Photoelectron Emission Study of Iron(II) and Cobalt(II) Complexes in Aqueous Solution. Reorganization Energies

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The photoelectron emission threshold energies of Fe^{II} and Co^{II} complexes in aqueous solutions have been determined. The values could be successfully used for obtaining the reorganization energies in the one-electron oxidation reaction of these complexes. The obtained reorganization energies were found to be correlated with the rate constants of the electron-self-exchange reactions of Fe^{II}/Fe^{III} and Co^{II}/Co^{III}.

A new spectroscopic technique, Photoelectron Emission Spectroscopy (PEES) of solution,[1-5] provides the photoelectron emission threshold energies, E_t, of molecules or ions in solution. The E_t values for organic molecules in solutions have been found to be linearly correlated with their ionization potentials, I_p, in the gas phase or the oxidation potentials, E_{ox}, in solutions.[4,5] The E_{ox} values used, however, are not of the equilibrium values but the peak potentials in cyclic voltammetry. Since E_{ox} is thermodynamically less meaningful than the standard redox potential, E°, it is essential to measure the E_t values of any samples for which the E° values are accurately known in order to study the correlation between E_t and E°. Iron(II) and cobalt(II) with various ligands or chelates are suitable for this purpose since it is easy to find a variety of E° values from these complexes.

The E_t and E° for a one-electron redox reaction pertain to the energy changes of the following reactions:

$$X^{nz} \rightarrow {}^*X^{nz+1} + e^-(\text{vacuum}) \qquad E_t \quad (1)$$

$$X^{nz} \rightarrow X^{nz+1} + e^-(\text{electrode at the potential of NHE})^{6} \qquad E^\circ \quad (2)$$

Since the $^*X^{nz+1}$ in Eq. 1 is the product of an optical process (the Franck-Condon transition), the $^*X^{nz+1}$ has a geometrical structure which is exactly the same as that of the X^{nz} with respect to the geometries both in the inner- and the outer-sphere regions, and is in a vibrationally excited state. The vibrational relaxation energy of the $^*X^{nz+1}$, or the reorganization energy, ΔG_r, in the one-electron oxidation reaction of X^{nz}, is defined by

$$^*X^{nz+1} \rightarrow X^{nz+1} \qquad \Delta G_r \quad (3)$$

and given as follows:

$$\Delta G_r = (E^\circ + \Delta G_H) - E_t \qquad (4)$$

where $\Delta G_H (\approx 4.5\text{eV})$[7] is the potential energy of the vacuum level with respect to NHE.

In the Marcus theory for outer-sphere electron transfer reactions, the ΔG_r is a key parameter closely related to the activation energy.[8] Its evaluation is thus essential for the study of the kinetics. Considering the importance of ΔG_r, the potentiality of the PEES of solution providing the ΔG_r value must be fully explored.

Only a few studies have taken place in which ΔG_r values have been obtained from PEES experiments,[9-11] or the values so obtained treated in discussions concerning electron transfer kinetics.[12-16] In the present study, the experimentally obtained ΔG_r values for iron(II)/(III)[17] and cobalt(II)/(III) complexes are compared with the values calculated with the following equations, which are considered to be the only practical method for estimating the ΔG_r values:

$$\Delta G_r = \Delta G_r(\text{in}) + \Delta G_r(\text{out}), \qquad (5)$$

$$\Delta G_r^{\text{calc}}(\text{in}) = -(1/2) N f_o (\Delta r)^2, \qquad (6)$$

and

$$\Delta G_r^{\text{calc}}(\text{out}) = -(e^2/2a)(\varepsilon_{op}^{-1} - \varepsilon_s^{-1}), \qquad (7)$$

where ΔG_r(in) and ΔG_r(out) are the inner- and outer-sphere components of the reorganization energy, respectively; N is the coordination number of the complex (6 in this study), f_o the force constant for the bond between the central metal and its coordinating atom for the oxidized species (X^{nz+1}), Δr the difference in the coordination bond distances for the X^{nz} and X^{nz+1}, a the mean radius of the assumed boundaries between the inner- and outer-sphere regions for the X^{nz} and X^{nz+1}, and ε_{op} and ε_s the optical and the static dielectric constants of water.

