Fig. 3. Variation of the distribution ratio for Zn(II), Cd(II) and Hg(II) tracers in 0.1 M oxalate solution as a function of amine concentration in chloroform. Graphs: A, Zn(II); B, Cd(II); C, Hg(II). Curves: 1, Aliquat 336; 2, Primene JM-T.

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Kinetics and mechanism of Cu(II) catalysed oxidation of malic acid by the peroxydisulphate ion

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Catalysis by copper (II) in peroxydisulphate oxidation has been reported for many systems[1-12]. Insufficient kinetic data do not provide evidence for the mechanism of the catalytic action[13]. Kinetics of Cu(II) catalysed oxidation of malic acid by the peroxydisulphate ion have been studied in order to elucidate the catalytic role of Cu(II).

EXPERIMENTAL
All chemicals used were either BDH "AnalaR" or E. Merck G.R. samples and reactants solutions were prepared in double-distilled water. Kinetics were followed by estimating residual peroxydisulphate iodometrically at different intervals of time[14].

The $S_2O_8^{2-}$ equivalents of Cu(II) concentration ($\approx 5 \times 10^{-4} \text{M}$) in terms of titre volume (of 0.04 N) have been subtracted from the observed titre volume to obtain $(a-x)$. (At lower Cu(II) concentrations it was not necessary). Table I shows how the first order rate constants $(k_1)$ were calculated; data reported in different tables were similarly evaluated.

RESULTS

Stoichiometry. One molecule of malic acid reacts with two molecules of peroxydisulphate.

The rate law. Table I gives the results of the kinetic run at 60°C.

The first order rate constant value increases with time for an initial period of 900-3600 sec, thereafter a fair constancy is obtained. The later slight increase is due to further consumption of $S_2O_8^{2-}$ by the reaction product which proceeds slowly. The concentration time curve (Fig. 1) is somewhat "S" shaped, typical of autocatalytic reactions. Such kinetic features are reproduced at other reactant concentrations. To explain this disturbed autocatalytic nature of the first order constant it is presumed that the reaction starts as an uncatalysed one and that after a period a catalysed reaction starts; after about an hour both reactions occur simultaneously. This view is supported by results obtained with uncatalysed oxidation under identical conditions. The value of first order rate constant for the uncatalysed reaction was
Table 1. (Malic acid) = (K₂S₂O₈) = 0.02 M, (CuSO₄) = 0.0005 M, Temp. 60°C

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Vol. of 0.04 N Na₂S₂O₃</th>
<th>(a - x) mole/l</th>
<th>10⁴ k (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.06</td>
<td>5.00</td>
<td>0.0200</td>
</tr>
<tr>
<td>900</td>
<td>4.89</td>
<td>4.83</td>
<td>0.0193</td>
</tr>
<tr>
<td>1800</td>
<td>4.51</td>
<td>4.45</td>
<td>0.0178</td>
</tr>
<tr>
<td>2700</td>
<td>4.02</td>
<td>3.96</td>
<td>0.0158</td>
</tr>
<tr>
<td>3600</td>
<td>3.54</td>
<td>3.48</td>
<td>0.139</td>
</tr>
<tr>
<td>4500</td>
<td>3.12</td>
<td>3.06</td>
<td>0.0122</td>
</tr>
<tr>
<td>5400</td>
<td>2.78</td>
<td>2.72</td>
<td>0.0109</td>
</tr>
<tr>
<td>7200</td>
<td>2.24</td>
<td>2.18</td>
<td>0.0087</td>
</tr>
<tr>
<td>9000</td>
<td>1.80</td>
<td>1.74</td>
<td>0.0070</td>
</tr>
<tr>
<td>10800</td>
<td>1.40</td>
<td>1.34</td>
<td>0.0054</td>
</tr>
<tr>
<td>12600</td>
<td>1.12</td>
<td>1.06</td>
<td>0.0042</td>
</tr>
<tr>
<td>14400</td>
<td>0.90</td>
<td>0.84</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

Average value 1.2
Slope value 1.1

*Mean calculated hereafter.

Concentration-time plot

0.5 × 10⁻⁴ sec⁻¹, in good agreement with the value 0.4 × 10⁻⁴ sec⁻¹ obtained at the initial stage of the catalysed reaction.

The pH changes quasi-linearly during the reaction as shown in Table 2.

