EPR Studies at High-Pressure. VI. Spin-Exchange Reaction of Nitroxide Radical with Copper(II) and Iron(III) Complexes

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(Received May 7, 2001)

The spin exchange of nitroxide with copper(II) and iron(III) complexes was studied by means of a high-pressure EPR technique. The spin exchange with Cu^{II} complexes exhibited the aspect of weak exchange, independent of the kinds of coordinated ligands, while the spin exchange with Fe^{III} complexes was found to vary from weak exchange to a strong one, dependent of the solvent viscosity. Based on the results, the spin exchange with Cu^{II} and Fe^{III} complexes is discussed in detail.

Exchange-broadening experiments give much more interesting information about the mechanism of the exchange interaction.[1] Based on the temperature dependence of the spin exchange rates, Skubnevskaya and Molin distinguished the cases of strong and weak exchanges.[2] For the diffusion-controlled spin-exchange reaction, the viscosity of the solvent plays an important role. However, since any viscosity variation with temperature inevitably involves unfavorable energetic problems, we have pointed out the usefulness of studying the pressure dependence of the spin-exchange rates.[1] In a previous paper,[1] the spin exchange of nitroxide with various kinds of Co^{II} and Ni^{II} complexes was examined in detail. Based on the results, it was suggested that the degree of screening of the Co^{II} and Ni^{II} metals by coordinated ligands is important for the efficiency of spin exchange. However, we have found that the spin exchanges with Cu^{II} and Fe^{III} complexes can not be explained simply by shielding of the central metal by coordinated ligands. In the present study, we examined the spin exchanges of nitroxide with Cu^{II} and Fe^{III} complexes, in which the dipole contribution to the broadening of lines can be neglected,[3] and have demonstrated experimental results for segregating the cases of strong and weak exchanges.

Experimental

2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxyl (TANONE) and acetylacetonate complexes ([Cu(acac)$_2$], [Fe(acac)$_3$], and [Co(acac)$_2$]) were purchased from Aldrich Chemical Company Inc., and were used as received. 1,4,8,11-tetraazacyclo-tetradecane (cyclam) was obtained from Lancaster Synthesis Lid. and a complex between cyclam and Cu^{II} ion was obtained.[1] *N*,*N′*-disalicylidene-*o*-phenylenediamine (H_2saloph) was prepared by the reported method,[4] and [Cu(saloph)] was obtained.[4,5] The high-pressure technique and procedures for EPR measurements were almost the same as those described elsewhere.[1,6] The peak-to-peak width of the central component of the nitroxide radical (5×10^{-4} mol dm^{-3}) was measured at 298 K. The rate constants of the spin exchange were determined at pressures up to 63.7 MPa.

Results and Discussion

Spin Exchange with Cu^{II} Complexes. The rate constants (k_{ex}) for the spin exchange of TANONE with Cu^{II} complexes were estimated from the slope of a plot of the linewidth of the TANONE EPR-spectra against the metal-complex concentrations (Eq. 1),[7]

$$\Delta H = (k_{ex}/A)\, C + \Delta H_0, \tag{1}$$

where ΔH and ΔH_0 are the linewidths of TANONE in the presence and absence of spin exchange, respectively. C denotes the concentration of metal complexes. The A-value is 1.52×10^8 mT^{-1} s^{-1} for spin exchange between nitroxide and a transition metal.[1] The rate constants obtained at 10^5 Pa were on the order of 10^9: $k_{ex} = 0.701 \times 10^9$ mol^{-1} dm^3 s^{-1} for [Co(acac)$_2$] in CCl_4, 2.75×10^9 mol^{-1} dm^3 s^{-1} for [Cu(acac)$_2$] in $CHCl_3$, 3.16×10^9 mol^{-1} dm^3 s^{-1} for [Cu(acac)$_2$ (C_5H_5N)$_2$] in $CHCl_3$, 1.30×10^9 mol^{-1} dm^3 s^{-1} for [Cu(saloph)] in $CHCl_3$, and 2.33×10^9 mol^{-1} dm^3 s^{-1} for [CuCl$_2$(cyclam)] in 1-propanol.

