Kinetics of oxidation of tris-(2,2'-bipyridyl)cobalt(II) by iron(III)-2,2'-bipyridyl complex—Micellar effect of sodium dodecyl sulphate

P V Subba Rao*, G Krishna Rao, K Ramakrishna, G Ramababu & A Selayanaryana
Department of Physical Chemistry, School of Chemistry, Andhra University, Visakhapatnam 530 003, India
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Iron(III)-2,2'-bipyridyl complex obtained, in situ, by direct mixing of iron(III) and 2,2'-bipyridyl, oxidises Co(Bipy)_{3}^{+} and the reaction is markedly accelerated by sodium dodecyl sulphate. The rate-surfactant profile exhibits a maximum. The kinetic analysis of the micellar effect has been carried out using Berezin's approach. The binding constants of 2,2'-bipyridyl and Co(Bipy)_{3}^{+} have been determined.

Micellar effects on electron transfer reactions of metal ion complexes attracted the attention of a large number of workers due to their importance in biological processes. However, the reactions mostly investigated were of simple bimolecular type without the involvement of pre-equilibria. But most of the electron transfer reactions involve equilibrium prior to the rate-determining step and it is interesting to test the applicability of pseudophase model to such systems. Keeping this in view, we have taken up the study of micellar effects on the oxidation by iron(III)-2,2'-bipyridyl complex, obtained, in situ, by direct mixing of iron(III) and 2,2'-bipyridyl with the composition [Fe(bipy)]_{2}(H_{2}O)^{+} (ref. 1) in the presence of H'. This bis complex is labile1 and is different from tris(2,2'-bipyridyl)iron(III) which cannot be obtained by the direct mixing of iron(III) and bipyridyl but by the oxidation of the corresponding tris iron(II) complex.2 The reactions of tris iron(III) complexes3-5 do not show any dependence of rate on ligand concentration. On the other hand, the oxidations by labile iron(III)-bipyridyl complex have dependence on square of the ligand concentration. Subba Rao and co-workers6-10 reported systematic investigations on electron transfer reactions of the labile complex which were shown to follow a general mechanism.

H^{+} + Bipy = HBipy^{+}
Fe^{3+} + 2HBipy^{+} = Fe(Bipy)_{2}^{3+} + 2H^{+}
d
Fe(Bipy)_{3}^{2+} + Substrate -> Products

Materials and Methods
A known concentration of (0.1 mol dm^{-3}) iron(III) in aqueous perchloric acid medium was prepared and standardised according to literature methods. Fluka sample of sodium dodecyl sulphate (SDS) has been used in the preparation of 0.1 mol dm^{-3} solution. The purity of the sample was tested by determining the cmc (8.0 x 10^{-3} mol dm^{-3}) conductometrically. The cmc of SDS corresponding to the present experimental conditions (μ = 0.1 mol dm^{-3}) has been reported to be 1.0 x 10^{-3} mol dm^{-3}, ref. 11. 0.05 mol dm^{-3} solutions of cobaltous nitrate, perchloric acid and bipyridyl were prepared and estimated by standard methods. A 0.1 mol dm^{-3} solution of tris(2,2'-bipyridyl)cobalt(II) [log β = 16.02] was prepared by mixing cobalt(II)nitrate and 2,2'-bipyridyl in 1 : 3 mole ratio.

The course of reaction is followed by measuring the absorbance of tris(bipyridyl)iron(II) formed at various times at 510 nm using Milton Roy (spectronic 1201) spectrophotometer with kinetic attachment. At this wavelength, all the other materials concerned have negligible absorbance. All the kinetic runs were carried out keeping [SDS] in large excess such that the micellar surface covered by the binding of products is negligible. In the kinetic runs, the ionic strength was maintained constant at 0.1 mol dm^{-3} with sodium perchlorate. The concentration of H^{+} is at least 100 times more than iron(III) and no change in pH has been observed during the course of the reaction. Duplicate kinetic runs were made in
Table 1—Effects of [SDS] on rate

