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(24) N$_4$P$_4$(NHEt)$_2$(NMe$_2$)$_6$[5] is obtained (75%).

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The Hexaamminecobalt Electron-Exchange Reaction

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In this paper we present a theoretical study of the extraordinarily slow electron-exchange reaction $\mathrm{Co^{3+}(NH_3)_6 + Co^{2+}(NH_3)_6 \xrightarrow{k_1} Co^{2+}(NH_3)_6 + Co^{3+}(NH_3)_6}$. With the utilization of multiphonon theory for nonadiabatic electron-transfer reactions, k_1 was expressed as a product of a two-center electron-exchange term, $|V_{\mathrm{if}}|^2$, and a nuclear Franck–Condon factor, G. $|V_{\mathrm{if}}|^2$ was evaluated by invoking the effects of spin–orbit coupling, while G was calculated by incorporating the effects of configurational changes and of frequency changes in the first coordination layer, as well as the Marcus–Levich solvent reorganization energy. We demonstrate that both electronic spin multiplicity restrictions and the nuclear reorganization energy contribute significantly to the retardation of the rate of this reaction. The mechanism considered herein is more efficient than the alternative reaction paths which involve thermally excited electronic states.

I. Introduction

There have been extensive experimental[1-3] and theoretical[4,5] studies of electron-transfer reactions between coordination complexes in solution. An unsolved problem in this area pertains to the enormous difference between the rates of the symmetric electron-exchange reactions[6-8] (1) and (2), where

$$\mathrm{Co(NH_3)_6{}^{3+} + Co(NH_3)_6{}^{2+} \xrightarrow{k_1} Co(NH_3)_6{}^{2+} + Co(NH_3)_6{}^{3+}} \qquad (1)$$

$$k_1 \le 10^{-9}\ \mathrm{M^{-1}\ s^{-1}} \quad \text{at } 65\ {}^\circ\mathrm{C}$$

$$\mathrm{Ru(NH_3)_6{}^{3+} + Ru(NH_3)_6{}^{2+} \xrightarrow{k_2} Ru(NH_3)_6{}^{2+} + Ru(NH_3)_6{}^{3+}} \qquad (2)$$

$$k_2 = 10^{3}\ \mathrm{M^{-1}\ s^{-1}} \quad \text{at } 25\ {}^\circ\mathrm{C}$$

at room temperature (25 °C) $k_1/k_2 \simeq 10^{-13}$–10^{-15}. The extraordinarily slow rate of some electron-exchange reactions has been attributed by Libby[9] about 25 years ago to small Franck–Condon vibrational overlap, originating from large configurational changes in the first coordination layer.[6] However, recent classical calculations of this activation barrier[10] result in a contribution of 6.8 kcal mol^{-1} to the activation energy, which is too low to account for the small value of k_1. Alternatively, spin multiplicity restrictions have been introduced to account for the slow exchange rate k_1.[10] These two effects are interrelated. As was pointed out by Orgel,[11] high spin–low spin exchange results in large configurational changes in the first coordination layer.

In this paper we report a quantum mechanical calculation of the relative exchange rate k_1/k_2. We show that both the electronic spin multiplicity restriction and the Franck–Condon reorganization energy contribute significantly to the retardation of the electron exchange reaction (eq 1). Both effects should be incorporated in a quantitative theory of electron transfer in this system. We shall utilize a quantum mechanical rate equation developed for nonadiabatic outer-sphere electron-exchange reaction. It incorporates the following contributions: (1) the electronic-exchange matrix element, (2) the Marcus–Levich reorganization energy of the classical polar solvent outside the first coordination layer, (3) the Franck–Condon overlap factors originating from configurational changes in the first coordination layer.

The transition probability, W, for the reaction

$$\mathrm{A}^{z} + \mathrm{B}^{y} \rightarrow \mathrm{A}^{z+1} + \mathrm{B}^{y-1} \qquad (3)$$

can be expressed in the form[5,12]

$$W = \frac{2\pi}{\hbar}|V_{\mathrm{if}}|^2 G(\Delta E, E_{\mathrm{s}}, \{\Delta d_x\}, \{\omega_x'\}, \{\omega_x''\}) \qquad (4)$$

The factor V_{if} is the two-center electron-exchange term between the two ions

$$V_{\mathrm{if}} = \langle \Psi_{\mathrm{f}} | V | \Psi_{\mathrm{i}} \rangle \qquad (5)$$

with Ψ_{i} and Ψ_{f} corresponding to the electronic wave functions of the initial state ($\mathrm{A}^{z} + \mathrm{B}^{y}$) and in the final state ($\mathrm{A}^{z+1} + \mathrm{B}^{y-1}$), respectively. The interaction V may be approximated as a sum of one-electron Coulomb interactions between the two ions. The function $G(\Delta E, E_{\mathrm{s}}, \{\Delta d_x\}, \{\omega_x'\}, \{\omega_x''\})$ appearing in eq 4 is the equilibrium-averaged Franck–Condon factor, which takes into account the solvent and the vibrations of the first coordination layer. It is characterized by the set of its arguments: ΔE is the energy gap between the initial and final electronic states, E_{s} is the Marcus–Levich solvent reorganization energy, $\{\Delta d_x\}$ is the set of reduced displacements in the first coordination layer, $\{\omega_x'\}$ and $\{\omega_x''\}$ are the sets of vibrational frequencies in the initial and final states. All the electronic and nuclear terms appearing in eq 4 are evaluated at a fixed interionic separation.

