Kinetics and Mechanism of the Oxidation of Diols by 2,2′-Bipyridinium Chlorochromate

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The oxidation of diols by 2,2′-bipyridinium chlorochromate involves a hydride-ion transfer *via* a chromate ester intermediate.

In continuation of earlier work[2–5] on the oxidation by 2,2′-bipyridinium chlorochromate (BPCC), we report in this paper the kinetics of oxidation of some vicinal diols, non-vicinal diols and two of their monoethers by BPCC in dimethyl sulfoxide (DMSO). The mechanistic aspects are discussed.

The reactions were followed under pseudo-first order conditions by keeping a large excess (× 15 or greater) of the diols over BPCC. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of BPCC spectrophotometrically at 365 nm for up to 80% of the reaction. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear (r 0.990–0.999) plots of log [BPCC] against time. The second-order rate constant, k_2, was determined using the relation; $k_2 = k_{obs}/[\text{diol}]$. Since the reductants are monohydric and dihydric alcohols, a statistical factor of 2 was applied to the rates of oxidation of monohydric compounds, wherever a kinetic correlation of the rates of the two groups of compounds was attempted.

The oxidation of the diols by BPCC resulted in the formation of the corresponding hydroxycarbonyl compounds. The overall reaction may therefore be written as eqn. (1).

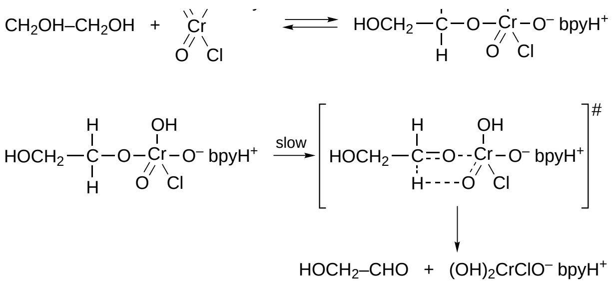
$$\begin{aligned}&HOCH_2\text{—}CH_2OH + O_2CrClO^- \ bpyH^+ \\ &\longrightarrow HOCH_2\text{—}CHO + H_2O + OCrClO^- \ bpyH^+ \qquad (1)\end{aligned}$$

BPCC undergoes a two-electron change. This is an accord with our earlier observations with both PFC[6] and BPCC.[2] There is no noticeable oxidation of pinacol by BPCC. The isolation of the hydroxycarbonyl compounds as the products and the resistance of the pinacol towards oxidation by BPCC indicate that the diols behave as monohydric alcohols towards BPCC.

The reactions were found to be first-order with respect to BPCC and the diol. The reaction is catalysed by hydrogen ions, though the degree of catalysis is moderate. The hydrogen-ion dependence takes the form: $k_{obs} = c + d[H^+]$. The oxidation of [1,1,2,2-$^2H_4$]ethane-1,2-diol showed the presence of a substantial primary kinetic isotope effect ($k_H/k_D = 6.35$ at 303 K). This confirmed that an α-C—H bond is cleaved in the rate-determining step. The rate constants for the oxidation of the diols were obtained at different temperatures and the activation parameters were evaluated.

The oxidation of diols by BPCC, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Furthermore, the addition of acrylonitrile had no effect on the rate. This indicates that a hydrogen-abstraction mechanism, giving rise to free radicals, is unlikely.

The oxidation of ethane-1,2-diol was studied in nineteen different organic solvents. The kinetics were similar in all the solvents. The rate constants for the oxidation, k_2, in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) did not exhibit any significant correlation in terms of the linear solvation energy relationship of Kamlet *et al.*[12]



Scheme 1

The data on the solvent effect were analysed also in terms of Swain's equation[14] of cation- and anion-solvating concept of the solvents [eqn. (5)].

$$\log k_2 = aA + bB + C \qquad (5)$$

The rates of oxidation of ethane-1,2-diol in the different solvents show an excellent correlation in Swain's equation[14] [eqn. (6)] with the cation-solvating power playing the major role. In fact, the cation solvation alone accounts for *ca.* 98% of the data. Here n is the number of data points and is Exner's statistical parameter.[13]

$$\log k_2 = 0.27(\pm 0.04)A + 1.68(\pm 0.03)B - 5.64 \qquad (6)$$

$$R^2 = 0.9948; \quad \text{sd} = 0.03; \quad n = 19; \quad \psi = 0.05$$

The rate constants for the oxidation of the four vicinal diols showed an excellent correlation with Taft's σ^* values[15] with negative reaction constants. The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The formation of a carbocationic transition state is supported by the greater role of the cation-solvating power of the solvents. Thus a mechanism involving a hydride transfer is likely for the reaction. The hydride-ion transfer may take place either by a single bimolecular step or *via* a chromate ester. Kwart and Nickle[16] have shown that a study of the dependence of the kinetic isotope effect on temperature can be gainfully employed to resolve this problem.

The data for protio- and deuterio-ethane-1,2-diols, fitted to the familiar expression $k_H/k_D = A_H/A_D\ (\exp(\Delta E_a/RT)$,[16,17] show a direct correspondence with the properties of a symmetrical transition state in which the activation-energy difference (ΔE_a) for k_H/k_D is equal to the zero-point energy difference for the respective C—H and C—D bonds ($\approx$4.5 kJ mol^{-1}) and the frequency factors and the entropies of activation of the respective reactions are nearly equal. It is thus evident that in the present studies the hydrogen transfer does not occur by an acyclic biomolecular process. The only truly symmetrical processes involving linear transfer of hydrogen are intrinsically concerted sigmatropic reactions characterized by transfer with cyclic state.[19] Littler[20] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr^{VI}, involves six electrons and, being a Hückel-type system, is an allowed process. The mechanism shown in Scheme 1 accounts for all the observed data.

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Techniques used: Spectrophotometry, correlation analysis

References: 22

Equations: 8

Table 1: Analyses of products in the oxidation of diols by BPCC

Table 2: Rate constants for the oxidation of ethane-1,2-diol by BPCC a 303 K

Table 3: Dependence of the reaction rate on hydrogen-ion concentration

Table 4: Rate constants and the activation parameters for the oxidation of diols by BPCC

Table 5: Solvent effect in the oxidation of ethane-1,2-diol by BPCC at 303 K

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