Copper(II) Catalysed Oxidation of Hydroxylamine. A Kinetic Study of the Reaction between Vanadium(V) and Hydroxylamine in Strongly Acid Solutions

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The previous kinetic studies of the oxidation of hydroxylamine by vanadium(V) in strongly acid solutions have been continued by a corresponding study of this reaction in the presence of copper(II), acting as a catalyst with only a moderate catalytic effect. The experimental rate law of the catalysed reaction is analogous to that of the uncatalysed reaction, i.e.

$$-d[VO_2^+]/dt = k[VO_2^+][NH_3OH^+] + k'[VO_2^+]^2[NH_3OH^+]$$

Both rate constants increase with increasing copper(II) concentration and finally reach limiting values such that $k_{lim}/k_0=3$ and $k'_{lim}/k'_0=2$ (index 0 represents [Cu(II)] = 0). At the same time, the stoichiometry increases to the limiting value $\Delta[VO_2^+]/\Delta[NH_3OH^+] = 2.0$. The limiting values of both the stoichiometry and the rate constants are attained at much lower copper(II) concentrations in the presence of chloride ions or bromide ions than in the absence of halide ions.

A reaction mechanism of the catalysed reaction, giving a reasonable interpretation of the experimental results, is proposed. This includes the same initial steps as those of the uncatalysed reaction, i.e. a rapid reversible complex formation between the reactants, followed by two parallel slow electron transfer steps. In the catalysed reaction, these are followed by rapid reactions between copper(II) and nitrogen-containing intermediates. At sufficiently large copper(II) concentrations, all intermediates formed in the slow reaction steps are oxidised by copper(II). The copper(I) formed is reoxidised by vanadium(V).

Previous studies of the reaction between hydroxylamine and vanadium(V) in strongly acid solution ([H+] = 0.005–1.0 M) have shown that this reaction is slow, yields vanadium(IV) and dinitrogen and probably some dinitrogen oxide, and for [H+] ≥ 0.2 M obeys the rate equation

$$-d[VO_2^+]/dt = k[VO_2^+][NH_3OH^+] + k'[VO_2^+]^2[NH_3OH^+]$$

At lower hydrogen ion concentrations the reaction is still slow, but the kinetics become more complicated. Within the hydrogen ion concentration range of these studies, vanadium(V) is present as VO_2^+ and hydroxylamine as hydroxylammonium ion NH_3OH^+. The studies at [H+] = 0.2–1.0 M indicate a mechanism with a rapid, reversible complex formation between VO_2^+ and NH_3OH^+ followed by two parallel rate-determining electron transfer reactions. The $k$ term of the rate law might be supposed to correspond to the reaction path yielding dinitrogen, and the $k'$ term to the one yielding dinitrogen oxide. The rate of nitrogen gas evolution and the fact that the stoichiometry $\Delta[VO_2^+]/\Delta[NH_3OH^+]$ decreases with increasing initial vanadium(V) concentration indicate, however, that nitrogen gas is formed also in the reaction path corresponding to the third order term, possibly as a result of the reaction between an intermediate in this reaction series and NH_3OH^+.

According to Gowda et al., the rate of the
oxidation of hydroxylamine by vanadium(V) is increased by the addition of copper sulfate to solutions being 5–6 M with respect to hydrochloric acid. In these catalytic reactions, dinitrogen oxide is the only product emanating from hydroxylamine, while in the absence of copper(II) one obtains a mixture of nitrogen gas and dinitrogen oxide. These observations indicate that a kinetic study of the copper(II) catalysed reaction might give some further information about the mechanism of the oxidation of hydroxylamine with vanadium(V).

EXPERIMENTAL

The chemicals used were of the same kind and quality as those described in Refs. 1–3, i.e., vanadium pentoxide, hydroxylammonium chloride (Riedel de Haeën), hydroxylammonium sulfate (Merck), perchloric acid and sodium perchlorate, all of analytical grade. So were the methods used to prepare stock solutions and to determine the concentrations of these.

