THEORETICAL ANALYSIS OF CROSS ELECTRON TRANSFER REACTIONS BETWEEN COMPLEX IONS.
COMMUNICATION 3. COMPLEXES WITH MONO- AND BIDENTATE LIGANDS

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The electron transfer (ET) reactions between complexes with water and ammine ligands (effective radius of the complex \( r = 3.5 \) Å) were examined in [1], and reactions between complexes with bipyridyl and phenanthroline ligands \( (r = 7 \) Å) were examined in [2]. A comparison with the experimental data for these systems revealed the soundness of the values of the parameters which determine the rate constant and activation energy of the ET used in the calculations. The cross ET reactions (in an aqueous medium) involving both groups of complexes were investigated within the framework of the system of calculation described in [1].

The thermodynamic characteristics (free energies and enthalpies) of the reactions, reported in Table 1, were estimated with the data tabulated in [1] for complexes with water and ammine ligands and in [2] for complexes with bipyridyl and phenanthroline ligands. The values of the inner-shell parameters of the complexes are given in the same articles.

The outer-shell energy of reorganization, \( E_s \) (in water) for the reactions was set at 30 kcal/mole. This value is -3 kcal/mole higher than the estimation of \( E_s \) with the cross ratio \( (E_s^1 \cdot 2 = (E_s^1 + E_s^2)/2) \) but fits the experimental data better.

The energy of the electrostatic reaction and the reaction volume for this group of reactions was 2.5 kcal/mole and 0.5 liter/mole, respectively. The effective frequency of the nuclear motion \( (\omega/2\pi) \) was equal to \( 10^{13} \) sec\(^{-1} \) [1].

DISCUSSION OF THE RESULTS

As in the two previous articles, the results of the calculations were compared with the experimental data extrapolated to zero ionic strength (see Table 1). The available information on the effect of the ionic strength on the rate constant and enthalpy of the ET reactions examined here is even more limited than for the redox systems discussed in [1] and [2]. Co-(aq)\(^{3+} \)/Cr(bipy)\(^{2+} \) is the only system for which the rate constants and activation energies were measured with several values of the ionic strength. However, the corresponding constants are the observed and not the true constants, although they could be close to the true constants. Extrapolation of the observed constants to \( \mu = 0 \) with the Debye-Hückel equation at coordinates of \( log k - \mu^{1/2}/(1 + 3.3\mu^{1/2}) \) results in \( log k_0 = 1.1 \). Application of the Debye-Hückel equation to the true rate constant with \( \mu = 0.11 \) gives \( log k_0 = 1.3 \). The last value was used for the comparison with the theory. A similar increment of the transition from \( \mu = 0.1 \) to \( \mu = 0 \) (\( \Delta log k = log k(\mu = 0.9) - log k_0(\mu = 0) = 1.2 \)) was used for the Co(phen)\(^{3+} \)/Ru(aq)\(^{2+} \) system.

As the data in Table 1 indicates, a decrease in \( \mu \) results in a small increase in the rate for the Fe(phen)\(^{3+} \)/Fe(aq)\(^{2+} \) and Ru(bipy)\(^{3+} \)/Fe(aq)\(^{2+} \) systems. This tendency is opposite to the predicted tendency based on the Debye-Hückel equation and is most likely due to the inaccuracy of the increment. If extrapolation to \( \mu = 0 \) is performed for the Ru(bipy)\(^{3+} \)/Fe-(aq)\(^{2+} \) system using the rate constant with \( \mu = 0.1 \), the corresponding value of \( log k_0 \) will be equal to 5.2. If the rate constant with \( \mu = 1.0 \) is used, the value of \( log k_0 \) will be equal to 4.6 (in the condition that the increment of \( \Delta log k = log k(\mu = 1) - log k_0(\mu = 0) = 1.2 \) is the average value for the ET reactions between complexes with radius \( r = 3.5 \) Å; [1, 2]). For ET reactions between complexes with a radius of 7 Å, the last value of \( log k_0 \) is given in Table 1 in parentheses. For the Fe(phen)\(^{3+} \)/Fe(aq)\(^{2+} \) system, extrapolation resulted in \( log k_0 \sim 4 \) (or 3.3) based on the value of the constant with \( \mu = 0.5 \) (or \( \mu = 1.0 \)).

For ET reactions between \( \text{Co(phen)}_{3}^{3+} \) and aqua cations \( \text{V}^{2+}, \text{Cr}^{2+}, \text{Ru}^{2+}, \) and \( \text{Fe}^{2+} \) and for the \( \text{Fe(aq)}_{6}^{3+}/\text{Cr(dipy)}_{3}^{2+}, \text{Co(am)}_{5}(\text{aq})^{3+}/\text{Cr(bipy)}_{6}^{2+}, \) and \( \text{Os(bipy)}_{3}^{3+}/\text{Ru(aq)}_{6}^{2+} \) systems, the increment of \( \Delta \log k \) was set at 1.2. The rate constants extrapolated in this way could also be slightly high.