Experimental

Photoelectron Emission Spectrometer for Solution. Details concerning the spectrometer have been described elsewhere.[3,4] Since this technique is extremely sensitive to any surface contamination of a sample solution, a surface scratcher was newly provided to the rotating glass disk. The scratcher is made of a thin plastic film and presses the glass surface very lightly at a few millimeters above the sample solution; it thus prevents organic contaminants floating on the surface of the solution from entering the photoionization region. This greatly improved the cleanliness of the observing surface. Therefore, the slower rotation rate of the glass disk could be utilized, resulting in

smaller capacitive noise currents and better S/N ratios.

Samples. The reagents used to prepare the solutions were of guaranteed reagent grade and were used without further purification. The abbreviations used in this paper are: edta=*N,N,N′,N′*-ethylenediaminetetraacetate, pdta=1,2-diaminopropane-*N,N,N′,N′*-tetraacetate, cydta=1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetate, bpy=2,2′-bipyridine, dmbpy=4,4′-dimethyl-2,2′-bipyridine, phen=1,10-phenanthroline, tmp=3,4,7,8-tetramethyl-1,10-phenanthroline, Cl-phen=5-chloro-1,10-phenanthroline, tpy=2,2′:6′,2″-terpyridine, N4=1,4,8,11-tetraazacyclotetradecane.

The constituents of the solutions measured were: $[Fe(H_2O)_6]^{2+}$; 2M(M=mol dm^{-3}), 1M, 0.5M in 3M H_2SO_4, $[Fe(edta)]^{2-}$; 0.2M, 0.1M, 0.05M, $[Fe(CN)_6]^{4-}$; 0.2M in 0.1M KOH, $[Fe(bpy)_3]^{2+}$; 0.8M, 0.4M, 0.2M, $[Fe(dmbpy)_3]^{2+}$; 0.05M, 0.025M, $[Fe(phen)_3]^{2+}$; 0.8M, 0.4M, 0.2M, $[Fe(tmp)_3]^{2+}$; 0.05M, 0.025M, $[Fe(tpy)_2]^{2+}$; 0.05M, 0.025M, $[Co(H_2O)_6]^{2+}$; 0.2M in 2M H_2SO_4, $[Co(NH_3)_6]^{2+}$; saturation in 4M ammonia water, $[Co(edta)]^{2-}$; 0.2M, 0.1M, $[Co(pdta)]^{2-}$; 0.2M, 0.1M, $[Co(cydta)]^{2-}$; 0.2M, 0.1M, $[Co(bpy)_3]^{2+}$; 0.2M, 0.1M 0.02M, $[Co(dmbpy)_3]^{2+}$; 0.2M, 0.1M, $[Co(phen)_3]^{2+}$; 0.2M, 0.1M, 0.04M, $[Co(Cl\text{-}phen)_3]^{2+}$; 0.05M, 0.01M, $[Co(tpy)_2]^{2+}$; 0.025M, 0.0125M, $[Co(N4)]^{2+}$; 0.1M.

The solutions containing edta or its analogues were prepared from $FeSO_4\cdot 7H_2O$, or $CoSO_4\cdot 7H_2O$, and $Na_2H_2edta\cdot 2H_2O$, H_4pdta, or H_4cydta, and the acidities were adjusted to pH ca. 7 with $NaHCO_3$. The solutions containing the bpy, phen, N4 or their analogues were prepared by adding excess amounts of the metal ions so that the free ligands would not exist in the solutions. If a ligand exists in excess of the metal ion, it is possible that the free ligand molecules can coagulate on the solution surface, while perturbing photoelectron emission from the solute.

The $[Co(NH_3)_6]^{2+}$, $[Fe(edta)]^{2-}$ and some others are extremely sensitive to oxidation by air. These samples were therefore prepared under a nitrogen gas atmosphere.

The solutions were cooled to around +1 °C, except for aqueous ammonia solutions, which were cooled to −15 °C since the vapor pressure of ammonia was too high at +1 °C.

Determination of E_t Values. The photoelectron emission yield Y is a function of the exciting photon quantum energy $h\nu$ and the E_t as follows:[1)]

$$Y=A(h\nu-E_t)^n, \tag{8}$$

where A is a proportional constant and n is known to be either 2 or 2.5. A plot of $Y^{1/n}$ gives a straight line and its extrapolation to Y=0 gives the E_t value. In this study, after testing both n values, that which gave better statistics to be fitted on a straight line was chosen. Consequently, a value of 2 was used for $[Fe(dmbpy)_3]^{2+}$, $[Co(bpy)_3]^{2+}$, $[Co(phen)_3]^{2+}$, and $[Co(tpy)_2]^{2+}$, and 2.5 was used for the other samples. The E_t values obtained with this extrapolation method are considered to correspond to the energy change of the reaction given in Eq. 1.

