 1). Alternatively, BTPPD may react, as a neutral molecule, with the alcohol to form a diester. After protonation, the diester disproportionates to the products (Scheme 2). 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 are shown as single steps, these must be taking place in two steps each.



Scheme 1

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Table 1. Rate constants for the oxidation of benzyl alcohol BTPPD at 298 K

Table 2. Dependence of the reaction rate on the hydrogen-ion concentration

Table 3. Kinetic isotope effect in the oxidation of benzyl alcohol by BTPPD

Table 4. Effect of solvent on the oxidation of benzyl alcohol by BTPPD at 298 K

Table 5. Rate constants and the activation parameters for the oxidation of substituted benzyl alcohols by BTPPD.

Table 6. Correlation of rate constants of the oxidation of para- and meta- substituted benzyl alcohols with dual substituent parameters

Table 7. Temperature dependence of the reaction constants for the oxidation of para- and meta-substituted benzyl alcohols by BTPPD

Techniques used: Spectrophotometry; Correlation analysis

References: 29 Equations: 13

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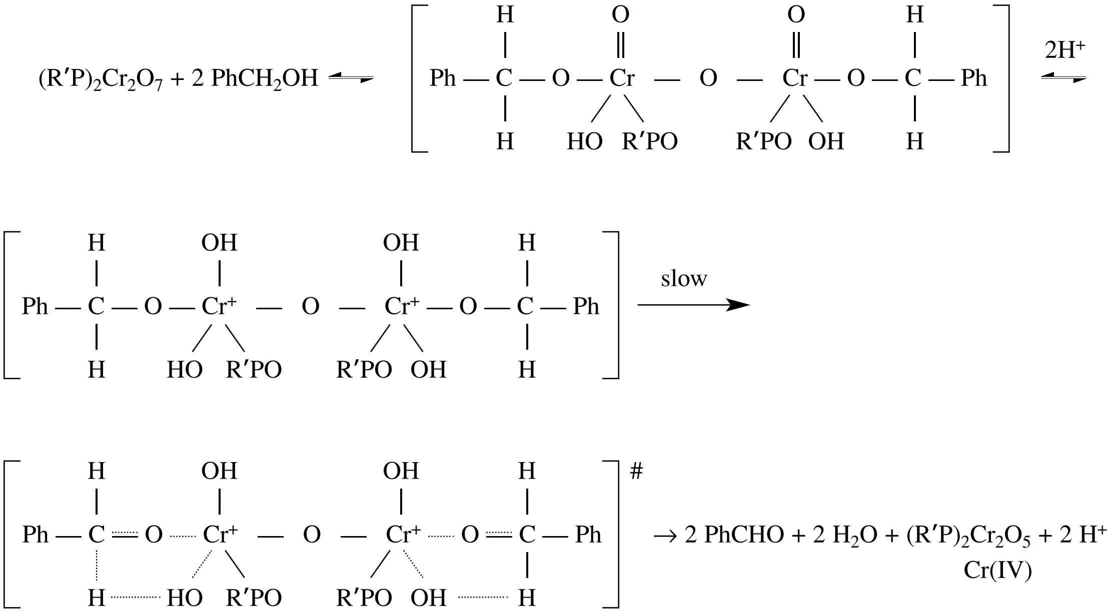

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \xrightarrow{\text{fast}} \mathrm{Cr\ (V)}$$

$$\mathrm{Cr\ (V)} + \mathrm{PhCH_2OH} \xrightarrow{\text{fast}} \mathrm{PhCHO} + \mathrm{Cr\ (III)} + 2\mathrm{H^+}$$

R′ = butyltriphenyl

Scheme 2

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