<table>
<thead>
<tr>
<th>[SDS] (mol dm$^{-3}$)</th>
<th>$10^{-3} k_{r}$</th>
<th>$10^{3} k_{b}$</th>
<th>$10^{-1} k_{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.08</td>
<td>4.4</td>
<td>11.85</td>
</tr>
<tr>
<td>0.64</td>
<td>0.56</td>
<td>4.8</td>
<td>10.3</td>
</tr>
<tr>
<td>1.28</td>
<td>5.54</td>
<td>5.6</td>
<td>8.92</td>
</tr>
<tr>
<td>1.60</td>
<td>10.22</td>
<td>6.4</td>
<td>7.6</td>
</tr>
<tr>
<td>1.92</td>
<td>10.94</td>
<td>7.2</td>
<td>6.4</td>
</tr>
<tr>
<td>2.56</td>
<td>15.0</td>
<td>8.0</td>
<td>5.75</td>
</tr>
<tr>
<td>3.2</td>
<td>17.0</td>
<td>9.6</td>
<td>4.55</td>
</tr>
<tr>
<td>3.6</td>
<td>16.5</td>
<td>12.8</td>
<td>3.10</td>
</tr>
<tr>
<td>4.0</td>
<td>13.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Each case and the rate constants were found to be reproducible within ±5%.

The products of oxidation have been found to be Co(Bipy)$_2^+$ and tris(2,2'-bipyridyl)iron(II).

The tris iron(II) complex has a molar extinction coefficient of 8750 cm$^{-1}$ mol$^{-1}$ dm$^3$ at A = 510 nm. In the presence of SDS, the molar extinction coefficient of Fe(2,2'-bipyridyl)$_3^+$ decreases to 8250 cm$^{-1}$ mol$^{-1}$ dm$^3$ at the cmc and remains constant with further increase in [SDS]. This shows that at [SDS] ≥ cmc, the product is completely bound by the micelle.

Results and Discussion

Determination of binding constants

For determining binding constants of 2,2'-bipyridyl and Co(Bipy)$_2^+$ with SDS micelles at [H$^+$] = 2.0 × 10$^{-2}$ mol dm$^{-3}$ and [bipyridyl] = 1.0 × 10$^{-3}$ mol dm$^{-3}$; $\mu$ = 0.1 mol dm$^{-3}$; temp. = 30.0 ± 0.1 °C.

Each absorbance in the presence of micelle, 1/([A$_M$] - A$_M^*$) is plotted against C (i.e. stoichiometric concentration of SDS-cmc) and from slopes and intercepts of these plots, the binding constants of 2,2'-bipyridyl and Co(Bipy)$_2^+$ have been found to be 20.0 ± 2.0 dm$^3$ mol$^{-1}$ and (9.2 ± 0.3) × 10$^2$ dm$^3$ mol$^{-1}$ respectively.

The reaction obeys first order kinetics in iron(III) as shown by the linear plots of log (A$_M$ - A$_M^*$) versus time under the conditions [Fe(III)] = [Co(II)] and first order with respect to Co(Bipy)$_2^+$ but the second order rate constant, $k_r$ (obtained from the slopes of the linear plots of 1/(A$_M$ - A$_M^*$) versus time and multiplying the slopes with molar extinction coefficient of Fe(Bipy)$_3^+$ under the conditions [Co(II)] = [Fe(III)]) is directly proportional to [bipyridyl]. Further the $k_r$ is proportional to 1/H$^+$ (Fig. 2). The reaction is markedly accelerated by SDS up to a certain limit (Table 1). The acceleration in the presence of the micelle may be due to (i) the binding of the reactants in a small volume of Stern layer of the micelle thus leading to considerable concentration effect and (ii) due to the possibility that the transition state is stabilized more than the initial state in the micellar pseudophase leading to the lowering of the activation energy.