In the next section we discuss and evaluate the electronic-exchange matrix element. Section III is devoted to the evaluation of the factor G and the overall rate constant. The results are presented in section IV, and alternative schemes

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Table I. Structural and Spectroscopic Input Data

	Co-$(NH_3)_6^{2+}$	Co-$(NH_3)_6^{3+}$	Ru-$(NH_3)_6^{2+}$	Ru-$(NH_3)_6^{3+}$
M-L, Å[a]	2.114	1.936	2.144	2.104
$\omega_1(A_{1g})$, cm^{-1}[b]	357	494	350[c]	500
$\omega_2(E_g)$, cm^{-1}	255	442		475
$\omega_3(F_{14})$, cm^{-1}	325	474.7		463
$\omega_4(F_{14})$, cm^{-1}	192	331		273
$\omega_5(F_{2g})$, cm^{-1}	187[d]	322		248
$\omega_6(F_{24})$, cm^{-1}	143[d]	246[e]		

[a] Reference 10. [b] Skeletal vibrational frequencies were taken from ref 15. [c] Estimated according to the relation $\omega_1(\mathrm{II}) = 0.7\omega_1(\mathrm{III})$. [d] Calculated from the ratio $\omega_4(\mathrm{II})/\omega_4(\mathrm{III}) = \omega_5(\mathrm{II})/\omega_5(\mathrm{III}) = \omega_6(\mathrm{II})/\omega_6(\mathrm{III})$. [e] Evaluated from the comparison with $\omega_6(\mathrm{Cr(NH_3)_6}^{3+})$.

are discussed in section V. Some computations and mathematical details are postponed for the appendixes.

II. Electronic Matrix Elements

Symmetry and spin restrictions are important factors in the evaluation of electronic matrix elements and therefore have to be analyzed carefully. In the scheme in which the spin is a good quantum number, the ground states of $\mathrm{Co^{II}}$ and $\mathrm{Co^{III}}$ are $^4T_{1g}$ and $^1A_{1g}$, respectively. The electron exchange amounts to a transfer of one electron from $\mathrm{Co^{II}}$, which is a quartet whose spin quantum number is $s = {}^3/_2$. The resultant state of $\mathrm{Co^{III}}$ must have either $s = 1$ or $s = 2$, both states being orthogonal to the ground state of $\mathrm{Co^{III}}$, which is a singlet, and therefore one obtains $V_{\mathrm{if}} = 0$ for pure spin states. On the other hand, in the ruthenium case the ground-state terms are $^1A_{1g}$ and $^2T_{2g}$. Therefore, the removal of an electron from $\mathrm{Ru^{II}}$ results in a doublet which is necessarily $^2T_{2g}$, thus $V_{\mathrm{if}} \neq 0$. The electronic configurations of $^1A_{1g}$ and $^2T_{2g}$ are $(t_{2g})^6$ and (t_{2g}),^{5} respectively. They differ only in one electron in t_{2g}, and accordingly the interaction matrix element may be written as eq 6, where $t_{2g}(a)$ is localized on one ion and $t_{2g}(b)$ is localized on the second ion.

$$V_{\mathrm{if}} = \langle t_{2g}(a)|v|t_{2g}(b)\rangle \tag{6}$$

Owing to spin–orbit coupling, the true ground states of the cobalt ions are not pure spin states. In such a case, the previous argument does not hold, and the matrix element V_{if} has a finite value. Nonvanishing matrix elements are obtained between the two low-lying excited states of $\mathrm{Co^{III}}$, $^3T_{1g}$ and $^3T_{2g}$, and the ground state $^4T_{1g}$ of $\mathrm{Co^{II}}$. The true eigenstates can be represented as a linear combination of several pure spin states. However, since spin–orbit coupling mixes only states which belong to the same double-group representation, it can mix the ground state $^1A_{1g}$ only with $^3T_{1g}$ (common representation Γ_1).[13] Thus, we can write the ground state of $\mathrm{Co^{III}}$ as the linear combination in eq 7.

$$\Psi(\mathrm{Co^{III}}) = {}^1A_{1g}[(t_{2g})^6] + c_1{}^3T_{1g}[(t_{2g})^5(e_g)^1] \tag{7}$$

In the case of $\mathrm{Co^{II}}$ only one low-lying excited state, ^2E_g, gives a nonvanishing contribution to V_{if} with the ground state $^1A_{1g}$ of $\mathrm{Co^{III}}$. The spin–orbit coupling splits the ground state $^4T_{1g}$ into three components ($J = {}^1/_2, {}^3/_2, {}^5/_2$) with relative energies $E_{1/2} = 0$, $E_{3/2} = {}^1/_2\zeta$, and $E_{5/2} = {}^4/_3\zeta$, where ζ is the spin–orbit coupling constant.[13] Double-group representation analysis shows that only the components with $J = {}^3/_2$ and $J = {}^5/_2$ mix with the term ^2E_g. We therefore write the three states as in eq 8.