The E_t values were reproducible within 0.1 eV or less, irrespective of the concentrations of the metal complexes.

Results and Discussion

The E_t values obtained are listed in Table 1 together with the E° values for the X^{nz}/X^{nz+1} couples. Since both the E_t and E° values pertain to the energy necessary for removing an electron from X^{nz} (cf. Eqs. 1 and 2), one may well expect that they are related with each other. No correlation, however, was observed between them. This is because the complexes presently studied had quite different ΔG_r values. This is in contrast with the results concerning the organic molecules which have been reported.[4,5)]

The ΔG_r values determined by the PEES technique with Eq. 4 are plotted as ΔG_r^{exp} in Fig. 1 against the ΔG_r^{calc} values given by Eqs. 5—7.

The values of Δr in Eq. 6 were collected from reports concerning the X-ray diffraction and EXAFS (Extended X-ray Absorption Fine Structure). The values of a in Eq. 7 are determined according to

$$a=d_{X-L}+r_L, \tag{9}$$

where d_{X-L} is the distance between the central metal atom X and an atom L in the ligand at the most distant position from X, and r_L is the van der Waals radius of L. The values of Δr and a are included in Table 1.

As shown in Fig. 1, the experimental ΔG_r values are in excellent agreement with the calculated ones. The line in the figure indicates the position where both values are the same. It should be noted that both ΔG_r values are the result of a number of approximations and simplifications, as follows. In the derivation of Eq. 6, (1) only the bond length between the metal and the atom directly coordinating to the metal is taken into account; thus, the other differences in geometries of the X^{nz} and X^{nz+1} are neglected. (2) A harmonic potential is adopted for the bond deformation. (3) In Eq. 7, the outer-sphere component is calculated by using the Born model, i.e. the spherical conductor of radius a in a continuous medium with dielectric constants of ε_{op} and ε_s. In the derivation of Eq. 4, there exists (4) the uncertainty in ΔG_H, and (5) the double layer potential or the surface potential at the solution/gas interface is neglected. In Eq. 8, there is (6) the uncertainty in the value of n, and (7) the density of states for the ion solvated is represented by a delta function; thus, the concept of adiabatic and vertical ionization energies is abandoned.[18)] However, considering the excellent agreement between the experimental and calculated ΔG_r values, it seems that the approximations used here are adoptable within the present experimental accuracy.

Due to a spin-state change during the oxidation process for many of the cobalt complexes, i.e. the high-spin state for Co^{II} to the low-spin state for Co^{III}, these complexes have the large bond differences, Δr, and thus large ΔG_r values compared to the iron complexes whose spin states remain high. It is now important to note that the electronic state of cobalt complexes just after photoionization is not of the low-spin cobalt(III)(^1A: t_{2g}^6, e_g^0) but of a ^3T state as expressed by

Table 1. Standard Redox Potentials E°, Photoelectron Emission Threshold Energies E_t of M^{II}, Parameters to Calculate Reorganization Energies ΔG_r^{calc}, and Experimentally Determined Reorganization Energies ΔG_r^{exp} for Iron and Cobalt Complexes in Aqueous Solutions