Table 2. Variation of pH during the course of the reaction conditions same as Table 1

| Time (sec) | pH  | 2.6 | 2.5 | 2.4 | 2.2 | 2.1 | 2.0 | 1.7 | 1.8 |

Copper (II) dependence. A plot of rate constant against [Cu(II)]¹/² (Fig. 2) gives a straight line not passing through origin, indicating again that the uncatalysed reaction occurs simultaneously with the catalysed reaction. The first order rate constants obtained experimentally are governed by the expression

\[ k = 5 \times 10^{-5} + 2.5 \times 10^{-3} [\text{Cu(II)}] \text{(sec}^{-1} \text{)} \]

at 60°C.

This expression supports the view that if the reaction starts by an uncatalysed pathway the second term is absent at the initial stage.

Temperature dependence. The effect of temperature on K is shown in Table 5.

Table 5. (K₂S₂O₈) = (Malic acid) = 0.02 M, (CuSO₄) = 0.0005 M, Temp. 60°C

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>50</th>
<th>55</th>
<th>60</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁴ k (sec⁻¹)</td>
<td>0.3</td>
<td>0.7</td>
<td>1.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The arrhenius plot is linear and gives \( k = 2.2 \times 10^{12} \exp(-25/RT) \text{sec}^{-1} \). The entropy of activation is 0.3 cal deg⁻¹ mole⁻¹.

Influence of acids, salts and gases. The reaction is retarded by acids, K₂SO₄ and KCl while sodium acetate accelerates it; oxygen gas is observed to inhibit the reaction.

DISCUSSION

For the interpretation of the kinetic data any proposed mechanism must incorporate (a) the first order dependence on

![Plot of K vs [Cu(II)]¹/²](image-url)
peroxydisulphate (b) independence on malic acid and (c) linear
development in Cu(I) dependence on malic acid.
It is therefore obvious that the rate determining step involves
peroxydisulphate and not malic acid. Moreover, the formation of
copper complexes now seems to be well founded [16–19].

Since a bimolecular reaction between oxidant and the catalyst
is ruled out on kinetic grounds [20], a reasonable mechanism which
accounts for the smaller oxidation rate in the presence of Cu(I)
(k Cu(I)-cat uncat is 3.25) may involve:

\[
\begin{align*}
\text{SO}_4^{2-} & \xrightarrow{k_1} \text{S}_2\text{O}_5^{2-} \quad (1) \\
\text{SO}_4^{2-} + \text{Cu}^{II}(\text{C}_6\text{H}_5\text{O}_4)^{2-} & \xrightarrow{k_2} \text{Cu}^{II}(\text{C}_6\text{H}_5\text{O}_4)^{2-} + \text{SO}_2^{2-} \quad (2) \\
\text{Cu}^{II}(\text{C}_6\text{H}_5\text{O}_4)^{2-} & \xrightarrow{k_3} \text{Cu}^{II}\text{C}_6\text{H}_5\text{O}_4 + \text{CO}_2 + \text{CH}_2\text{COO} \\
\end{align*}
\]

(3)

\[
\begin{align*}
\text{CH}_2\text{COO} + \text{OH} & \xrightarrow{\text{pace}} \text{CH}_2\text{COOH} \quad (3a) \\
\text{CH}_2\text{COO} & \xrightarrow{\text{pace}} \text{COOH} \\
\text{Cu}^{II}\text{C}_6\text{H}_5\text{O}_4 + (\text{C}_6\text{H}_5\text{O}_4)^{2-} & \xrightarrow{k_4} \text{Cu}^{II}(\text{C}_6\text{H}_5\text{O}_4)^{2-} \\
\text{CO}_2 + \text{SO}_2^{2-} + \text{SO}_4^{2-} & \xrightarrow{k_5} \text{CO}_2 + \text{SO}_2^{2-} \quad (6) \\
\end{align*}
\]

Reaction (2) is rate determining as it does not involve malate ion
directly but in a complex state; this is in accordance with the
view of Kovats [21]. The Cu(II) state is postulated in the
mechanism, which is well established [22–26, 28]. Moreover, it is
also reported that the metal ion after forming a complex with the
organic substrate decays to produce the CO$_2^-$ radical [27–29].

Alternatively reactions (2) and (3) may be combined in a single
classical concerted step. This change avoids a Cu(III) complex.

With the production of the CO$_2$ radical-ion the higher
concentration of CO$_2$ is explained (reaction 6). That
CO$_2$ is produced is evident from the fact that the system
reduces Hg(II) chloride [27] and oxygen inhibits the reaction rate.