$$\begin{aligned}\Psi_1(\mathrm{Co^{II}}) &= {}^4T_{1g(J=1/2)}[(t_{2g})^5(e_g)^2]\\ \Psi_2(\mathrm{Co^{II}}) &= {}^4T_{1g(J=3/2)}[(t_{2g})^5(e_g)^2] + c_2{}^2E_g[(t_{2g})^6(e_g)^1]\\ \Psi_3(\mathrm{Co^{II}}) &= {}^4T_{1g(J=5/2)}[(t_{2g})^5(e_g)^2] + c_3{}^2E_g[(t_{2g})^6(e_g)^1]\end{aligned} \tag{8}$$

Their relative energies are approximately those of the components of $^4T_{1g}$. Taking the value $\zeta = 515$ cm^{-1} for the spin–orbit coupling constant,[14] we obtain $E_1 = 0$, $E_2 = 257$ cm^{-1}, and $E_3 = 687$ cm^{-1}. It is quite clear that at room temperature the thermal populations of the two excited states cannot be neglected. They should be considered in the evaluation of the electron-transfer rate constant. As a result, we have to evaluate nine different rate constants, and the overall rate constant is their thermal average. The first stage is to evaluate the nine matrix elements between the three possible initial states and the three final states. As we discussed above, considerations of spin multiplicity show that there is a restricted set of pure spin states that gives nonvanishing contributions. The contributing components in the wave functions of $\mathrm{Co^{III}}$ and $\mathrm{Co^{II}}$ in Ψ_i and Ψ_f are either $^1A_{1g}$ and ^2E_g or $^3T_{1g}$ and one of the three components of $^4T_{1g}$. In the combination $^1A_{1g}$ and ^2E_g the electronic configurations in the strong-field approximation are $(t_{2g})^6$ and $(t_{2g})^5e_g$, while in the combination $^3T_{1g}$ and $^4T_{1g}$ they are $(t_{2g})^5e_g$ and $(t_{2g})^4(e_g)^2$. In each pair the configurations differ only by one electron in the e_g orbital. Therefore, all the interaction matrix elements are proportional to the same one-electron matrix element $\langle e_g(a)|v|e_g(b)\rangle$. The nine matrix elements may be expressed as eq 9, where k and l are the indices of

$$V_{kl} = \alpha_{kl}\langle e_g(a)|v|e_g(b)\rangle \tag{9}$$

the $\mathrm{Co^{II}}$ wave function (eq 8) in the initial and final states, respectively. The coefficients α_{kl} (eq 10) are evaluated by using the explicit form

$$\begin{aligned}\alpha_{11} &= c_1^2\\ \alpha_{12} = \alpha_{21} &= c_1(c_1 + c_2)\\ \alpha_{13} = \alpha_{31} &= c_1(c_1 + c_3)\\ \alpha_{22} &= (c_1 + c_2)^2\\ \alpha_{23} = \alpha_{32} &= (c_1 + c_2)(c_1 + c_3)\\ \alpha_{33} &= (c_1 + c_3)^2\end{aligned} \tag{10}$$

of the wave functions (eq 7 and 8). The numerical values of the coefficients c_i are evaluated in Appendix A.

Using the general expression for the individual rate constants (eq 4), we can write the overall rate constant as the thermal average over the nine processes (eq 11). On the other hand, in the ruthenium case

$$\begin{gathered}W_{\mathrm{Co}} = \frac{2\pi}{\hbar}\,\frac{1}{Z}\sum_{k=1}^{3} 2ke^{-E_k/k_BT}\sum_{l=1}^{3}|V_{kl}|^2 G(\Delta E_{lk},E_s,\{\Delta d_x\},\{\omega_x'\},\{\omega_x''\})\\ Z = \sum_{k=1}^{3} 2ke^{-E_k/k_BT}\\ \Delta E_{lk} = E_l - E_k\end{gathered} \tag{11}$$

one may simply use eq 4 with V_{if} from eq 6 and $\Delta E = 0$, obtaining eq 12.

$$W_{\mathrm{Ru}} = \frac{2\pi}{\hbar}|\langle t_{2g}(a)|v|t_{2g}(b)\rangle|^2 G(\Delta E(=0),E_s,\{\Delta d_x\},\{\omega_x'\},\{\omega_x''\}) \tag{12}$$

