Kinetics and mechanism of oxidation of formic and oxalic acids by tetrakis(pyridine) silver dichromate

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Received 15 July 2008; revised 8 October 2008

Kinetics and mechanism of oxidation of formic and oxalic acids by tetrakis(pyridine) silver dichromate (TPSD) in DMSO have been studied. The main product of oxidation is carbon dioxide. The reaction is first order each with respect to TPSD and the organic acids. The reaction is acid-catalysed and the acid dependence has the form, $k_{obs} = a + b[H^+]$. The oxidation of $\alpha$-deuterioformic acid exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.65$ at 298 K). The reaction has been studied in nineteen different organic solvents and the solvent effect has been analysed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical cyclic transition state in the rate determining step. Suitable mechanisms have been proposed.

IPC Code: Int. Cl. 8 CO7B33/00

Inorganic salts of Cr(VI) are well-known oxidants for organic compounds. However, these salts are rather drastic and non-selective oxidants. Further, they are insoluble in most organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic syntheses as mild and selective oxidants in non-aqueous solvents. One such compound is tetrakis(pyridine)silver dichromate (TPSD) reported by Firouzabadi et al.² We have been interested in the kinetics and mechanism of the oxidation by complex salts of Cr(VI) and several reports have emanated from our laboratories³−⁵. The oxidation of formic and oxalic acids by chromic acid has been studied by several workers and different mechanisms have been postulated⁶. It is, known that the mode of oxidation depends on the nature of the counter-ion attached to the chromium anion. There seems to be no report on the kinetics of oxidation by TPSD. Therefore, we have undertaken a systematic study of kinetics of oxidation of oxalic acid (OA) and formic acid (FA) by TPSD in DMSO as solvent. The mechanistic aspects are discussed.

Experimental

TPSD and $\alpha$-deuterioformic acid ($\text{DCO}_2\text{H}$ or DFA) were prepared by the literature methods. Due to the non-aqueous nature of the medium, toluene-$p$-sulphonic acid (TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar solvent like DMSO, it is likely to be completely ionized. Solvents were purified by the usual methods.

To determine the stoichiometry, an excess of TPSD ($\times 5$ or greater) was reacted with the organic acid in DMSO (100 cm$^3$) and the amount of residual TPSD after the completion of reaction was measured spectrophoto-metrically at 365 nm. Formation of carbon dioxide was confirmed by the lime water test. No quantitative determination of carbon dioxide formed was carried out.

Kinetic studies

The reactions were followed under pseudo-first order conditions by keeping a large excess ($\times 15$ or greater) of the organic acid over TPSD. The temperature was kept constant to ±0.1 K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of TPSD spectrophotometrically at 365 nm for up to 80% of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first-order rate constants, $k_{obs}$, were evaluated from the linear plots of log [TPSD] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%.

Results and discussion

The oxidation of organic acids leads to the formation of carbon dioxide. The stoichiometric determination indicated the following overall reactions:
The reactions are of first order with respect to TPSD. Further, the values of \( k_{\text{obs}} \) are independent of the initial concentration of TPSD. The reaction exhibits a first order dependence on the concentration of organic acid also (Table 1).

The reaction is catalyzed by hydrogen ions. The values of \( 10^4 k_{\text{obs}} \) (s\(^{-1}\)) for the oxidation of oxalic acid at \([\text{H}^+] = 0.1, 0.2, 0.4, 0.6, 0.8 \) and \( 1.0 \) mol dm\(^{-3}\) are 8.17, 9.72, 12.2, 14.0, 17.1 and 19.4 respectively with \([\text{TPSD}] = 0.001 \) mol dm\(^{-3}\) and temp. = 308 K. The corresponding values for the oxidation of formic acid are 2.23, 2.56, 3.33, 3.74, 4.71 and 5.29. The hydrogen-ion dependence has the form. \( k_{\text{obs}} = a + b [\text{H}^+] \). The values of \( a \) and \( b \), for oxalic acid, are \( 7.08 \pm 0.23 \times 10^4 \) s\(^{-1}\) and \( 12.3 \pm 0.37 \times 10^4 \) mol\(^{-1}\) dm\(^3\) s\(^{-1}\) respectively \((r^2 = 0.9982)\). The corresponding values for the oxidation of formic acid are \( 1.88 \pm 0.09 \times 10^4 \) and \( 3.41 \pm 0.15 \times 10^4 \) mol\(^{-1}\) dm\(^3\) s\(^{-1}\) \((r^2 = 0.9963)\). The data fit into the following experimental kinetic dependence.