	Complex	E°	E_t	a	Δr	$-\Delta G_r^{calc}$ (in)	$-\Delta G_r^{calc}$ (out)	$-\Delta G_r^{calc}$	$-\Delta G_r^{exp}$
		V	eV	pm	pm	eV	eV	eV	eV
1	$[Fe(H_2O)_6]^{2+/3+}$	0.77	7.09	390	13	0.81	1.01	1.82	1.82
2	$[Fe(edta)]^{2-/-}$	0.117	7.06	(547)[a]			(0.72)[a]		2.44
3	$[Fe(CN)_6]^{4-/3-}$	0.36	5.60	456	1	0.01	0.86	0.87	0.74
4	$[Fe(bpy)_3]^{2+/3+}$	1.085	6.15	697	0	0	0.57	0.57	0.57
5	$[Fe(dmbpy)_3]^{2+/3+}$	0.905	6.12	729	0	0	0.54	0.54	0.72
6	$[Fe(phen)_3]^{2+/3+}$	1.056	6.14	735	0	0	0.54	0.54	0.58
7	$[Fe(tmp)_3]^{2+/3+}$	0.832	5.73	838	0	0	0.47	0.47	0.40
8	$[Fe(tpy)_2]^{2+/3+}$	1.062	6.05	591	0	0	0.64	0.64	0.49
9	$[Co(H_2O)_6]^{2+/3+}$	1.82	8.04	374	21	2.06	1.06	3.12	1.72
10	$[Co(edta)]^{2-/-}$	0.40	7.18	548	22	1.84	0.72	2.56	2.28
11	$[Co(pdta)]^{2-/-}$	0.33	7.34	548	22	1.84	0.72	2.56	2.51
12	$[Co(cydta)]^{2-/-}$	0.31	7.57	548	22	1.84	0.72	2.56	2.76
13	$[Co(bpy)_3]^{2+/3+}$	0.315	6.25	708	20	1.83	0.56	2.39	1.44
14	$[Co(dmbpy)_3]^{2+/3+}$	0.239	7.15	740	20	1.83	0.54	2.37	2.41
15	$[Co(phen)_3]^{2+/3+}$	0.37	7.48	741	20	1.83	0.53	2.36	2.61
16	$[Co(Cl\text{-}phen)_3]^{2+/3+}$	0.43	7.26	740	20	1.83	0.54	2.37	2.33
17	$[Co(tpy)_2]^{2+/3+}$	0.31	5.89	706	14	0.93	0.53	1.46	1.08
18	$[Co(N4)(H_2O)_2]^{2+/3+}$	0.421	7.12	524[b]	0	0	0.76	1.44	2.20
				374[c]	22	0.68	1.00	1.68	
19	$[Co(NH_3)_6]^{2+/3+}$	0.058	7.58	380	22	2.21	1.04	3.25	3.02

The structural information is collected from the following reports for each sample. Some of the parameters are estimated from the data for the samples having similar structure. (1) Ref. 22; J. K. Beattie, S. P. Best, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, **1981**, 2105; J. Strouse,S. W. Layten, and C. E. Strouse, *J. Am. Chem. Soc.*, **99**, 562 (1977). (2) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964). (3) Ref. 22; B. I. Swanson, S. I. Hamburg, and R. R. Ryan, *Inorg. Chem.*, **13**, 1685 (1974); K. Yanagi, Y. Ohashi, Y. Sasada, Y. Kaizu, and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **54**, 118 (1981). (4) M. E. G. Posse, M. A. Juri, P. J. Aymonino, O. E. Piro, H. A. Negri, and E. E. Catellano, *Inorg. Chem.*, **23**, 948 (1984). (5) Estimated. (6) Ref. 22; A. Zalkin, D. H. Templeton, and T. Ueki, *Inorg. Chem.*, **12**, 1641 (1973); J. Baker, L. M. Engelhardt, B. N. Figgis, and A. H. White, *J. Chem. Soc., Dalton Trans.*, **1975**, 530. (7) Estimated. (8) A. T. Baker and H. A. Goodwin, *Aust. J. Chem.*, **38**, 207 (1985). (9) The Refs. for sample (1); S. Ray, A. Zalkin, and D. H. Templeton, *Acta Crystallogr., Sect. B*, **29**, 2741 (1973); T. B. Vance, Jr., E. M. Holt, C. G. Rierpont, and S. L. Holt, *Acta Crystallogr., Sect. B*, **36**, 150 (1980); A. F. K. McCandish, T. K. Michael, J. A. Neal, E. C. Lingafelter, and N. J. Rose, *Inorg. Chem.*, **17**, 1383 (1978). (10) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959). (11) Estimated. (12) Estimated. (13) The Refs. for sample (3); D. J. Szalda, C. Creutz, D. Mahajan, and N. Sutin, *Inorg. Chem.*, **22**, 2372 (1983). (14) Estimated. (15) Ref. 22. (16) Estimated. (17) C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, **1976**, 7; B. N. Figgis, E. S. Kucharski, and A. H. White, *Aust. J. Chem.*, **36**, 1537 (1983); B. N. Figgis, E. S. Kucharski, and A. H. White, *Aust. J. Chem.*, **36**, 1527 (1983), and B. N. Figgis, E. S. Kucharski, and A. H. White, *Aust. J. Chem.*, **36**, 1563 (1983). (18) J. F. Endicott, B. Durham, M. D. Glick, T. J. Anderson, J. M. Kuszaj, W. G. Schmonsees, and K. P. Balakrishnan, *J. Am. Chem. Soc.*, **103**, 1431 (1981); J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsees, M. G. Simic, M. D. Glick, and D. P. Rillema, *J. Am. Chem. Soc.*, **99**, 429 (1977). (19) Ref. 22. The force constants are collected from K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, Wiley-Interscience, New York (1978), and J. T. Hupp and M. J. Weaver, *J. Phys. Chem.*, **89**, 2795 (1985). Some are estimated from the data for the complexes having similar structure. a) Estimated from the data for $[Fe(edta)]^-$. b) The parameters for equatorial bonds, and c) for axial bonds.