III. Average Franck–Condon Factors

In order to evaluate eq 11 and 12, we have to estimate the nuclear factors $G(\Delta E,E_s,\{\Delta d_x\},\{\omega_x'\},\{\omega_x''\})$. These Franck–Condon factors express the contributions of the solvent and of the internal vibrational degrees of freedom of the ions to the rate constant. In what follows we discuss some features of G, while its evaluation by the saddle-point method is presented in Appendix B. To obtain a numerical estimate of $G(\Delta E,E_s,\{\Delta d_x\},\{\omega_x'\},\{\omega_x''\})$, one needs as an input the information about the energetic parameters ΔE and E_s, the structural information on $\{\Delta d_x\}$, and the spectroscopic information concerning the vibrational frequencies. The energy gap between the initial and final electronic states, ΔE, can be evaluated from the information about the splitting of the ground state of $\mathrm{Co^{II}}$, as discussed in the previous section. The reorganization energy of the solvent, E_s, is given by the Marcus expression (eq 13) where, in the symmetric exchange, r_1 and r_2 are

$$E_s = e^2\left(\frac{1}{n^2} - \frac{1}{D}\right)\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R}\right) \tag{13}$$

the radii of the first coordination layer of A^{z+1} and A^z, n is the solvent index of refraction, and D is its dielectric constant. Expression 13 was evaluated by taking, for the solvent, $e^2((1/n^2) - (1/D)) = 200$ Å kcal mol^{-1} and by using the following values for the radii[10] (see Table I) and the distances between ions: $r_1(\mathrm{Co^{III}}) = 3.5$ Å, $r_1(\mathrm{Ru^{III}}) = 3.7$ Å, $r_2(\mathrm{Co^{II}}) = 3.7$ Å, $r_2(\mathrm{Ru^{II}}) = 3.7$ Å, $R_{\mathrm{Co^{II}-Co^{III}}} = 7.3$ Å, and $R_{\mathrm{Ru^{II}-Ru^{III}}} = 7.5$ Å. The resultant solvent reorganization energy is 28 kcal mol^{-1} for the cobalt case and 27 kcal mol^{-1} for the ruthenium case.

The geometry and force constants of the ligands are almost unaffected by the change in oxidation states of the complexes. Therefore, we have to deal only with the metal–ligand vibrations. In the present case of a symmetrical electron exchange between octahedral complexes, we have 3(6 + 1) − 6 = 15 modes in each complex. Furthermore, we assume that the nature of the normal modes is the same in the two oxidation states. The change in the equilibrium metal–ligand distance between the two oxidation states is denoted by Δr. This bond length change is not reflected in the asymmetric modes, for which one has $\Delta r_\kappa = 0$. Only for the totally symmetric A_{1g} vibration $\Delta r(A_{1g}) \neq 0$ and is actually equal to $6^{1/2}(\Delta r)$. The reduced displacement (in reciprocal frequency units) is given by eq 14, where m is the mass of a single ligand. The available experimental

$$[\Delta d(A_{1g})]^2 = (1/\hbar)(6(\Delta r)^2 m) \qquad (14)$$

data on bond lengths and vibrational frequencies in the cobalt and ruthenium complexes are reproduced in Table I. From Table I we find that $\Delta r(\mathrm{Co}) = 0.178$ Å; the corresponding $\Delta d(A_{1g})$ is evaluated according to eq 14, and, together with the information about the vibrational frequencies, it is possible to estimate the factor G. Numerical values for G (in units of cm) for the relevant values of ΔE_{kl} are given in Table II, together with the statistical weights at 300 K, the corresponding values of α_{kl}^2, and the energy gaps ΔE_{kl}.

IV. Results

In the last column in Table II we give the values of $W' = W_{kl}|\langle e_g(a)|v|e_g(b)\rangle|^{-2}$ for the $Co^{3+}(NH_3)_6$–$Co^{2+}(NH_3)_6$ system, each multiplied by its statistical weight. Their sum is the total averaged transition probability divided by the square of the one-electron matrix element. The final result at 300 K is given by eq 15, where the electronic matrix element is expressed in

$$\bar{W}_{\mathrm{Co}} = 6.0 \times 10^{-10}|\langle e_g(a)|v|e_g(b)\rangle|^2\ \mathrm{s}^{-1} \qquad (15)$$

units of cm^{-1}. It is interesting to note that, as may be seen from Table II, one would obtain a very similar result on neglecting the splitting of the $\mathrm{Co^{II}}$ ground state. In the case of ruthenium there is only one transition for $\Delta E = 0$. Computation based on the data given in Table I gives eq 16

$$W_{\mathrm{Ru}} = 1.8 \times 10^2|\langle t_{2g}(a)|v|t_{2g}(b)\rangle|^2\ \mathrm{s}^{-1} \qquad (16)$$

at 300 K. The ratio between the transition probabilities for the two-electron-transfer reactions is given by eq 17.

$$\frac{\bar{W}_{\mathrm{Co}}}{W_{\mathrm{Ru}}} = 3.3 \times 10^{-12}\frac{|\langle e_g(a)|v|e_g(b)\rangle|_{\mathrm{Co}}{}^2}{|\langle t_{2g}(a)|v|t_{2g}(b)\rangle|_{\mathrm{Ru}}{}^2} \qquad (17)$$

The bimolecular rate constant is related to the transition probability by the relation in eq 18, where N_0 is Avogadro's

$$k = N_0\int W(R)\ \exp[-U(R)/k_BT]\ \mathrm{d}^3R \qquad (18)$$

number, $U(R)$ is the potential of average force between the two complexes as function of their separation R, and $W(R)$ is the separation-dependent transition probability. This expression may be approximated as eq 19, where $\bar{R}$ is an effective

$$k = N_0[4\pi\bar{R}^2\beta(W(\bar{R}))\ \exp[-U(\bar{R})/k_BT]] \qquad (19)$$

distance for the electron transfer and $\beta \approx 1$ Å is a typical width. The factor $4\pi\bar{R}^2\beta\ \exp[-U(R)/k_BT]$ in eq 19 is expected to be practically identical for the cobalt and ruthenium electron-exchange reactions. Therefore, the ratio of the rate constants for reactions 1 and 2 is given by eq 17.