\[
\text{Rate} = k_2 [\text{Organic acid}] [\text{TPSD}] + k_3 [\text{Organic acid}] [\text{TPSD}] [\text{H}^+] \quad \ldots(3)
\]

The oxidation of organic acids by TPSD, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, rate of oxidation was not affected by the addition of acrylonitrile (Table 1). 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.

To ascertain the importance of the cleavage of the \( \alpha\)-C-H bond in the rate-determining step, the oxidation of DFA was studied. The results recorded in Table 2 show the presence of a substantial primary kinetic isotope effect \((k_d/k_I = 5.65 \) at 298 K\). The rates of oxidation of oxalic and formic acids were determined at four different temperatures and the activation parameters were calculated (Table 2).

The oxidation of formic acid was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of TPSD and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The dependence of the rate on the oxidant and reductant concentration were obtained in all the solvents and were similar. The values of \( k_2 \) are recorded in Table 3.

The rate constants, \( k_2 \), in eighteen solvents (CS\(_2\) was not considered, as the complete range of solvent parameters was not available) did not show any significant correlation in terms of the linear solvation energy relationship of Kamlet \( et \ al.\)

\[
\text{Table 1} \quad \text{Rate constants for the oxidation of oxalic and formic acids by TPSD at 308 K}
\]

<table>
<thead>
<tr>
<th>( 10^4 ) [TPSD] ( (\text{mol dm}^{-3}) )</th>
<th>[Organic acid] ( (\text{mol dm}^{-3}) )</th>
<th>( 10^4 k_{\text{obs}} ) (s(^{-1}))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.00 )</td>
<td>( 0.10 )</td>
<td>( 7.02 )</td>
<td>( 1.92 )</td>
</tr>
<tr>
<td>( 1.00 )</td>
<td>( 0.20 )</td>
<td>( 13.8 )</td>
<td>( 3.76 )</td>
</tr>
<tr>
<td>( 1.00 )</td>
<td>( 0.40 )</td>
<td>( 27.2 )</td>
<td>( 7.47 )</td>
</tr>
<tr>
<td>( 1.00 )</td>
<td>( 0.60 )</td>
<td>( 41.6 )</td>
<td>( 11.2 )</td>
</tr>
<tr>
<td>( 1.00 )</td>
<td>( 0.80 )</td>
<td>( 55.4 )</td>
<td>( 15.1 )</td>
</tr>
<tr>
<td>( 1.00 )</td>
<td>( 1.00 )</td>
<td>( 71.1 )</td>
<td>( 18.9 )</td>
</tr>
<tr>
<td>( 1.00 )</td>
<td>( 2.00 )</td>
<td>( 139 )</td>
<td>( 37.4 )</td>
</tr>
<tr>
<td>( 2.00 )</td>
<td>( 0.40 )</td>
<td>( 28.8 )</td>
<td>( 8.10 )</td>
</tr>
<tr>
<td>( 4.00 )</td>
<td>( 0.40 )</td>
<td>( 26.1 )</td>
<td>( 6.21 )</td>
</tr>
<tr>
<td>( 6.00 )</td>
<td>( 0.40 )</td>
<td>( 29.0 )</td>
<td>( 7.74 )</td>
</tr>
<tr>
<td>( 8.00 )</td>
<td>( 0.40 )</td>
<td>( 27.6 )</td>
<td>( 8.91 )</td>
</tr>
<tr>
<td>( 1.00 )</td>
<td>( 0.20 )</td>
<td>( 14.4^a )</td>
<td>( 3.60^a )</td>
</tr>
</tbody>
</table>