Besides the chemicals used previously the following ones were also used in this study: Copper perchlorate, Cu(ClO₄)₂·6H₂O (G. Frederick Smith Chemical Co., Columbus, Ohio) for the preparation of copper(II) stock solutions. The copper concentrations of these were determined electrogravimetrically or by a spectrophotometric method. In the latter, the absorbance of a sample of the solution to be analysed was measured at the wavelength 610 nm in the presence of 5 M ammonia (molar absorption coefficient: 53.1±0.1 M⁻¹ cm⁻¹). The two methods gave consistent results. Sodium chloride and sodium bromide were used in those measurements in which the effect of halide ions on the reaction rate was investigated.

For a series of measurements, solutions of hydroxylammonium perchlorate were prepared by addition of equivalent amounts of barium perchlorate (Ba(ClO₄)₂·3H₂O; G. F. Smith Chemical Co.) to hydroxylammonium sulfate solutions and filtering out the barium sulfate precipitated. These solutions gave within the experimental error limits the same results as hydroxylammonium sulfate solutions. Also the chemicals described here were of analytical grade.

The kinetic and stoichiometric measurements were carried out spectrophotometrically using a Zeiss PMQ II Spektralphotometer, mainly at the wavelength 340 nm. Some kinetic measurements (with the vanadium(V) concentration 0.2–0.4 mM) were, however, carried out at 280 nm. The reactions were initiated by mixing the proper volumes of reactant solutions by pipette or, for more rapid reactions, by means of an all-glass syringe equipped with a device to allow the delivery of a well-defined volume of the solution in question directly into the absorption cell.

Initial rates were evaluated graphically from absorbance versus time plots or, for more rapid reactions, reciprocal absorbance versus time plots which give a more gentle curvature. In general, the rate did not change appreciably during the first 5% of a complete run. Every initial rate value given in this paper represents the mean value of 3–5 separate measurements. Rate constants were calculated from linear relationships by means of a least squares program. The error limits given in this paper represent a confidence level of 99.9%.

The temperature was 25.0±0.1 °C and the ionic strength for most of the measurements 1.0–1.1 M. At copper perchlorate concentrations exceeding 30 mM and when sodium perchlorate, sodium chloride or sodium bromide was added, the ionic strength could be much larger. The effect of minor changes of the ionic strength fell within the normal experimental error limits, whereas major changes had appreciable effects.

SYMBOLS, NOTATIONS, AND EQUATIONS

\[ M = V(V) = VO_2^+ \]

\[ L = NH_2OH^+ \]

\[ C_M = \text{overall initial concentration of vanadium(V) (mol·L}^{-1}). \quad C_M = [M]+[ML]= [M] (1+\beta_1 [L]) = [M] (1+\beta_1 C_L) \text{ where } \beta_1 = 12.5±0.4 \text{ M}^{-1} \text{ (cf. Ref. 2) is the stability constant of ML.} \]

\[ C_L = \text{overall initial concentration of hydroxylamine (mol·L}^{-1}). \quad C_L = [L] \quad (1+\beta_1 [M]) = [L] (1+\beta_1 C_M). \]

\[ C_{Cu} = \text{overall concentration of copper(II) (mol·L}^{-1}). \]

\[ C_{Cl} = \text{overall concentration of chloride ions (mol·L}^{-1}). \]

\[ C_{ClO_4} = \text{overall concentration of perchloric acid (mol·L}^{-1}). \quad \text{Generally, } [H^+] = C_{ClO_4} - C_M. \]

\[ b = \text{path length of the absorption cell (cm).} \]

\[ A = \text{absorbance.} \]

\[ \varepsilon_M, \varepsilon_{ML} = \text{molar absorption coefficients of the species indicated (M}^{-1} \text{cm}^{-1}). \]

\[ \varepsilon = A/b C_M. \]
\( t = \) time (s).
\( v_0 = \) initial reaction rate (M s\(^{-1}\)).
\( -(\Delta A/a \cdot \Delta t)_{t=0} = -(\Delta C_M/\Delta t)_{t=0} = -(1+\beta_1[L]) (\Delta [M]/\Delta t)_{t=0} = -(1+\beta_1 C_M)(d[M]/dt)_{t=0} \)
\( (\Delta A/b \Delta t)_{t=0} = -(A^2 \Delta (1/A)/\Delta t)_{t=0}. \)

Indices \( o, i, \) and \( \infty \) denote the time after mixing of the reactants.

