Kinetics and Mechanism of the Oxidation of Oxalic and Formic Acids by 2,2′-Bipyridinium Chlorochromate

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The oxidation of formic and oxalic acids by 2,2′-bipyridinium chlorochromate (BPCC) involves initial formation of an anhydride intermediate and its subsequent decomposition *via* a symmetrical cyclic transition state.

2,2′-Bipyridinium chlorochromate has been used as a mild and selective oxidizing reagent.[1] Here we report the kinetics of oxidation of oxalic acid (OA) and formic acid (FA) by 2,2′-bipyridinium chlorochromate (BPCC) in dimethyl sulfoxide (DMSO) as a solvent. The mechanistic aspects are discussed. The oxidation of these acids by pyridinium fluoro-, chloro- and bromo-chromates (PFC, PCC, PBC) have been previously reported from this laboratory.[6–8]

The reactions were studied under pseudo-first-order conditions by keeping an excess (15× or greater) of the organic acid over BPCC. The solvent was DMSO, unless otherwise specified. The reactions were followed by monitoring the decrease in the concentration of BPCC at 365 nm for up to 80% reaction extent. Pseudo-first-order rate constants, k_{obs}, were evaluated from linear plots ($r > 0.990$) of log[BPCC] against time.

The oxidation of organic acids by BPCC resulted in the formation of carbon dioxide. The overall reaction may, therefore, be written as eqns (1) and (2).

$$(COOH)_2 + O_2CrClO^-bpyH^+ \longrightarrow 2CO_2 + 2H_2O + OCrClO^-bpyH^+ \quad (1)$$

$$HCOOH + O_2CrClO^-bpyH^+ \longrightarrow CO_2 + H_2O + OCrClO^-bpyH^+ \quad (2)$$

The reactions were found to be first order with respect to BPCC. Michaelis–Menten type kinetics were observed with respect to the organic acids. This leads to the postulation of the following overall mechanism [eqns (3) and (4)] and the rate law (5).

$$\text{organic acid} + \text{BPCC} \overset{K}{\rightleftharpoons} [\text{complex}] \quad (3)$$

$$[\text{complex}] \xrightarrow{k_2} \text{products} \quad (4)$$

$$-\text{d[BPCC]}/\text{d}t = k_2K[\text{BPCC}]\,[\text{organic acid}]/(1 + K[\text{organic acid}]) \quad (5)$$

The dependence on the concentration of the organic acid was studied at different temperatures and the values of K and k_2 were calculated from the double reciprocal plots. The thermodynamic parameters for the complex formation and the activation parameters for the decomposition of the complex were calculated.

To ascertain the importance of the cleavage of the α-CH bond in the rate-determining step, the oxidation of α-deuterioformic acid (DCO_2H) was studied. The results showed that the formation constants of the formic acid–BPCC complex for ordinary and deuteriated acids do not differ much. The decomposition of the complex showed the presence of a substantial primary kinetic isotope effect ($k_H/k_D = 5.77$ at 303 K).

The addition of acrylonitrile had no effect on the reaction rate. This indicates that a hydrogen abstraction mechanism, giving rise to free radicals, is unlikely.

Solvent Effect.—The oxidation of formic acid was studied in 19 different solvents. There was no reaction with the solvents chosen and the kinetics were similar in all the solvents. It was observed that the formation constant, K, of the formic acid–BPCC complex does not vary much with the solvent but there is a considerable variation in the values of k_2.

The correlation of k_2, in 18 solvents (CS_2 was not considered, as the complete range of solvent parameters was not available), in terms of the linear solvation energy relationship of Kamlet *et al.*[10] is not significant.