V. Discussion

In order to obtain quantitative information from eq 17 one has to estimate the ratio of the transfer matrix elements $\langle e_g(a)|v|e_g(b)\rangle$ for cobalt and $\langle t_{2g}(a)|v|t_{2g}(b)\rangle$ for ruthenium. The explicit evaluation of each of these terms requires a detailed knowledge of the electronic wave functions and is not practical at present. On the other hand, it is possible to advance arguments for the estimate of their relative magnitudes. The orbitals e_g and t_{2g} in the hexaammine complexes should be described not by the pure metal orbitals but by a linear combination of the metal orbitals with an appropriately symmetrized combination of the ligand orbitals. The coefficient of the symmetrized ligand orbital combination is known as the covalency parameter.[16] For the hexaammine complexes of transition-metal ions they are known to have values in the range of 0.1–0.5.[17] The two-center electron-exchange integrals are very sensitive to the behavior of the wave function far from the metal nuclei. Therefore, one expects that the major contribution comes from the ligand part of the wave function. In the present case of the two-electron-exchange reactions, one has the same ligands on both metal ions. Thus, we may conclude that the difference between the two matrix elements originates mainly from the differences in the covalency parameters between the hexaammine complexes of $\mathrm{Co^{II}}$ and $\mathrm{Ru^{II}}$. As we have already mentioned, the covalency parameters of the two complexes are comparable. The matrix elements are proportional to their square, and, therefore, the rate constants are proportional to their fourth power. As a result, all we can do without more information about the covalency parameters is to estimate the square ratio of the exchange matrix elements as unity within an uncertainty of 2 orders of magnitude. The resultant ratio between the rate constants for reactions 1 and 2 is $k_1/k_2 \simeq 10^{-12\pm2}$ at 300 K. The ratio k_1/k_2 consists of two factors. First, one contribution of about 10^{-4} is due to spin-multiplicity effects (α^2 in Table II). Second, the remaining contribution, which originates from the thermal average of Franck–Condon factors between excited vibrational states, amounts to 10^{-8}. It is interesting to compare this average contribution to the Franck–Condon factor between the vibrational ground states which amounts to about 10^{-18}. From the huge 10 orders of magnitude difference, one can conclude that in the present case transitions between excited vibrational states are most important. Stynes and Ibers[10] have estimated the effect of the difference in bond lengths by evaluating the classical reorganization energy. They obtained a value of 6.8 kcal mol^{-1} which corresponds at room temperature to a factor of 10^{-5}. This classical calculation is based on the assumption that the Franck–Condon factor between vibrational states at the intersection of the potential energy curves is about 1. Actually, it is much smaller, and, as we have shown, the detailed quantum mechanical calculation gives the factor 10^{-8} instead of 10^{-5}.

The important role of the geometric factor relative to spin-multiplicity effects was nicely demonstrated by Endicott and co-workers.[18] They found that the electron-exchange rate for the couple $\mathrm{Co([14]\text{-}dieneN_4)(H_2O)_2{}^{2+,3+}}$ is slow ($k_{ex} = 2 \times 10^{-5}$ M^{-1} s^{-1} at 25 °C) as compared to $\mathrm{Co([14]\text{-}tetraeneN_4)(H_2O)_2{}^{2+,3+}}$ ($k_{ex} = 6 \times 10^{-2}$ M^{-1} s^{-1} at 25 °C) and

Table II. Evaluation of Franck–Condon Factors for the $Co^{3+}(NH_3)_6$–$Co^{2+}(NH_3)_6$ System

k	l	$(2k/z)e^{-E_k/k_BT}$	$10^4\alpha_{kl}^2$	ΔE_{kl}, cm^{-1}	G, cm × 10^{-18}	W', cm^2 s^{-1} × 10^{-10}
1	1	0.59	1.45	0	2.63	2.66
1	2	0.59	0.85	258	1.40	0.83
1	3	0.59	0.13	687	0.49	0.04
2	1	0.34	0.85	−258	4.88	1.67
2	2	0.34	0.50	0	2.63	0.53
2	3	0.34	0.008	429	0.92	0.03
3	1	0.07	0.13	−687	13.44	0.14
3	2	0.07	0.08	−429	7.33	0.05
3	3	0.07	0.01	0	2.63	0.002

vitamin B_{12} ($k_{ex} = 2.10^3$ M^{-1} s^{-1} at 35 °C). In these three couples both the Co^{II} and Co^{III} ions have a low-spin electronic configuration. Therefore, the large differences in the electron-exchange rates may be attributed only to differences in the Franck–Condon factors. Indeed, X-ray analysis of ([14]-dieneN$_4$) cobalt complexes[19] reveals a large difference of the axial bond lengths between the Co^{II} and Co^{III} complexes. A quantitative evaluation of the average Franck–Condon factors is made difficult by the fact that the crystallographic studies were done on the Co^{III} complex with ammonia molecules as axial ligands, whereas in the Co^{II} complex the ligands were water molecules.