**MEASUREMENTS AND RESULTS**

**Stoichiometry.** The stoichiometry of the reaction was determined by measuring the decrease in absorbance at complete reaction for solutions initially containing both vanadium(V) (in excess, \( C_I/C_M\leq0.4 \)) and hydroxylamine, as compared to solutions with the same value of \( C_M \) but \( C_I=0 \). The stoichiometry is independent of the proportion between the reactants and of the hydrogen ion concentration (0.2 M \( \leq [H^+] \leq 1.0 \) M). It increases with increasing values of \( C_Cu \) and finally reaches the limiting value \( \Delta C_M/\Delta C_L = 2.0 \). The results shown in Table 1 have been obtained with hydroxylammonium chloride. A similar trend, and the same limiting value, is obtained with hydroxylammonium sulfate, but the increase is less rapid than in the presence of chloride ions.

**Rate equation.** The rate law with respect to hydroxylamine and vanadium(V), respectively, was determined by the method of initial rates at different values of \( C_Cu \). Fig. 1 shows \( v_0 \) versus \( C_L \) at constant \( C_M \) for \( C_Cu = 0 \) and 24.7 mM, respectively. It can be noted that, at least for low values of \( C_L \), the initial rate is proportional to \( C_L \). Fig. 2 shows \( v_o(1+\beta_1 C_M)/C_M \) versus \( C_M \) at a constant value of \( C_L \) for a series of \( C_Cu \) values. \( v_o(1+\beta_1 C_M)/C_M \) is a linear function of \( C_M \), and it appears that both the intercept and the slope increase with increasing values of \( C_Cu \) and tend towards limiting values. The rate equation of the catalysed reaction is, accordingly, analogous to that of the uncatalysed reaction, and can be written as

\[-(\Delta [M]/\Delta t)_o = k[M][L] + k'[M]^2[L] \]

or

\[ v_o = k \frac{C_M C_L}{1+\beta_1 C_M} + k' \frac{C_M^2 C_L}{(1+\beta_1 C_L)(1+\beta_1 C_M)} \]

Both the second order and the third order term increase with increasing \( C_Cu \) and the experimental rate constants at sufficiently large copper concentrations attain limiting values such that \( k_{lim}/k_0 = 3.1 \pm 0.4 \) and \( k'_{lim}/k'_0 = 2.1 \pm 0.3 \) (cf. Table 2). \( k_{lim} \) and \( k'_{lim} \) have been calculated from the initial rates at \( C_Cu = 19.8 \) and 24.7 mM which can be accommodated to the same straight line \( v_o(1+\beta_1 C_M)/C_M \) versus \( C_M \).

For an actual verification of the rate law given above as regards the dependence on \( C_L \) at constant \( C_M \), it should be shown that the experimental values of quantities such as \( v_o/C_L \) or \( v_o(1+\beta_1 C_L)/C_L \) are linearly dependent on \( 1/(1+\beta_1 C_L) \) and \( C_L \), respectively. Although these functions do fit straight lines, they are very sensitive to experimental error, because \( v_o/C_L \) and \( v_o(1+\beta_1 C_L)/C_L \) do not change more than, at

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**Table 1.** The stoichiometry \( \Delta C_M/\Delta C_L \) as a function of \( C_Cu/C_M=5.00 \) mM; \( C_I=0 \); \( C_HOO=1.00 \) M; \( C_Cu=0 \); 24.7 mM.

<table>
<thead>
<tr>
<th>( C_Cu/\text{mM} )</th>
<th>( \Delta C_M/\Delta C_L )</th>
<th>( C_Cu/\text{mM} )</th>
<th>( \Delta C_M/\Delta C_L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.21</td>
<td>5.92</td>
<td>1.98</td>
</tr>
<tr>
<td>0.99</td>
<td>1.62</td>
<td>11.84</td>
<td>1.98</td>
</tr>
<tr>
<td>1.97</td>
<td>1.78</td>
<td>17.8</td>
<td>2.01</td>
</tr>
<tr>
<td>2.96</td>
<td>1.86</td>
<td>24.7</td>
<td>2.00</td>
</tr>
</tbody>
</table>

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most, about 40% within the $C_L$ range where reliable measurements of $v_0$ could be made ($C_L \leq 50$ mM). The linearity of these functions is, therefore, of only limited value in establishing the detailed dependence of $v_0$ on $C_L$. At low hydroxylamine concentrations, $v_0$ should, according to the rate law, be expected to be proportional to $C_L$. The two plots in Fig. 1 have the slopes $5.5 \times 10^{-3}$ s$^{-1}$ and $15 \times 10^{-3}$ s$^{-1}$ for $C_{Cu}=0$ and 24.7 mM, respectively, in good agreement with the values that can be calculated with the appropriate rate constant values of Table 2.