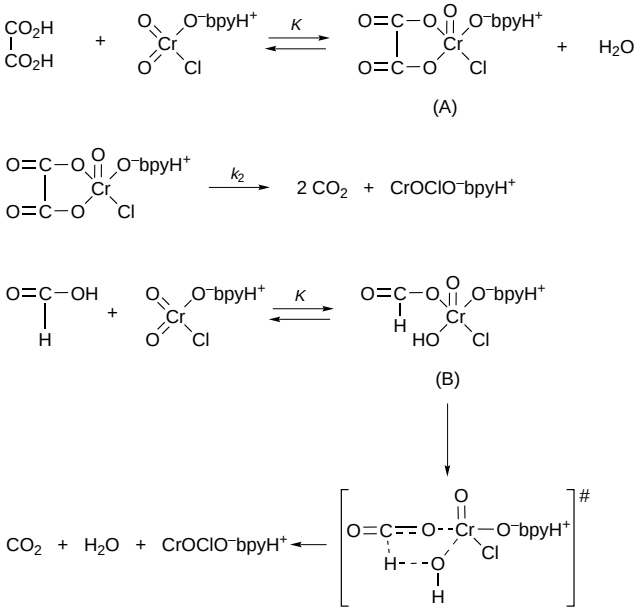
The data on the solvent effect were analysed in terms of Swain's equation[12] of the cation- and anion-solvating concept of the solvents [eqn. (12)].

$$\log k_2 = aA + bB + C \quad (12)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power and C is the intercept term. The rates of oxidation in the different solvents show an excellent correlation in terms of the Swain's equation [eqn. (12)], with cation-solvating power playing the major role.

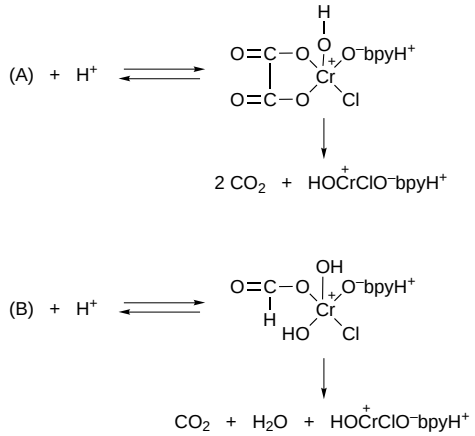
$$\log K_2 = 1.43(\pm 0.04)A + 1.72(\pm 0.03)B - 5.76 \quad (13)$$
$$R^2 = 0.9970;\ sd = 0.03;\ n = 19$$

The presence of a substantial kinetic isotope effect confirmed that an α-C—H bond is cleaved in the rate-determining step. The highly unfavourable entropy term observed in the complex formation of the oxalic acid–BPCC



Scheme 1

*To receive any correspondence.



Scheme 2

reaction suggests that oxalic acid acts as a didentate ligand and forms a cyclic intermediate complex. In chromic acid oxidation also, the formation of a cyclic anhydride intermediate, oxalyl chromate, has been postulated.[13]

For the formic acid oxidation, the cation-solvating power of the solvents plays a relatively more important role. Therefore, formation of an electron-deficient carbon centre in the transition state is indicated. Thus the decomposition of the BPCC–formic acid complex may involve a hydride ion transfer *via* an anhydride intermediate (Scheme 1). However, there is no real evidence for a hydride-ion transfer. In a concerted cyclic process, the difference between proton, atom and hydride-ion transfer is very subtle and cannot be established experimentally. The large kinetic isotope effect simply shows that a hydrogen transfer is involved in the transition state.

The involvement of a concerted cyclic process is supported by a study of the temperature dependence of the kinetic isotope effect. The data for protio- and deuterio-formic acids when fitted in the familiar expression $k_H/k_D = A_H/A_D \exp(-\Delta H^*/RT)$ show a direct correspondence with the properties of a symmetrical transition state in which the differences in the activation energies for the protio and deuterio compounds are equal to the differences in the zero point energies of the corresponding C—H and C—D bonds (*ca.* 4.5 kJ mol^{-1}) and the entropies of the activation of the respective reactions are almost equal.[14,15]

The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence has the following form: $k_{obs} = a + b[H^+]$. This suggests a reversible protonation of the anhydride with both the unprotonated and protonated forms being reactive. The protonated anhydride decomposes at a rate higher than the decomposition of the unprotonated anhydride (Scheme 2).

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Techniques used: Spectrophotometry, correlation analysis

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Equations: 16

Table 1: Rate constants for the oxidation of organic acids by BPCC in DMSO at 303 K

Table 2: Formation constants and thermodynamic parameters for the organic acid–BPCC complexes in DMSO

Table 3: Rate constants and activation parameters for the oxidation of organic acids by BPCC in DMSO

Table 4: Dependence of the reaction rate on hydrogen ion concentration

Table 5: Solvent effect on the oxidation of formic acid by BPCC at 303 K

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