\(^a\) contained 0.001 mol dm\(^{-3}\) acrylonitrile.

\[
\text{Table 2} \quad \text{Rate constants and activation parameters of the oxidation of organic acids by TPSD}
\]

<table>
<thead>
<tr>
<th>Subst.</th>
<th>( 10^4 k_2 ) ( (\text{dm}^3 \text{ mol}^{-1} \text{s}^{-1}) )</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
<th>( \Delta S^\circ ) (J mol(^{-1}) K(^{-1}))</th>
<th>( \Delta G^\circ ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA</td>
<td>17.1</td>
<td>51.5 ± 0.6</td>
<td>-120 ± 2</td>
<td>87.0 ± 0.5</td>
</tr>
<tr>
<td>FA</td>
<td>4.68</td>
<td>50.8 ± 0.7</td>
<td>-133 ± 2</td>
<td>90.2 ± 0.6</td>
</tr>
<tr>
<td>DFA</td>
<td>0.80</td>
<td>53.7 ± 0.8</td>
<td>-135 ± 3</td>
<td>94.5 ± 0.7</td>
</tr>
<tr>
<td>( k_d/k_I )</td>
<td>5.85</td>
<td>5.65</td>
<td>5.43</td>
<td>5.20</td>
</tr>
</tbody>
</table>
log \( k_2 = aA + bB + C \) \hspace{1cm} \cdots(4)

Here \( A \) represents the anion-solvating power of the solvent and \( B \) the cation-solvating power. \( C \) is the intercept term. \( (A + B) \) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of Eq. (4), separately with \( A \) and \( B \) and with \( (A + B) \).

\[ \log k_2 = 1.28(\pm 0.04)A + 1.40(\pm 0.03)B - 3.68 \] \hspace{1cm} \cdots(5)

\[ R^2 = 0.9959; \text{ sd } = 0.03; \text{ n } = 19; \psi = 0.07 \]

\[ \log k_2 = 0.08(\pm 0.46)A - 2.72 \] \hspace{1cm} \cdots(6)

\[ r^2 = 0.2440; \text{ sd } = 0.37; \text{ n } = 19; \psi = 0.89 \]

\[ \log k_2 = 1.30(\pm 0.23)B - 3.27 \] \hspace{1cm} \cdots(7)

\[ r^2 = 0.6577; \text{ sd } = 0.25; \text{ n } = 19; \psi = 0.60 \]

\[ \log k_2 = 1.36(\pm 0.03)(A + B) - 3.68 \] \hspace{1cm} \cdots(8)

\[ r^2 = 0.9938; \text{ sd } = 0.03; \text{ n } = 19; \psi = 0.08 \]

Here \( n \) is the number of data points and \( \psi \) is the Exner’s statistical parameter. The rates of oxidation in different solvents showed an excellent correlation in Swain’s equation (cf. Eq. (5)) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for ca. 66% of the data. The solvent polarity, represented by \( (A + B) \), also accounted for ca. 99% of the data. In view of the fact that solvent polarity is able to account for ca. 99% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of \( \log (\text{rate}) \) against the inverse of the relative permittivity is not linear \((r^2 = 0.4838; \text{ sd } = 0.31; \psi = 0.74)\).

**Mechanism**

A one-electron oxidation, giving rise to free radicals, is not likely to be operative in this reaction, in view of the failure to induce polymerization of acrylonitrile and recovery of unchanged BHT. The presence of a substantial kinetic isotopic effect confirmed that an \( \alpha-C-H \) bond is cleaved in the rate-determining step in the oxidation of formic acid. The observed solvent effect also indicated the importance of cation solvation. It also indicated that the transition state of the reaction is more polar than the reactants.