As discussed previously,[1] the rate constant (k_{ex}) can be related to the probability (P) of a spin exchange upon collision, as follows:

$$k_{ex}\eta \propto P, \tag{2}$$

where η is the viscosity coefficient of the medium. We have pointed out that P for weak exchange is susceptible to η, and that $k_{ex}\eta$ increases with η. On the other hand, $P \approx 1$ holds for a strong exchange, and $k_{ex}\eta$ is independent of η.[1] Figure 1 shows the relationship between $k_{ex}\eta$ and η for spin exchanges with Cu^{II} complexes. As can be seen in Fig. 1, $k_{ex}\eta$ for a spin exchange with [Co(acac)$_2$] is independent of η, suggesting that the spin exchange is strong. Though [Cu(acac)$_2$] and [Cu(saloph)] are tetracoordinated complexes similar to the structure of [Co(acac)$_2$], the $k_{ex}\eta$ value for these Cu^{II} complexes increases with η, indicating that the spin exchanges are weak. Further, the spin exchange with the octahedral Cu^{II} complex [Cu(acac)$_2$(C_5H_5N)$_2$] is also a weak exchange. Since halide ligands undergo spin transfer from a metal ion to a ligand by a superexchange mechanism, the spin exchange is expected to be strong even in the cyclam complex, having most severe shielding of the central metal.[1] However, a plot of $k_{ex}\eta$ against η for the spin exchange of [CuCl$_2$(cyclam)] complex shows saturation curvature. As reported previously,[8] the P-values become progressively larger and approach unity with increasing solvent viscosity (η). Though the spin exchange with [CuCl$_2$(cyclam)] approximates to a strong exchange, the increase in the plot of $k_{ex}\eta$ against η suggests that the spin exchange at 10^5 Pa is weak. The spin exchanges of Cu^{II} complexes used in the present study are weak, and can not be explained in terms of the shielding of central metal by ligands.[1]

The strength of the spin exchanges is related to the magni-

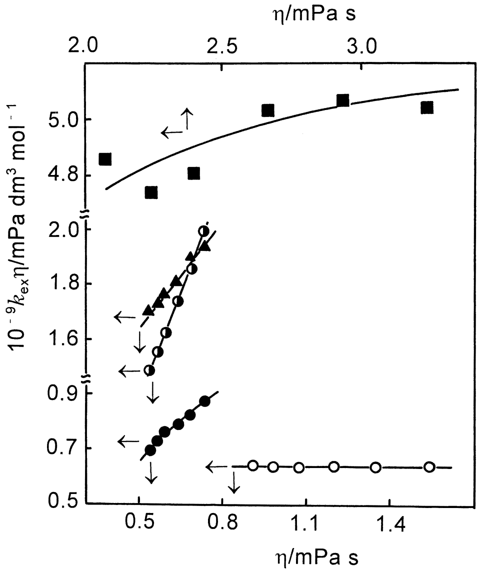

Fig. 1. Relationship between $k_{ex}\eta$ and η for spin exchange of TANONE with Cu^{II} and Co^{II} complexes: (○) [Co(acac)$_2$] in CCl$_4$, (◑) [Cu(acac)$_2$] in CHCl$_3$, (▲) [Cu(acac)$_2$(C$_5$H$_5$N)$_2$] in CHCl$_3$, (●) [Cu(saloph)] in CHCl$_3$, and (■) [CuCl$_2$(cyclam)] in 1-propanol.