Reaction with peroxydisulphate ion (step 5) regenerates SO$_4^{2-}$
Thus CO$_2$ and SO$_4^{2-}$ act as chain carrier to control the
mechanism of reduction of S$_2$O$_5^{2-}$. Step [6] is chain terminating.

With the limitations that step (3a) is instantaneous and
4 $k_1k_4/Cu^{II}(\text{C}_6\text{H}_5\text{O}_4)^{2-} \times k_5k_6$, the following rate expression is

\[
-d(S_2O_5^{2-})/dt = k'_4k_5(S_2O_5^{2-} + Cu^{II}(\text{C}_6\text{H}_5\text{O}_4)^{2-})^{1/2} \quad (A)
\]

The derived rate law is first order in peroxydisulphate and
shows a linear order dependence on (Cu$^{II}(\text{C}_6\text{H}_5\text{O}_4)^{2-}$)$^{1/2}$ (which
can be taken as representing Cu(II) concentration).

Experimental results suggest that an uncatalysed mechanism is
also operative [12, 30]. In this mechanism SO$_4^{2-}$ generate OH radicals as follows:

\[
\begin{align*}
\text{SO}_4^{2-} + \text{H}_2\text{O} & \xrightarrow{k_5k_6} \text{HSO}_4^- + \text{OH}^- \\
\end{align*}
\]

(7)

which react with uncomplexed malate ion to yield products in the
following manner.

\[
\begin{align*}
\text{CH}_2\text{COO} + \text{OH} & \xrightarrow{+} \text{CH}_2\text{COOH} + \text{OH}^- + \text{CO}_2 \quad (8) \\
\text{CH}_2\text{COOH} & \xrightarrow{+ OH} \text{CH}_2\text{COO} + \text{CO}_2 \\
\end{align*}
\]

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Thallium isotope exchange in TiCl₄

(Received 30 August 1978; received for publication 14 November 1978)

In a recent paper Fernandez Valverde, Duplatre and Maddock have described the exchange of ²⁰⁵Tl between the Tl(II) and Tl(III) fractions in TiCl₄ [1]. A striking dependence of the extent and rate of exchange on the condition of the TiCl₄ was reported.

We have made similar observations on samples of this compound prepared and analyzed in a different way.

Inactive TiCl₄ was prepared by adding three equivalents of TlCl to a solution of TiCl₄ in dilute nitric acid and boiling the mixture. The TiCl₄ was then recrystallized from 0.01 N HCl containing some 2e4Tl⁺.

The two thallium fractions were separated by treating the TiCl₄ with methanol for a number of hours. This dissolved the TiCl₄ together with a smaller part of the TiCl₂, leaving most of the TiCl₃ as an insoluble residue. After washing with methanol the TiCl₃ was dried and its specific activity compared to that of the original TiCl₄ by measuring the mercury K-line.

A serious difficulty occurred in that we were unable to combine preparation and analysis in such a way as to give zero exchange for the unannealed samples. At 300°C the exchange process has reached equilibrium distribution within a few minutes. At 200°C the exchange does not seem to be the same for the samples A, C and D.

Two activations of inactive TiCl₄ were performed with fast neutrons. The activity distribution of the product of the ²⁰⁵Tl(n,2n)²⁰⁶Tl reaction was not very different from equilibrium distribution, 21.3 and 21.0% of the ²⁰⁵Tl being found in the (TiCl₄)²⁻-ion.

Table 1. Annealing ²⁰⁵Tl (TiCl₄) per cent activity in the Ti (Cl₄)²⁻-ion

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>C</th>
<th>D</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing temp.</td>
<td>200°</td>
<td>300°</td>
<td>200°</td>
<td>300°</td>
<td>200°</td>
<td>300°</td>
</tr>
<tr>
<td>Duration annealing</td>
<td>unannealed</td>
<td>4</td>
<td>13.5</td>
<td>10.2±0.3</td>
<td>10.2±0.3</td>
<td>6.5±0.3</td>
</tr>
<tr>
<td>3 min</td>
<td>14.0±1.6</td>
<td>24.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 min</td>
<td>11.1±1.0</td>
<td>23.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 min</td>
<td>10.6±1.5</td>
<td>23.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 hr</td>
<td>21.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 hr</td>
<td>24.5</td>
<td>11.7±1.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 hr</td>
<td>12.5</td>
<td>18.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 hr</td>
<td>13</td>
<td>23.0</td>
<td>13.8±1.6</td>
<td>22.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>