The reaction rate is independent of $[H^+]$ within the hydrogen ion concentration range of this study. It is also unaffected by the removal of dissolved air from the solutions.

Table 2. The experimental rate constants $k$ and $k'$ as functions of $C_{Cu}$. $C_{Cu}=(1-10)$ mM; $C_L=10.0$ mM; $C_{CI}=C_L$; $C_{HCOO}^{-}=1.00$ M.

<table>
<thead>
<tr>
<th>$C_{Cu}$/mM</th>
<th>$k/10^{-3}$M$^{-1}$s$^{-1}$</th>
<th>$k'/M^{-2}s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.7±0.5</td>
<td>1.28±0.07</td>
</tr>
<tr>
<td>4.94</td>
<td>14±1</td>
<td>2.0±0.2</td>
</tr>
<tr>
<td>9.87</td>
<td>16±2</td>
<td>2.5±0.3</td>
</tr>
<tr>
<td>14.8</td>
<td>17±2</td>
<td>2.6±0.3</td>
</tr>
<tr>
<td>19.8</td>
<td>17±2</td>
<td>2.7±0.3</td>
</tr>
<tr>
<td>24.7</td>
<td>18±1</td>
<td>2.6±0.2</td>
</tr>
</tbody>
</table>

Table 3. The rate constant $k$, obtained from pseudo first order plots, as a function of $C_{Cu}$. $C_{M}=0.200$ mM; $C_L=20.0$ mM; $C_{CI}=C_L$; $C_{HCOO}^{-}=1.00$ M.

<table>
<thead>
<tr>
<th>$C_{Cu}$/mM</th>
<th>$k/10^{-3}$M$^{-1}$s$^{-1}$</th>
<th>$C_{Cu}$/mM</th>
<th>$k/10^{-3}$M$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.9</td>
<td>14.7</td>
<td>16.1</td>
</tr>
<tr>
<td>2.45</td>
<td>14.7</td>
<td>19.6</td>
<td>17.2</td>
</tr>
<tr>
<td>4.91</td>
<td>15.9</td>
<td>39.5</td>
<td>16.8</td>
</tr>
<tr>
<td>9.81</td>
<td>16.8</td>
<td>49.5</td>
<td>17.6</td>
</tr>
</tbody>
</table>

At very low $C_M$ values ($C_M \leq 5 \times 10^{-4}$ M) the $k'$ term of the rate law can be neglected, and if $C_I \gg C_M$ the reaction becomes pseudo first order with the rate constant $kC_L$. Table 3 shows the values obtained.

Effect of halide ions. The results of Tables 2 and 3 have been obtained with hydroxylammonium chloride, i.e. $C_{CI}=C_L=10.0$ or 20.0 mM, respectively. In solutions free from chloride ions, the increase of the reaction rate with increasing $C_{Cu}$ is considerably less marked, as it is illustrated by the rate constant values of Table 4. Furthermore, the attainment of the limiting values of the rate constants seems to be masked by an increase of the reaction rate which might be due to the large increase of ionic strength obtained at high copper perchlorate concentrations.

Table 5 shows the dependence of the initial rate on $C_{Cu}$ and $C_{CI}$. The effect of chloride ions in the absence of copper(II) falls almost within the error limits. In the presence of copper(II), there is, however, a marked influence of $C_{CI}$.

Bromide ions have about the same effect as chloride ions.

Table 4. The experimental rate constants $k$ and $k'$ as functions of $C_{Cu}$ in the absence of chloride ions. $C_{M}=(2-10)$ mM; $C_L=10.0$ mM; $C_{CI}=0$, $C_{HCOO}^{-}=1.00$ M.