The rate-[surfactant] profile has been found to have a maximum which is typical of bimolecular micellar-catalyzed processes. According to Romsted the maximum in the rate-[surfactant] profiles is produced by two opposing effects. Binding of the reactants in the Stern layer begins.
Table 2—Experimental and calculated values of $k_w$

\[
\begin{array}{cccc}
[\text{Co}^{2+}] &=& 4.0 \times 10^{-5} \text{ mol dm}^{-3};
\mu &=& 0.1 \text{ mol dm}^{-3};
[SDS] &=& 4.0 \times 10^{-3} \text{ mol dm}^{-3};
temp. &=& 30.0 \pm 0.1 \text{°C};
K_s &=& 20.0 \text{ mol}^{-1} \text{ dm}^3;
\end{array}
\]

$K_i = K_i^{+}P/K_i^{−} = 2.22 \times 10^{−1} \text{ mol}^{-1} \text{ dm}^3$.

\[
\begin{array}{cccc}
10^3 [H^+] & 10^3 [\text{Bipy}] & 10^2 k_{obs} dm^3 & 10^2 k_{calc} dm^3
\end{array}
\]

<table>
<thead>
<tr>
<th>$10^3 [H^+]$</th>
<th>$10^3 [\text{Bipy}]$</th>
<th>$10^2 k_{obs} dm^3$</th>
<th>$10^2 k_{calc} dm^3$</th>
</tr>
</thead>
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<tr>
<td>2.0</td>
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<td>1.32</td>
<td>1.31</td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>0.65</td>
<td>0.58</td>
</tr>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>0.30</td>
<td>0.33</td>
</tr>
<tr>
<td>5.0</td>
<td>1.0</td>
<td>0.22</td>
<td>0.21</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8</td>
<td>0.70</td>
<td>0.84</td>
</tr>
<tr>
<td>2.0</td>
<td>1.6</td>
<td>3.60</td>
<td>3.36</td>
</tr>
<tr>
<td>2.0</td>
<td>2.4</td>
<td>7.70</td>
<td>7.55</td>
</tr>
</tbody>
</table>

at the cmc and they are transferred into small volume of the micellar pseudophase. There is thus concentration effect which is responsible for acceleration. This concentration effect is opposed by the continuous dilution of the reactants within the micellar pseudophase with increasing surfactant concentration. The former effect is predominant at lower surfactant concentration whereas the latter becomes important at higher concentrations of surfactant resulting in maximum in the rate-[surfactant] profile.

In the range of $H^+$ ion concentration employed in the present study, all bipyridyl can be considered to be in the protonated form, HBipy$^+$. (The $pK_a$ of HBipy$^+$ is 4.35 (ref. 14)). Iron(III) can be expected to be mainly present in the form of Fe$^{3+}$. The dimeric form is present in negligible concentration at the low iron(III) concentrations employed ($10^{-5}$ mol dm$^{-3}$). The first stage hydrolysis constant, $K_{11}$, for the hydrolysis of iron(III) has a value of $1.07 \times 10^{-3}$ mol dm$^{-3}$ (ref. 15). In the presence of SDS micelles which bind Fe$^{3+}$ more strongly than FeOH$^2+$, the hydrolysis constant, $K_{11}$, can be expected to decrease. $K_{11}$ is related to $K_{11}$ by Eq. (2):

\[
K_{11}^{+} = K_{11} (1 + K_A C) (1 + K_A C)
\]

$K_A$ and $K_A$ are the binding constants of FeOH$^2+$ and Fe$^{3+}$ respectively. Assuming that the binding is electrostatic in nature, $K_A$ and $K_A$ can be calculated using the equation, $K = P/V$ where $P$ is the standard molar volume of SDS (0.246 dm$^3$ mol$^{-1}$ (ref. 16). The partition coefficient, $P$, of charged species between micellar and aqueous phase is given by the equation $P = e^{zφ/25}$ at 25°C where $ψ$ is the surface potential of the micelle ranging between 85-110 mV and $z$ is the charge of the ion bound at the micelle. Assuming that $ψ$ has a value of 85 mV, $K_A$ the binding constant of Fe$^{3+}$ is $5.0 \times 10^{3}$ dm$^3$ mol$^{-1}$ and $K_A$ has a value of $1.8 \times 10^{2}$ dm$^3$ mol$^{-1}$; the value of $K_{11}$ becomes equal to $9.3 \times 10^{-5}$ mol dm$^{-3}$. Thus in the presence of SDS, the concentration of FeOH$^2+$ [{(K$_{11}$/[Fe(III)]$_{total}$)/(K$_{11}$+[H$^+$])}] can be considered to be present in insignificant amounts. Further, if the hydrolysis of iron(III) is to an appreciable extent, a more complex acid dependence of rate would have been observed.