tude of the electron relaxation time (T_1) and the collision time (τ_c).[2,3] The τ_c value can be given by[9]

$$\tau_c = \frac{2\pi\eta\lambda^2}{k_BT}\frac{r_Ar_B}{r_A + r_B}, \qquad (3)$$
$$\lambda = (\rho_0/\rho)^{1/3}\lambda_0$$

where r_A and r_B denote the effective hydrodynamic radius of the radical and the complex, respectively, and were estimated by referring to the size of their Corey–Pauling–Koltum models (CPK). λ and ρ are the jump length and the liquid density, respectively, and λ_0 and ρ_0 represent them at the freezing point.[1,10] The τ_c value in solvents, used in the present study, can be calculated as being on the order of 10^{-11} s. The T_1 value for [Cu (acac)$_2$] has been reported to be 9.3×10^{-9} s.[3] We thus consider that the [Cu(acac)$_2$(C$_5$H$_5$N)$_2$] and [Cu(saloph)] complexes have T_1 values on the order of 10^{-9} s, though T_1 for [CuCl$_2$(cyclam)] may be somewhat smaller than the others. This value is sufficiently large compared with the τ_c value, which is responsible for the weak exchange of Cu^{II} complexes. When $T_1 < \tau_c$, the efficiency of the spin exchange is dependent on the degree of shielding of metal by coordinated ligands, as shown by Co^{II} and Ni^{II} complexes ($T_1 = 10^{-13}$ and 10^{-12} s).[1,3]

Spin Exchange with Fe^{III} Complex. To clarify the relationship between the strength of spin exchange and the T_1 value, it is useful to examine the pressure dependence of the spin exchanges of [Fe(acac)$_3$] in various solvents. The T_1 value of [Fe(acac)$_3$] has been reported to be 6×10^{-11} s at 10^5 Pa,[3] which is comparable to the τ_c value in the used solvents. As expected from Eq. 3, the τ_c value is dependent on the solvent viscosity. Therefore, by changing the solvent viscosity, we can examine the efficiency of the spin exchanges in solvents having shorter or longer τ_c values than the T_1 values. The τ_c values increase with increasing external pressure. For example, the τ_c value in CHCl$_3$ becomes 8.1×10^{-11} s up to 63.7 MPa from 6.3×10^{-11} s at 10^5 Pa. Since the increment of τ_c accompanying compression in the present study was not very large, it is instructive to compare the τ_c value at 10^5 Pa with the T_1 one. The τ_c values at 10^5 Pa for the spin exchange of [Fe(acac)$_3$] in various solvents can be calculated according to Eq. 3: $\tau_c = 2.5 \times 10^{-11}$ s in acetone, 6.3×10^{-11} s in CHCl$_3$, 6.8×10^{-11} s in benzene, 8.4×10^{-11} s in toluene, 12×10^{-11} s in CCl$_4$, and 20×10^{-11} s in 1-propanol. In Fig. 2, plots of $k_{ex}\eta$ against η are shown. As discussed above, the plots in Fig. 2 afford good judgement for distinguishing the strength of exchanges during collisions. In acetone, CHCl$_3$, and benzene, $k_{ex}\eta$ increases with increasing η, and thus weak exchanges are realized. In toluene, CCl$_4$, and 1-propanol, strong exchanges are realized. As can be expected, those are roughly divided to two groups: weak exchange under $T_1 \gtrsim \tau_c$ and strong exchange under $T_1 < \tau_c$. The T_1 and τ_c values as well as the shielding of the metal by ligands play an important role for determining the strengths of exchanges.

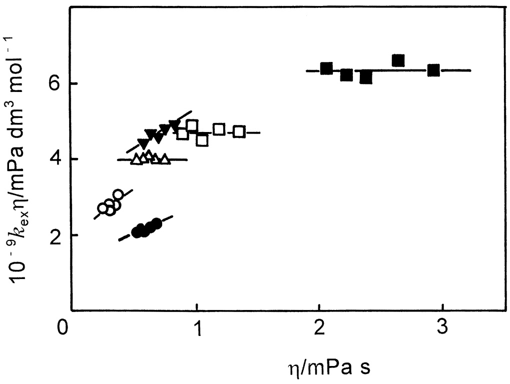

Fig. 2. Relationship between $k_{ex}\eta$ and η for spin exchange of TANONE with [Fe(acac)$_3$] in various solvents: (○) in acetone, (●) in CHCl$_3$, (▼) in benzene, (△) in toluene, (□) in CCl$_4$, and (■) in 1-propanol.

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