An alternative mechanism for reaction 1 was suggested by Orgel[11] and by Stynes and Ibers,[10] who propose a reaction path which proceeds via the thermally excited low-spin ^2E_g state of the Co^{II} ion. Under the reasonable assumption that the electronic-exchange matrix element for the cobalt system, when the Co^{II} is in the ^2E_g state, is of the same order of magnitude for the ruthenium system, one gets eq 20 for this alternative

$$\frac{k_{Co}}{k_{Ru}} \simeq \exp\left(-\frac{1}{k_BT}E(^2E_g)\right) \qquad (20)$$

mechanism. The excited-state (^2E_g) energy, relative to the ground state, has a value of about 9000 cm^{-1},[20] which gives a ratio of 10^{-19} for k_1/k_2 at 300 K, while our mechanism yields $k_1/k_2 = 10^{-12\pm2}$ providing a more efficient pathway for reaction 1. Another reaction path involves the excited electronic states of the Co^{III} ion either in the high-spin $(t_{2g})^4(e_g)^2$[10] configuration or in its $(t_{2g})^5(e_g)^1$ configurations. However, the excitation energies involved are 21 600 cm^{-1}[10] and 13 400 cm^{-1},[21] respectively, yielding, therefore, an even smaller k_1/k_2 ratio. Thus the rates of the reactions, which proceed via a thermally excited electronic state, are expected to be negligible as compared to the mechanism discussed in the present paper.

Appendix A. Electronic Matrix Elements

The relevant wave functions of the Co^{II} and Co^{III} ions, as given in eq 7 and 8 are in the form of a linear combination of pure spin wave functions Ψ_1 and Ψ_2:

$$\Psi = \Psi_1 + c\Psi_2 \qquad (A-1)$$

The mixing coefficient c is small, and, therefore, it can be evaluated by first-order perturbation theory as in eq A-2, where

$$c = \langle\Psi_2|H_{so}|\Psi_1\rangle/(E_2 - E_1) \qquad (A-2)$$

H_{so} is the spin–orbit interaction operator, and E_2 and E_1 are the pure spin-state energies. For the evaluation of the coefficients c_1, c_2, and c_3 (eq 7 and 8) one needs specific information about energies and matrix elements. The relevant matrix elements of the spin–orbit interaction operator are given in eq A-3.[13] The spin–orbit coupling constants have the

$$\langle{}^3T_{1g}|H_{so}|{}^1A_{1g}\rangle = 6^{1/2}\zeta(Co^{III})$$
$$\langle{}^2E_g|H_{so}|{}^4T_{1g}(3/2)\rangle = -(1/5^{1/2})\zeta(Co^{II})$$
$$\langle{}^2E_g|H_{so}|{}^4T_{1g}(5/2)\rangle = -(3/5^{1/2})\zeta(Co^{II}) \qquad (A-3)$$

values[14] $\zeta(Co^{II}) = 515$ cm^{-1} and $\zeta(Co^{III}) = 600$ cm^{-1}. The energy denominator for the Co^{III} is given by[21] $E(^3T_{1g}) - E(^1A_{1g}) = 13\,400$ cm^{-1} while for the Co^{II} ion, disregarding the splitting of the ground state, it is[20] $E(^2E_g) - E(^4T_{1g}) = 9000$ cm^{-1}. The resulting coefficients, computed on the basis of the above information, are $c_1 = 0.110$, $c_2 = -0.026$, and $c_3 = -0.077$.

Appendix B. Evaluation of Franck–Condon Factors

The theory of electron-transfer reactions in solution usually concentrates on the solvent degrees of freedom and treats the reactants as rigid systems.[4,5] This is a good approximation for a wide class of systems, but in some interesting situations, such as the hexaamminecobalt exchange, one cannot ignore the effects of internal vibrations. The frequencies of the internal vibrations are quite high (at room temperature $\hbar\omega \geq k_BT$), and, therefore, one ought to treat their effects quantum mechanically. It is possible to incorporate them either within a classical description of the solvent[22] or within the quantum mechanical (polaron-like) description.[12,23-25] For the present problem, we adopt the mathematical framework of the generating function and its evaluation through the saddle-point method.