The authors propose Scheme 1 to explain all the kinetic features.

Scheme 1

According to Scheme 1 the reaction in micellar as well as in aqueous phase involves a prior interaction between Fe$^{3+}$ and 2,2'-bipyridyl, (the latter mainly existing in the form of HBipy$^+$) leading to the formation of 1:2 complex, Fe(Bipy)$_2^{3+}$, (in successive equilibria) which is the active oxidising species. The complex formed between FeOH$^2+$ and bipyridyl, (Bipy)$_2$FeOH$^2+$ with smaller positive charge does not appear to be as effective. It is known$^{14}$ that FeOH$^2+$ is a poorer oxidant compared to Fe$^{3+}$. The reduction product of Fe(Bi-
pyH+ is Fe(Bipy)2+ which interacting with Hlsipy produces the tris(bipyridyl)iron(II).

Fe(Bipy)2+ + Hlsipy → Fe(Bipy)2+ + H+ (10)

This step should not be rate-determining, the only rate-determining steps being steps 8 and 9 required by the concentration dependence of rate on the reactants and bipyridyl. If the formation of tri(bispyridyl)iron(II) (step 10) is also rate-determining, plot of log (A_0 - A_t) should have been biphasic which is, however, not observed.

Combining equilibrium treatment and Berezin's approach it can be shown that the rate law is given by Eq. (11)

\[
\frac{\text{Rate}}{K_m K_m K_{2m} P_A [\text{Fe}^{3+}] [\text{Co(Bipy)}]^2}{[\text{H}_2\text{bipy}^+]} \left(1 + K_{1m} C \right) \left(1 + K_{2m} C \right)
\]

In Eq. (11), \( P_A, P_B, P_c \) represent the partition coefficients of \( \text{Fe}^{3+}, \text{Hbipy}^+ \) and substrate between micellar and aqueous pseudo phases, \( K_A, K_B, K_C \) are the corresponding binding constants and \( m \) and \( w \) signify micellar and aqueous phases. \( V \) is molar volume and \( C \) is ([SDS]-cmc). The equation though looking formidable, undergoes considerable simplification. The binding constant of iron(III) \( K_A \) has a value around \( 5.0 \times 10^5 \) dm\(^3\) mol\(^{-1}\) and hence \( [1 + K_{1m} C] \cong K_A \) at [SDS]>cmc. Thus iron(III) is mostly present in the micellar phase and hence the extent of reaction in aqueous phase (i.e., the second term in Eq. (11)) can be neglected. Further, the rate is directly proportional to \( 1/[\text{H}^+]^2 \) and [Bipy]\(^3\). Hence, the terms

\[
K_{1m} P_A [H^+]^2 [\text{Hbipy}^+] \quad \text{and} \quad K_{2m} P_B [\text{Hbipy}^+]^2 \left(1 + K_B C \right)^2
\]

in Eq. (11) can be considered to be negligible in comparison with \( [\text{H}^+]^2 \) and [Bipy]\(^3\). Hence under these conditions, Eq. (11) reduces to Eq. (12)

\[
\text{Rate} = \frac{k_m K_m K_{2m} P_A [\text{Fe}^{3+}] [\text{Co(Bipy)}]^2}{[\text{H}_2\text{bipy}^+]} \left(1 + K_B C \right)\left(1 + K_{1m} C \right)
\]

In Eq. (12), \([\text{H}^+]_m\) is the concentration of \( \text{H}^+ \) ion in moles per litre of micellar phase \((-m\text{V}/V\text{in Romsted's formulation})\) given by Eq.(13)

\[
[\text{H}^+]_m = \frac{0.82[H^+]}{[\text{Na}^+] V}
\]