<table>
<thead>
<tr>
<th>$C_{Cu}$/mM</th>
<th>$k/10^{-3}$M$^{-1}$s$^{-1}$</th>
<th>$k'/M^{-2}s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6±1</td>
<td>1.4±0.2</td>
</tr>
<tr>
<td>19.6</td>
<td>11±2</td>
<td>1.8±0.5</td>
</tr>
<tr>
<td>49.5</td>
<td>13±2</td>
<td>2.3±0.3</td>
</tr>
<tr>
<td>99.0</td>
<td>18±2</td>
<td>2.3±0.4</td>
</tr>
<tr>
<td>196</td>
<td>17±2</td>
<td>3.2±0.4</td>
</tr>
<tr>
<td>379</td>
<td>19±4</td>
<td>4.1±0.6</td>
</tr>
<tr>
<td>543</td>
<td>22±2</td>
<td>4.7±0.4</td>
</tr>
</tbody>
</table>

Table 5. The dependence of the initial rate on $C_{\text{Cl}}$ and $C_{\text{Cu}}$. $C_M = 5.00 \text{ mM}; C_L = 10.0 \text{ mM}; C_{\text{HClO}_4} = 1.00 \text{ M}$.

<table>
<thead>
<tr>
<th>$C_{\text{Cl}}$ (mM)</th>
<th>$v_0/10^{-7} \text{ M} \text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.4</td>
</tr>
<tr>
<td>2.00</td>
<td>5.4</td>
</tr>
<tr>
<td>10.0</td>
<td>5.6</td>
</tr>
<tr>
<td>20.0</td>
<td>5.7</td>
</tr>
<tr>
<td>40.0</td>
<td>5.7</td>
</tr>
<tr>
<td>60.0</td>
<td>5.8</td>
</tr>
<tr>
<td>80.0</td>
<td>5.9</td>
</tr>
<tr>
<td>100</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Table 6. The experimental rate constants $k$ and $k'$ as functions of the ionic strength at $C_{\text{Cu}} = 0$ and 19.8 mM. $C_M = (2-10) \text{ mM}; C_L = 10.0 \text{ mM}; C_{\text{Cl}} = C_L; C_{\text{HClO}_4} = 1.00 \text{ M}$.

<table>
<thead>
<tr>
<th>$\mu$ (M)</th>
<th>$C_{\text{Cu}}$/mM</th>
<th>$k/10^{-3} \text{M}^{-1} \text{s}^{-1}$</th>
<th>$k'/\text{M}^{-2} \text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.07</td>
<td>0</td>
<td>6±1</td>
<td>1.2±0.2</td>
</tr>
<tr>
<td>1.07</td>
<td>19.8</td>
<td>17±2</td>
<td>2.7±0.3</td>
</tr>
<tr>
<td>2.05</td>
<td>0</td>
<td>6±1</td>
<td>1.5±0.2</td>
</tr>
<tr>
<td>2.05</td>
<td>19.8</td>
<td>17±2</td>
<td>3.2±0.2</td>
</tr>
<tr>
<td>2.88</td>
<td>0</td>
<td>6±1</td>
<td>2.0±0.2</td>
</tr>
<tr>
<td>2.88</td>
<td>19.8</td>
<td>19±2</td>
<td>3.9±0.3</td>
</tr>
<tr>
<td>3.62</td>
<td>0</td>
<td>6±2</td>
<td>2.5±0.5</td>
</tr>
<tr>
<td>3.62</td>
<td>19.8</td>
<td>18±2</td>
<td>5.7±0.3</td>
</tr>
</tbody>
</table>

DISCUSSION

The mechanism suggested in Ref. 1 for the uncatalysed reaction may be represented by the following simplified formulae:

Path 1 ($k$ term).

\[
\begin{align*}
V(V) + N(-I) & \rightarrow V(V) \cdot N(-I) \quad (1) \\
V(V) \cdot N(-I) & \rightarrow V(IV) + N(O) \quad (2)
\end{align*}
\]

Path 2 ($k'$ term).

\[
\begin{align*}
V(V) + N(-I) & \rightarrow V(V) \cdot N(-I) \quad (1) \\
V(V) \cdot N(-I) + V(V) & \rightarrow 2 V(IV) + N(I) \quad (4) \\
N(I) & \rightarrow \frac{1}{2} N_2 \quad (5)
\end{align*}
\]

In these formulæ $V(V) = VO_2^+$, $N(-I) = NH_2OH^+$, and $V(V) \cdot N(-I) = VO_2NH_2OH^{++}$. The nature of $N(O)$ and $N(I)$ will be discussed below.