$$Co(II)(^4T: t_{2g}^5, e_g^2) \rightarrow {}^*Co(III)(^3T: t_{2g}^5, e_g^1) + e^-(vacuum). \quad (10)$$

Therefore, the ΔG_r^{exp} value for this process must be expressed as

$$\Delta G_r^{exp} = -(1/2)Nf_o(\Delta r)^2 - (e^2/2a)(\varepsilon_{op}^{-1} - \varepsilon_s^{-1}) + \Delta E_{spin}, \quad (11)$$

where ΔE_{spin} is the energy difference between the two spin states as follows and is regarded as having a positive value:

$${}^*Co^{III}(^3T: t_{2g}^5, e_g^1) \rightarrow {}^*Co^{III}(^1A: t_{2g}^6, e_g^0). \quad \Delta E_{spin} \quad (12)$$

The structure of the product with * in Eq. 12 still remains the same as that of Co^{II}. The present study

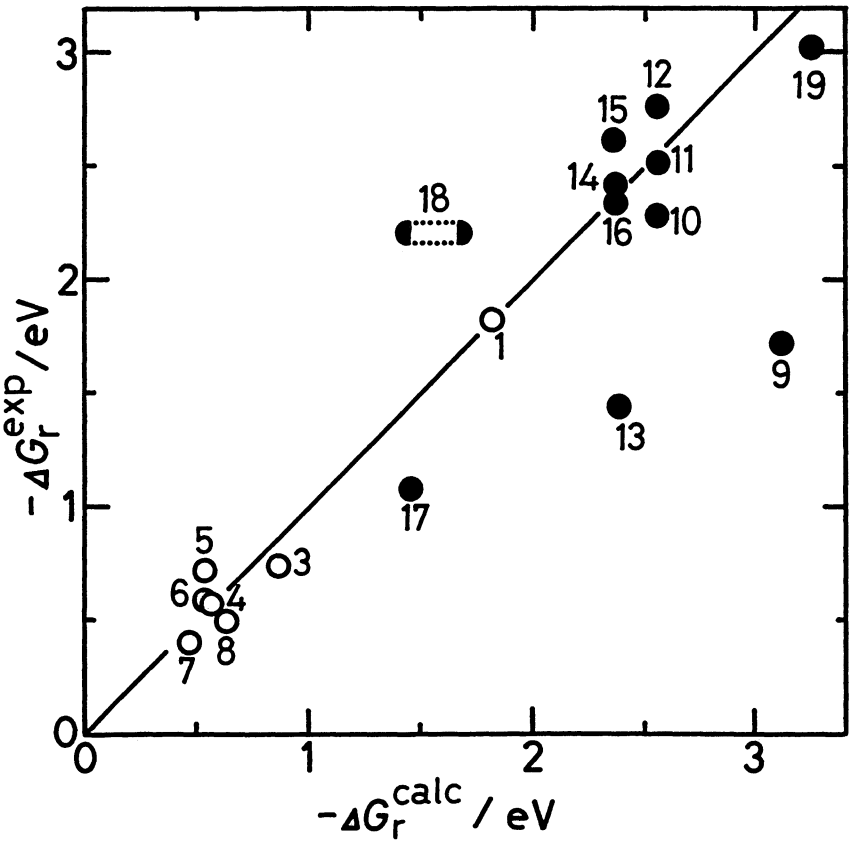

Fig. 1. Plot of the reorganization energies ΔG_r^{exp} determined by the photoelectron emission technique against the ΔG_r^{calc} values calculated by using Eqs. 5—7 for iron (○) and cobalt (●) complexes. The numbers are the same as those in Table 1.