This procedure was developed by Holstein[26] for the similar problem of small polarons, under the assumption that only equilibrium distances are changed and the frequencies remain constant. In the present case, the two oxidation states have different vibrational frequencies, and, therefore, one has to use more general expressions for the generating functions.[27,28] The formal expression for the averaged Franck–Condon factor may be written as eq B-1, where ΔE is the energy gap. The

$$G = \frac{1}{2\pi\hbar}e^{-S_s}\int_{-\infty}^{\infty}e^{it(\Delta E)/\hbar}[e^{f_s(t)} - 1]e^{f_c(t)}\,dt \qquad (B-1)$$

subscripts s and c specify the solvent degrees of freedom and the internal vibrations, respectively. Putting $f_c(t) = 0$, one gets the already well-known contribution of the solvent given by eq B-2. The solvent is characterized by its reorganization energy E_s (eq 13).

$$G_s = (4\pi E_sk_BT)^{-1/2}\exp\left[-\frac{(\Delta E + E_s)^2}{4E_sk_BT}\right] \qquad (B-2)$$

The factor $\exp(f_c(t))$ is the generating function of the internal vibrations, and it is given by

$$f_c(t) = \Phi_c(t) + \varphi_c(t) \qquad (B-3a)$$

$$\Phi_c(t) = -\sum_\kappa\frac{\omega_\kappa'\omega_\kappa''(\Delta d_\kappa)^2}{\omega_\kappa''\coth\lambda_\kappa' + \omega_\kappa'\coth\mu_\kappa''} \qquad (B-3b)$$

$$\varphi_c(t) = \sum_\kappa\ln\left\{\frac{2(\omega_\kappa'\omega_\kappa'')^{1/2}\sinh\dfrac{\hbar\omega_\kappa'}{2k_BT}}{[(\sinh 2\lambda_\kappa')(\sinh 2\mu_\kappa'')]^{1/2}}[(\omega_\kappa''\coth\mu_\kappa'' + \omega_\kappa'\coth\lambda_\kappa')(\omega_\kappa''\tanh\mu_\kappa'' + \omega_\kappa'\tanh\lambda_\kappa')]^{-1/2}\right\} \qquad (B-3c)$$

where

$$\lambda_\kappa' = \frac{1}{2}\left(i\omega_\kappa't + \frac{\hbar\omega_\kappa'}{k_BT}\right) \qquad \mu_\kappa'' = \tfrac{1}{2}i\omega_\kappa''t$$

The sum is taken over all internal modes, and the oxidation states are distinguished by one and two primes. The changes in the equilibrium configurations are characterized by the reduced displacements Δd_κ (eq 14). The second term in eq B-3 originates only from vibrational frequency differences, and in the present case its contribution is much smaller than that of the first term.

The integral in eq B-1 is evaluated by the saddle-point method. The saddle points are the solutions of the equation $F^I(t_0) = 0$ where $F^I \equiv dF/dt$ and

$$F(t) = it(\Delta E)/\hbar + f_s(t) - S_s + f_c(t) \qquad (B-4)$$

It can be shown that in the present case it is enough to consider only the saddle point t_0 which is closest to the axes origin (also $\mathrm{Re}(t_0) = 0$). The integral (B-1) is then given by (B-5). In

$$G = 1/\hbar[-2\pi(F^{II}(t_0))]^{-1/2}\exp F(t_0) \qquad (B-5)$$

general one has to solve the saddle-point equation (B-4) numerically; only if the energy gap vanishes ($\Delta E = 0$) can one find by inspection that $t_0 = i\hbar/2k_BT$. In this case one may write down the final result as

$$G = (2\pi)^{-1/2}\left[-f_s^{II}\left(\frac{i\hbar}{2k_BT}\right) - \Phi_c^{II}\left(\frac{i\hbar}{2k_BT}\right) - \varphi_c^{II}\left(\frac{i\hbar}{2k_BT}\right)\right]^{-1/2}\prod_{\varkappa}X_{\varkappa}\exp\left\{-\frac{E_s}{4k_BT} - \sum_{\varkappa}Y_{\varkappa}\right\} \quad \text{(B-6)}$$

$$X_{\varkappa} = 4\omega_{\varkappa}'\omega_{\varkappa}''/(\omega_{\varkappa}' \coth \nu_{\varkappa}' + \omega_{\varkappa}'' \coth \nu_{\varkappa}'') \times (\omega_{\varkappa}' \tanh \nu_{\varkappa}' + \omega_{\varkappa}'' \tanh \nu_{\varkappa}'') \quad \text{(B-7)}$$

$$Y_{\varkappa} = \frac{2(\Delta d_{\varkappa})^2\omega_{\varkappa}'\omega_{\varkappa}''}{\omega_{\varkappa}' \coth \nu_{\varkappa}'' + \omega_{\varkappa}'' \coth \nu_{\varkappa}'} \quad \text{(B-8)}$$

$$f_s^{II}(t_0) = -2E_sk_BT$$

where

$$\lambda_{\varkappa}'\left(\frac{i\hbar}{2k_BT}\right) \equiv \nu_{\varkappa}' = \frac{\hbar\omega_{\varkappa}'}{4k_BT} \qquad \mu_{\varkappa}''\left(\frac{i\hbar}{2k_BT}\right) \equiv \nu_{\varkappa}'' = \frac{\hbar\omega_{\varkappa}''}{4k_BT}$$