The results of the calculations of the rate constants of the ET reactions reported in Table 1 should essentially be considered as the results of estimations of the electronic matrix elements \( L \) (or transmission coefficients \( \kappa_{e} \)) (compare [17]). Such an estimation of \( L \) is of definite interest, since it can serve as the basis for constructing empirical approximations of \( L \).

Assuming that the value of \( \log k_{0} = 5.2 \) is more realistic for the related systems \( \text{Ru(bipy)}_{3}^{3+}/\text{Ru(aq)}_{6}^{2+} \) and \( \text{Ru(phen)}_{3}^{3+}/\text{Fe(aq)}_{6}^{2+} \), the value of \( L \) is equal to 55 cm\(^{-1} \) (see Table 1). Use of \( L = 55 \) cm\(^{-1} \) for calculation of the ET in the \( \text{Ru(bipy)}_{3}^{3+}/\text{Ru(aq)}_{6}^{2+} \) system results in the value of \( \log k = 8.8 \), which is in good agreement with the experimental value.

As suggested by Eq. (1) in [1], a comparison of the rate constants with the same ionic strength values gives \( \Delta \log k = \log k_{1} - \log k_{2} = 2 \Delta \log L + \Delta \log k_{0} \), where \( k = k/L^{2} \), and \( \kappa_{e} \sim L^{2} \).

Applying this ratio to the \( \text{Fe(bipy)}_{3}^{3+}/\text{Fe(aq)}_{6}^{2+} \) and \( \text{Ru(bipy)}_{3}^{3+}/\text{Fe(aq)}_{6}^{2+} \) systems and substituting the experimental difference in the corresponding values from Table 1 for \( \Delta \log k \) and the value calculated with \( \Delta \log L = 0 \) for \( \Delta \log k \), \( L - 30 \) cm\(^{-1} \) for the first system. The ET rate constants in the \( \text{Fe(bipy)}_{3}^{3+}/\text{Fe(aq)}_{6}^{2+} \) and \( \text{Fe(phen)}_{3}^{3+}/\text{Fe(aq)}_{6}^{2+} \) systems calculated with this value of \( L \) are close to the experimental values.

Matrix element \( L = 14 \) cm\(^{-1} \) for the group of reactions of \( \text{Co(phen)}_{3}^{3+}/\text{ML}^{2+} \) (\( \text{L} = \text{aq}, \text{am} \)), as follows from the calculation of the rate constant of the ET reaction between \( \text{Co(phen)}_{3}^{3+} \) and \( \text{Ru(am)}_{6}^{2+} \).

The \( \text{Co(am)}_{6}^{3+}/\text{Cr(bipy)}_{3}^{2+} \) system was used for estimating \( L \) in the group of related reactions involving bipyridyl and phenanthroline complexes of chromium. As Table 1 shows, the value of \( L = 28 \) cm\(^{-1} \) fits the corresponding experimental data for reactions with aqua complexes of iron. The fit is slightly worse when \( \text{Co(am)}_{5}(\text{aq})^{3+} \) is the oxidant, but this could be due to the fact that the energy of the inner-shell reorganization for this complex is not a well-known value and is set as the same as for hexammine complexes.

Finally, for reactions between \( \text{Os(bipy)}_{3}^{3+} \) and aqua complexes of iron and ruthenium, the value of \( L \) is ~90 cm\(^{-1} \). The values of \( L \) estimated with the approximate ratio* are reported in the last column in Table 1, where \( L_{11} \) and \( L_{22} \) are the matrix elements for the symmetrical reactions

\[
\begin{align*}
\text{Ox}_{1} + \text{Red}_{1} & \rightarrow \text{Red}_{1} + \text{Ox}_{1} \\
\text{Ox}_{2} + \text{Red}_{2} & \rightarrow \text{Red}_{2} + \text{Ox}_{2}
\end{align*}
\]

and \( L_{12} \) is the matrix element for the cross reaction

\[
\begin{align*}
\text{Ox}_{1} + \text{Red}_{2} & \rightarrow \text{Red}_{1} + \text{Ox}_{2}
\end{align*}
\]

Ratio (1) can be substantiated within the framework of the concept that the fundamental contribution to the integral of the overlapping of the molecular orbitals of the reaction complexes of the redox pair is made by overlapping of the orbitals of the ligands [17]. Designating the density of the transferred electron in the orbitals of the ligands by \( c_{z}^{2} \), it is possible to approximately write the molecular matrix elements \( L \) as

\[
L_{11} \sim l_{z}^{2}, \quad L_{22} \sim l_{z}^{2}, \quad L_{12} \sim l_{z}l_{z},
\]

where \( l \) is the matrix element between the contiguous N (or O) atoms of the ligands of the oxidant and reducing agent which are considered approximately constant. Expression (1) for \( L_{12} \) is directly derived from (2).

As Table 1 shows, the fit between the experimental values (\( L_{12} \)) and the values of \( L \) calculated with the approximate formula \( (L_{12})_{ap} \) is extremely good (values of \( L_{11} \) from [1] and [2]).

*Approximation of the geometric mean value was also proposed for estimation of the matrix elements of cross ET reactions in [18].