provides the value of ΔE_{spin} as the difference of $(\Delta G_r^{exp} - \Delta G_r^{calc})$. The results shown in Fig. 1 indicate that the ΔE_{spin} values are rather small for most of the cobalt complexes studied here. One exception is $[Co(H_2O)_6]^{2+/3+}$ the value of which is very large (ca. 1.6 eV). The abnormal behavior of this couple concerning the rate of the electron-self-exchange reaction (which has been known for long time[19]) will be studied elsewhere by taking into account their spin states.

The other two samples for which the ΔG_r values do not agree are $[Co(bpy)_3]^{2+/3+}$ and $[Co(N4)(H_2O)_2]^{2+/3+}$. The disagreement for the case of $[Co(bpy)_3]^{2+/3+}$ is not understandable since other complexes which are quite similar to this one give excellent agreement. For the case of $[Co(N4)(H_2O)_2]^{2+/3+}$, the shape of the complex is not spherical since ligand N4 is a flat ring molecule. The equatorial a value used for the calculation of ΔG_r may be too large and the Δr value used here too small, which is regarded as being the same as that of the $[Co(H_2O)_6]^{2+/3+}$.

The relatively small ΔG_r values for $[Co(tpy)_2]^{2+/3+}$ are in accordance with the fact that both ionic states of this complex have a low-spin electron configuration.[20]

It is almost impossible to estimate the ΔG_r value for $[Fe(edta)]^{2-/-}$. The $[Fe(edta)]^-$ is considered to take the heptacoordinate structure of $[Fe(edta)(H_2O)]^-$ in aqueous solution[21] and is too complex to be handled with Eq. 6 (all the metal-ligand atom bond lengths are different in crystals[22]). In addition, the structure in solution is not known for $[Fe(edta)]^{2-}$. In any case, it should be noted that the ΔG_r value (=2.44 eV) for this complex is the largest among the iron complexes. The fact that the $[Fe(edta)]^{2-}$ is an extremely stronger reductant than the $[Fe(H_2O)_6]^{2+}$ (cf. E°=0.117 and 0.77 V, respectively) can be understood as being caused by a large stabilization free energy (2.44 eV) gained after (vertical) one-electron oxidation. This is concluded from the experimental fact that removing an electron vertically from $[Fe(edta)]^{2-}$ requires the same enegy as that from $[Fe(H_2O)_6]^{2+}$ (E_t=7.09 and 7.06 eV, respectively).

It is interesting to compare the ΔG_r^{exp} values obtained by the PEES technique with the rate constants, k_{exch}, of electron-self-exchange reactions in solution. According to the Marcus-Hush theory, the ΔG_r value is closely related to the activation energy, ΔG^*, for the thermal electron-exchange reaction and, thus, to its rate constant. In the simplest model,