The fact that the rate law of the copper(II) catalysed reaction is analogous to that of the uncatalysed reaction implies that the initial steps of the two reactions are the same. The catalytic action of copper(II) must then be due to reactions between the catalyst and intermediates formed from hydroxylamine in the slow steps, or subsequent steps. Copper(I) is probably formed and rapidly reoxidised by reaction with vanadium(V). Since both terms of the rate law are increased by the presence of copper(II), intermediates from both reaction paths must be assumed to react with copper(II). Such a mechanism will give a proper explanation to the moderate catalytic effect of copper(II). To obtain the stoichiometry $\Delta C_M/\Delta C_L = 2$, one must assume that the nitrogen-containing intermediates, formed by the oxidations with copper(II), react with hydroxylationmonium ion, yielding dinitrogen oxide as the ultimate product. The mechanism outlined here can be summarised, using the same kind of simplified formulæ as before:

Path 3 (k term; catalysed).

\[
\begin{align*}
V(V) + N(-I) & \rightarrow V(V) \cdot N(-I) \quad (1) \\
V(V) \cdot N(-I) & \rightarrow V(IV) + N(O) \quad (2)
\end{align*}
\]

$2 Cu(II) + N(O) \rightarrow 2 Cu(I) + N(II)$

$2x[Cu(I) + V(V) \rightarrow Cu(II) + V(IV)]$

$N(II) + \frac{1}{2} N(-I) \rightarrow \frac{1}{2} N_2 O$

The identity of the intermediates denoted as N(O), N(I), N(II) and N(III) has not been established. These intermediates are supposed to be present only in very low concentrations and, in general, the identification of such species is difficult. Gutch and Waters \(^7\) have shown the existence of the radical NH\(_2\)O\(_2^\cdot\) as an intermediate in the oxidation of hydroxylamine by cerium(IV) in methanol and methanol–water solutions by means of ESR measurements. In these reactions, dinitrogen is the product formed, and it seems reasonable that N(O)=NH\(_2\)O\(_2^\cdot\) (cf. however Ref. 8, where :NH\(_2\)OH is suggested as a better alternative in the oxidation of hydroxylamine with IrCl\(_6^{2-}\)). The participation of free radicals in this reaction is implied by the fact that the reacting solution induces polymerisation of acrylonitrile. Nitroxy, HNO, has been suggested as an intermediate in several reactions yielding dinitrogen oxide as the product of oxidation of hydroxylamine. \(^9\)–\(^{17}\) although no real evidence for this has been put forward. The intermediate N(I) might be nitroxy, or some species derived from it.

The presence of chloride or bromide ions makes the rate attain the limiting value at lower copper(II) concentrations than in the absence of halide ions. This effect may, according to the mechanisms proposed above, be attributed to reactions (7) and (10) or perhaps reaction (8) being favoured at the expense of reactions (3) and (5), respectively.

The effect of ionic strength on the experimental rate constants is in agreement with the mechanisms suggested above. The value of \(k\) is only slightly dependent on the ionic strength, just as it might be expected if the rate-limiting step is monomolecular. The effect that does exist, may be a secondary salt effect. The fact that \(k\) changes little with increasing ionic strength indicates that \(\beta_1\) changes only slightly with \(\mu\). The value of \(\beta_1\) used for the calculation of the values of Table 6 is the one determined at \(\mu=1.00\) M.

The values of \(k\) and \(k'\) obtained from \(v_{\text{obs}}(1+\beta_1C_M)/C_M\) versus \(C_M\) are not, however, very sensitive to the value of \(\beta_1\) used in these calculations.

Reaction (4) might in fact be two consecutive reactions; a rapid reversible formation of a binuclear complex followed by a rate-limiting electron transfer reaction. The strong dependence of \(k'\) on the ionic strength indicates, however, that this reaction is truly bimolecular. Since the reacting species in reaction (4) are both positively charged, \(k'\) should be expected to increase with increasing ionic strengths. The studies on the pre-equilibrium reported in Ref. 2 gave no evidence for the rapid formation of any binuclear complex.

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REFERENCES


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