Finally, $\Phi_c^{II}(i\hbar/2k_BT)$ in eq B-6 is the second logarithmic derivative of the generating function for the symmetric exchange process, which accounts for changes in metal–ligand bond distances in a system where the A_{1g} vibrational modes are characterized by different frequencies $\omega_{\varkappa}'$ and $\omega_{\varkappa}''$ (eq B-9)

$$\Phi_c^{II}\left(\frac{i\hbar}{2k_B\mathrm{T}}\right) = \sum_{\varkappa}(\Delta d_{\varkappa}\hbar\omega_{\varkappa}'\omega_{\varkappa}'')^2 \times \left[\frac{\omega_{\varkappa}' \cosh \nu' \operatorname{cosech}^3 \nu' + \omega_{\varkappa}'' \cosh \nu'' \operatorname{cosech}^3 \nu''}{(\omega_{\varkappa}' \coth \nu_{\varkappa}'' + \omega_{\varkappa}'' \coth \nu_{\varkappa}')^2} - \omega_{\varkappa}'\omega_{\varkappa}''\frac{(\operatorname{cosech}^2 \nu_{\varkappa}' - \operatorname{cosech}^2 \nu_{\varkappa}'')^2}{(\omega_{\varkappa}' \coth \nu_{\varkappa}'' + \omega_{\varkappa}'' \coth \nu_{\varkappa}')^3}\right] \quad \text{(B-9)}$$

and contains contributions only from these vibrational modes where $\Delta d_{\varkappa} \neq 0$. The third term, $\varphi_c^{II}(i\hbar/2k_BT)$, in eq B-6 is responsible for frequency changes only (eq B-10).

$$\varphi_c^{II}\left(\frac{i\hbar}{2k_\beta T}\right) = -\hbar^2\sum_{\varkappa}\left[\frac{\omega\varkappa'^2}{\sinh^2 2\nu_{\varkappa}'} + \frac{\omega_{\varkappa}''^2}{\sinh^2 2\nu_{\varkappa}''} + \frac{1}{4}\,\frac{(\omega_{\varkappa}'^2 \operatorname{sech}^2 \nu_{\varkappa}' - \omega_{\kappa}''^2 \operatorname{sech}^2 \nu_{\varkappa}'')^2}{(\omega_{\varkappa}' \tanh \nu_{\varkappa}' + \omega_{\varkappa}'' \tanh \nu_{\varkappa}'')^2} + \frac{1}{2}\,\frac{\omega_{\varkappa}'^3 \sinh \nu_{\varkappa}' \operatorname{sech}^3 \nu_{\varkappa}' + \omega_{\varkappa}''^3 \sinh \nu_{\varkappa}'' \operatorname{sech}^3 \nu_{\varkappa}''}{\omega_{\varkappa}' \tanh \nu_{\varkappa}' + \omega_{\varkappa}'' \tanh \nu_{\varkappa}''} + \frac{1}{4}\,\frac{(\omega_{\varkappa}'^2 \operatorname{cosech}^2 \nu_{\varkappa}' - \omega_{\varkappa}''^2 \operatorname{cosech}^2 \nu_{\varkappa}'')^2}{\omega_{\varkappa}' \coth \nu_{\varkappa}' + \omega_{\varkappa}'' \coth \nu_{\varkappa}'')^2} - \frac{1}{2}\,\frac{\omega_{\varkappa}'^3 \cosh \nu_{\varkappa}' \operatorname{cosech}^3 \nu_{\varkappa}' + \omega_{\varkappa}''^3 \cosh \nu_{\varkappa}'' \operatorname{cosech}^3 \nu_{\varkappa}''}{\omega_{\varkappa}' \coth \nu_{\varkappa}' + \omega_{\varkappa}'' \coth \nu_{\varkappa}''}\right] \quad \text{(B-10)}$$

It is apparent that $\varphi_c^{II}(i\hbar/2k_BT) = 0$ when the frequencies in each mode are equal; i.e., $\omega_{\varkappa}' = \omega_{\varkappa}''$ for all $\varkappa$. Numerical evaluation for the hexaamminecobalt electron-exchange system gives $f_s^{II} = -4.1 \times 10^6\ \mathrm{cm}^{-2}$, $\Phi_c^{II}(i\hbar/2k_BT) = -5.2 \times 10^6\ \mathrm{cm}^{-2}$, and $\varphi_c^{II}(i\hbar/2k_BT) = -0.4 \times 10^6\ \mathrm{cm}^{-2}$; that is $|\varphi_c^{II}(i\hbar/2k_BT)| << |\Phi_c^{II}(i\hbar/2k_BT)|$. The factor $\prod_{\varkappa}X_{\varkappa}$, which originates only from vibrational frequency changes, amounts to 0.18 which is a relatively small contribution (if $\omega_{\varkappa}' = \omega_{\varkappa}''$, $X_{\varkappa} = 1$). The most important contribution is $\sum_{\varkappa}Y_{\varkappa} = 18$.

In order to obtain G for other values of the energy gap, one has to solve numerically the saddle-point equation (eq B-4) and then evaluate the different terms in eq B-5. For each value of ΔE_{kl} the saddle-point equation, eq B-4, was solved numerically, and the resulting value of t_0 was incorporated in eq B-5. The final numerical values of G are summarized in Table II. All calculations were performed at 300 K.

Registry No. $Co^{3+}(NH_3)_6$, 14695-95-5; $Co^{2+}(NH_3)_6$, 15365-75-0.

References and Notes

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