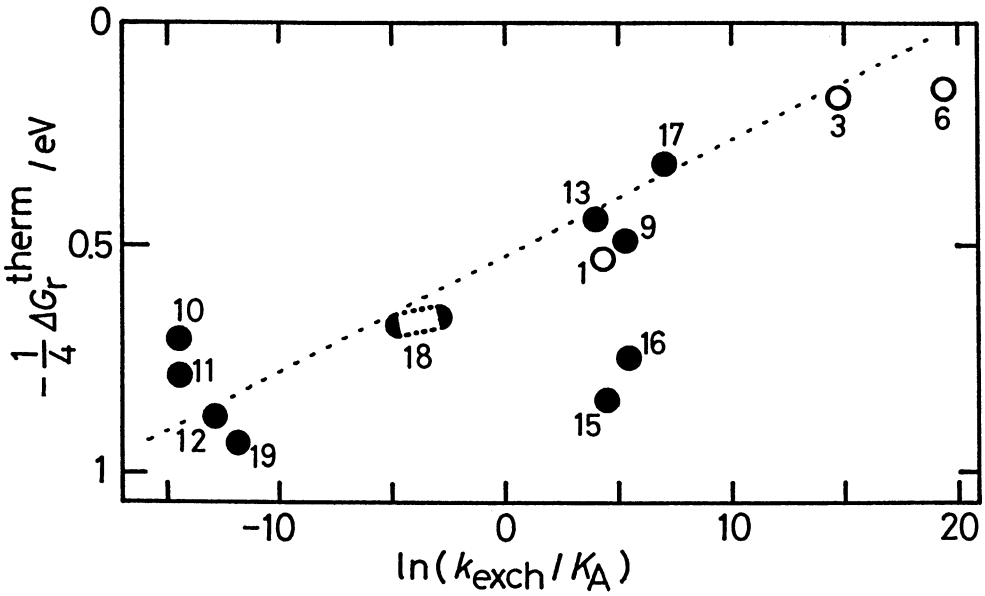

Fig. 2. Correlation between the logarithm of the rate constant k_{exch} for the electron-self-exchange reaction corrected for the formation constant K_A of the precursor complex and a quarter of the thermal reorganization energy ΔG_r^{therm} derived from the ΔG_r^{exp} determined by the photoelectron emission technique for iron (O) and cobalt (●) complexes. The numbers are the same as those in Table 1. The dotted line indicates the slope of RT(=25.7 meV). The k_{exch} and K_A values are collected from Ref. 23.

$\Delta G_r = -4\Delta G^{\neq}$. By using many transition metal(II)/(III) couples, Brunschwig and co-workers showed a linear correlation between $(\Delta r)^2$ and $\Delta G_r(in)$, as determined by the following equation:[23]

$$\Delta G_r(in) = 4RT \ln(k_{exch}/K_A) - \Delta G_r^{calc}(out), \quad (13)$$

where K_A is the equilibrium constant for the formation of the precursor complex for the electron exchange reaction and the $\Delta G_r^{calc}(out)$ was obtained by using Eq. 7. Their results support the classical model for evaluating the $\Delta G_r(in)$ from Δr, as described in Eq. 6.

The ΔG_r^{exp} determined in the present work is of the optical transition and is different from the ΔG_r^{therm} for the thermal one, like an electron-transfer reaction in solution. For the calculation of ΔG_r in an optical transition, only the force constant, f_o, for X^{nz+1} is used as in Eq. 6, while the f for ΔG_r^{therm} must be evaluated by using the mean value of f_o and f_r for X^{nz}.

According to the Delahay's treatment,[24,1]

$$\Delta G_r^{therm} = \Delta G_r^{opt} + \Delta G_r^{opt}(in) \cdot [(3f_r - f_o)/(f_r + f_o)], \quad (14)$$

where ΔG_r^{opt} is the reorganization energy pertaining to the optical electron-transfer reaction, i.e. the ΔG_r^{exp} determined by the PEES technique. It is then possible to evaluate ΔG_r^{therm} using $\Delta G_r^{opt}(in) = \Delta G_r^{exp} - \Delta G_r^{calc}(out)$. The values of the term $(3f_r - f_o)/(f_r + f_o)$ were calculated and found to be almost constant (0.37) for the complexes studied here.

The ΔG_r^{therm}, thus obtained, is obviously related to the k_{exch} corrected for the K_A, as shown in Fig. 2, with an expected slope of RT, which is indicated by the dotted line.

It is worth noting that the anomalous behavior of the $[Co(H_2O)_6]^{2+/3+}$ observed by Brunschwig and co-workers that the experimental k_{exch} value is several orders greater than the predicted value from the classical model,[23] now disappears in the k_{exch} vs. ΔG_r^{exp} relation (the point 9 in Fig. 2). The present results indicate that the thermal electron-transfer reaction proceeds not via the $Co^{III}(^1A)$ state, but via a state which is optically accessible and lies fairly below the $Co^{III}(^1A)$ state when the $[Co(H_2O)_6]^{2+}$ complex deforms its geometry in order to transfer its electron.

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6) The E° is commonly defined as the potential of an electrode in equilibrium with equi-activity X^{nz} and X^{nz+1} ions with respect to NHE (Normal Hydrogen Electrode). This means that the free energy of X^{nz} in solution is the same as that of the system consisting of X^{nz+1} in solution plus e^- in the electrode having the potential of E°, and that no energy is necessary to transfer an electron from X^{nz} to the electrode at E°. Thus, the transfer of the electron from X^{nz} to NHE requires the energy of $-eE^\circ$, where e is the charge of an electron. Equation 2 is the expression for this process.

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