For the formic acid oxidation, the cation solvating power of the solvents plays a relatively more important role, supporting the premise that an electron-deficient carbon centre is formed in the transition state. Thus, the transfer of a hydride-ion from the acid to the oxidant is indicated.

This hydride ion transfer may take place either via an anhydride or by an acyclic process. The involvement of a concerted cyclic process is supported by a study of the temperature dependence of the kinetic isotope effect. The data for proto- 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 symmetric transition state in which the differences in the activation energies for the proto- 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 \( \text{kJ mol}^{-1} \)) and the entropies of the activation of the respective reactions are almost equal. Similar phenomena have been observed earlier in the oxidation of aliphatic alcohols by butyltriphenyl phosphonium dichromate and of diols by 2,2'-bipyridinium chlorochromate. Littler 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. Thus a transition state having a planar, cyclic structure can be envisaged for the decomposition of the anhydride intermediate. Therefore, in the oxidation of formic acid by TPSD, the overall mechanism is proposed to involve the formation of a chromate anhydride in a fast pre-equilibrium step and then decomposition of the anhydride in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Schemes 1 and 2).

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**Table 3 — Effect of solvents on the oxidation of formic acid by TPSD at 308 K**

<table>
<thead>
<tr>
<th>Solvents</th>
<th>( 10^3 k_2 ) ( (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) )</th>
<th>Solvents</th>
<th>( 10^3 k_2 ) ( (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>79.4</td>
<td>Toluene</td>
<td>18.2</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>70.8</td>
<td>Acetophenone</td>
<td>69.1</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>66.1</td>
<td>THF</td>
<td>31.6</td>
</tr>
<tr>
<td>DMSO</td>
<td>189</td>
<td>t-Butyl alcohol</td>
<td>35.5</td>
</tr>
<tr>
<td>Acetone</td>
<td>56.2</td>
<td>1,4-Dioxane</td>
<td>33.1</td>
</tr>
<tr>
<td>DMF</td>
<td>107</td>
<td>1,2-Dimethoxyethane</td>
<td>19.1</td>
</tr>
<tr>
<td>Butanone</td>
<td>41.7</td>
<td>Carbon disulfide</td>
<td>8.91</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>85.1</td>
<td>Acetic acid</td>
<td>50.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>19.9</td>
<td>Ethyl acetate</td>
<td>26.9</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Acid-independent path

\[ [\text{AgPy}_2]_2 \text{Cr}_2 \text{O}_7 + \text{HCOOH} \rightleftharpoons (A) \]

\[ \text{H}^+ + \text{CO}_2 + \text{CrO(OH)OAgPy}_2 + [\text{CrO}_3 (\text{OAgPy}_2)]^- \]

\[ [\text{AgPy}_2]_2 \text{Cr}_2 \text{O}_7 + (\text{COOH})_2 \rightleftharpoons (B) \]

\[ \text{H}^+ + 2\text{CO}_2 + \text{CrO(OH)OAgPy}_2 + [\text{CrO}_3 (\text{OAgPy}_2)]^- \]

Acid-dependent path

Scheme 1

\[ (A) + \text{H}^+ \rightleftharpoons \text{H}^+ + \text{CO}_2 + [\text{Cr(OH)}_2 \text{OAgPy}_2]^+ + [\text{CrO}_3 (\text{OAgPy}_2)]^- \]

Scheme 2

\[ (B) + \text{H}^+ \rightleftharpoons \text{H}^+ + 2\text{CO}_2 + [\text{Cr(OH)}_2 \text{OAgPy}_2]^+ + [\text{CrO}_3 (\text{OAgPy}_2)]^- \]
The observed negative value of entropy of activation also supports the proposed mechanism. As the charge separation takes place in the transition state, the charged ends become highly solvated. This results in immobilization of a large number of solvent molecules, reflected in the loss of entropy. Initially Cr(VI) is reduced to Cr(VI). 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\(^\text{11}\).

**Acknowledgement**

Thanks are due to the CSIR New Delhi, India for financial support in the form of a major research project, No. 01/(2014)/05/EMR–II.

**References**