Equation (13) approximates to

\[
[H^+]_m = \frac{0.82[H^+]}{[\text{Na}^+] V}
\]

under the experimental conditions employed, \([\text{Na}^+] \approx [\text{H}^+]_m\). Hence, \([\text{H}^+]_m\) is directly proportional to \( [\text{H}^+] \). The rate constant,

\[
k_m = \text{Rate}/[[\text{Fe}^{3+}] [\text{Co(Bipy)}]^2]
\]

where \( k_m = (0.82[H^+]/[\text{Na}^+] V) \)

or

\[
1 = k_m (1 + K_B C)^2 = \frac{[\text{H}^+]^2}{k_m K_m K_{2m} P_A P_B [\text{Hbipy}^+]^2} + \frac{K_C [\text{H}^+]^2}{k_m K_m K_{2m} P_A P_B [\text{Hbipy}^+]^2}
\]

The validity of rate law has been tested by calculating \( 1/(k_m (1 + K_B C)^2) \) and plotting it against \( C \) using the values of \( K_B \) determined from UV spectral data. A linear plot is obtained with a positive intercept (Fig. 1) and \( K_B \), the binding constant of Co(Bipy)\(^{2+}\) has been calculated to be \((9.25 \pm 0.75) \times 10^2 \) dm\(^3\) mol\(^{-1}\) from the values of slopes and intercepts of the above plot. This is in reasonable agreement with the value obtained using spectral data \((9.2 \times 10^2 \) dm\(^3\) mol\(^{-1}\)). The value of \( k_m \) has been calculated from the intercept of this plot. The validity of the rate law is further tested by calculating \( k_m \) from the knowledge of \( k_n, K_{1m}, K_{2m}, P_A P_B, K_A, K_B \) and \( K_C \). The experimental and calculated values of \( k_m \) are in reasonable agreement (Table 2) further lending
support to the rate law. Thus the consistent results obtained for the oxidation of Co(Bipy)_2^+ by the iron(III)-bipyridyl complex in the presence of SDS micelles validate the validity of the kinetic model employed by the authors for interpreting the micellar effect of SDS on the electron-transfer reactions of the iron(III)-bipyridyl complex.

Appendix

Since the reaction is investigated under the conditions, [Fe(III)]_0 + [Bipy], [SDS], the mass balance for Fe(III) can be written in the form:

\[
[\text{Fe(III)}]_{\text{mic}} = [\text{Fe}^{3+}]_{\text{aq}} + [\text{Fe(Bipy)}]^3_{\text{mic}} + [\text{Fe(Bipy)}]^2_{\text{mic}} \quad \ldots (1)
\]

where [Fe(III)]_0 is the total Fe(III) concentration in micellar or aqueous phase, and [Fe(Bipy)]^3_{mic} and [Fe(Bipy)]^2_{mic} are the corresponding equilibrium concentrations in micellar or aqueous phases. The concentration of the reactive oxidising species [Fe(Bipy)]^2_{mic} in micellar or aqueous phases is given by:

\[
[\text{Fe(Bipy)}]^2_{\text{mic}} = K_1[\text{HBipy}^+][\text{Fe(III)}]_{\text{mic}}
\]

\[
[\text{Fe(Bipy)}]^2_{\text{mic}} = K_1[\text{HBipy}^+][\text{Fe(III)}]_{\text{mic}} \quad \ldots (2)
\]

According to Berezin, for solute, X, distributing between micellar and aqueous phases, the concentration in micellar phase is given by the equation,

\[
[X]_{\text{mic}} = \frac{P_X[X]}{1 + K_X[C]} \quad \ldots (3A)
\]

and

\[
[X]_{\text{aq}} = \frac{[X]}{1 + K_X[C]} \quad \ldots (3B)
\]

where [X] is the total concentration, \(P_X\) is partition coefficient between pseudo phases and \(K_X\) is the binding constant of X.

The total rate of the reaction according to the mechanism is given by the equation:

\[
\text{rate} = k_a[\text{Fe(Bipy)}]^2 + [\text{Co(Bipy)}]_0 \frac{\text{VC}}{1 + \text{VC}} 
\]

Using Eqs 1, 2, 3 and 4, the rate law for the system is given as:

\[
\text{Rate} = \frac{k_a[\text{Fe(Bipy)}]^2 [\text{Co(Bipy)}]_0 [\text{VC}]}{(1 + [\text{VC}])}
\]

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References