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Spin-Exchange Reactions of Nitroxide Radicals with Cobalt and Nickel Complexes

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The rate constants k_{ex} for the spin exchange of nitroxides with various kinds of cobalt(II) and nickel(II) complexes were determined from the EPR line-broadening of nitroxides. The rate constants estimated were in the range of 10^8—10^9 M^{-1} s^{-1} and this reaction was found to be diffusion-controlled. In order to distinguish cases of strong and weak spin exchange, we examined the pressure dependence of the spin exchange between nitroxide and the complexes. It was found that the ligand in the first coordination sphere of the complexes plays an important role for the efficiency of spin exchange. The presence of the coordinated halide ion provides strong exchange, regardless of any screening of the complex's internal atoms by organic molecules. From the pressure dependence of k_{ex}, the J^2f_s values (the exchange integral J and the steric factor f_s) for the spin exchange of nitroxides with cobalt and nickel complexes were estimated to be about 10^{20} s^{-2}. Based on the results, the steric hindrance for the reaction of spin exchange is discussed.

The spin exchange is utilized to study the role of steric hindrance during collisions as well as to measure the rate constant of diffusion collision in solutions. In the previous paper,[2] we have examined the spin exchange between nitroxides in various kinds of solvents, whose viscosities were changed by applying pressure. The usefulness of study for pressure dependence of the spin exchange is as follows: (1) The pressure dependence of the spin-exchange rate makes it possible to segregate cases of strong and weak spin exchange. (2) From the study of pressure dependence, we demonstrated the method for evaluating the steric factor and exchange integral which reflect on the exchange efficiency.[1] The exchange integral provides useful information concerning processes which involve a rearrangement of the spins and the weak overlap of electron orbials: for example, quenching of the triplet state and the outer-sphere electron transfer reactions.

It is recognized that nitroxide radical undergoes an interconversion of spin states with a paramagnetic metal complex upon collision, resulting in line-broadening of EPR spectra.[3] The attractive feature of the spin exchange for the radical-complex systems is to vary the structure of the complex by changing the composition of its first coordination sphere. Since the efficiency of spin exchange is related to the steric hindrance and overlapping of orbitals of colliding particles, shielding of the paramagnetic metal by organic molecules enables us to control the efficiency of spin exchange. Therefore, the spin exchange between nitroxide and complex is suitable for the study of a weak exchange. Such study will afford useful information on exchange interactions.[1]

The materials selected for the present study were complexes of cobalt(II) and nickel(II) ions with relaxation times T_1 short enough to neglect the dipole contribution to line-broadening. In order to obtain further information about the collision rate and the steric hindrance for the spin exchange between nitroxide and the complexes, we have examined the pressure effects on the spin exchange of nitroxide with the complexes in which bulky ligands were introduced. From the pressure effects, the exchange integrals J of the spin exchange for the nitroxide-complex collision have been estimated. Further, we have found that the halide ligands play an important role for the spin exchange, and hence we wish to report on studies that elucidate the role of halide ligands.

Experimental

The following nitroxide radicals were purchased from Aldrich Chemical Company, Inc., and were used as received (Chart 1): 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxyl (TANONE), di-*t*-butyl nitroxide (DTBN), and 10-doxylnonadecane (10-DOXYL). Acetylacetonate complexes and reagent grade cobalt(II) and nickel(II) halides were provided by Aldrich Chemical Company Inc., and were used without further purification. Complex $[Co(NCO)_4]^{2-}$ was prepared according to the method reported by Cotton and Goodgame.[4] 1,4,8,11-Tetraazacyclo-tetradecane (cyclam) was purchased from Lancaster Synthesis, Ltd. and used as received (Chart 1). The host–guest complexes between cyclam and metal ions (cobalt(II) and nickel(II)) were obtained by adding cyclam to a solution of cobalt(II) and nickel(II) halides.[5] The $[Ni(NCO)_2(cyclam)]$ and $[Ni(NCS)_2(cyclam)]$ complexes were formed by adding a 6-fold excess of KNCO and KNCS to the $[NiCl_2(cyclam)]$ solution, respectively: λ_{max} = about 515 nm in a methanol–water mixture. Solvents of reagent grade were used after distillation.

The instrumentation of a high-pressure EPR cell has already

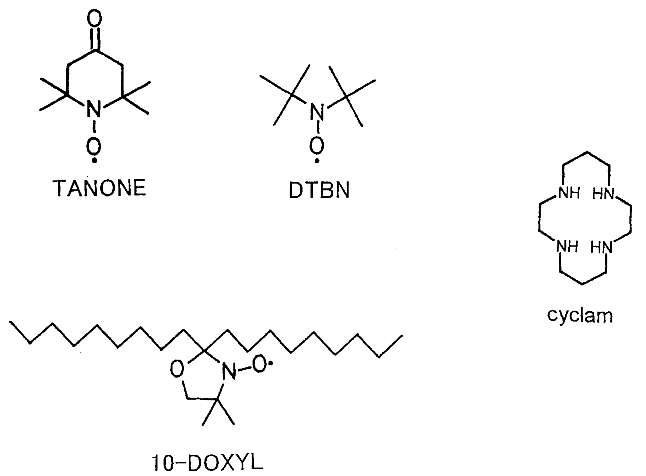

Chart 1.

been described elsewhere.[2)] EPR signals were recorded on a JEOL-FE3XG X-band spectrometer equipped with a 100 kHz field modulation. The concentration of nitroxide radical in all the experiments was selected small (5×10^{-4} M ($=\text{mol dm}^{-3}$)) enough that the influence of the spin exchange between nitroxide radicals could be neglected. The concentrations of cobalt(II) and nickel(II) complexes were varied in the range of 10^{-2} and 10^{-3} M. Sample solutions were deoxygenated by bubbling nitrogen. The peak-to-peak width of the central component of the hyperfine structure of the nitroxide radical was measured at 298 K. The accuracy of the linewidth obtained was $\pm1.5\%$.

Theoretical Background

The rate constant k_{ex} of spin exchange is determined from the line broadening of the nitroxide EPR signal by Eq. 1.

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

where ΔH and ΔH_0 are the linewidth in the presence and absence of spin exchange, respectively. A can be set to $1.52\times10^{7}\ \mathrm{G}^{-1}\,\mathrm{s}^{-1}$ for the spin exchange between nitroxide and transition metal.[7)] The exchange rate constant can be related to the rate constant k_{diff} for a diffusive process by

$$k_{\mathrm{ex}} = Pf_{\mathrm{s}}k_{\mathrm{diff}} \tag{2}$$

where f_{s} denotes the steric factor and P is the probability of a spin exchange upon collision. The spin-lattice relaxations for cobalt(II) and nickel(II) complexes are so rapid that the relaxation time T_1 is less than the collision duration τ_{c} ($T_1 = 1.6\times10^{-13}$ s for cobalt(II) and 4.0×10^{-12} s for nickel(II)).[3,7)] For $T_1 \ll \tau_{\mathrm{c}}$, the P value between nitroxide and the complexes is represented by the formula:[7)]

$$P = \frac{(2/3)J^2s(s+1)T_1\tau_{\mathrm{c}}}{1+(2/3)J^2s(s+1)T_1\tau_{\mathrm{c}}}. \tag{3}$$

Here, J is the exchange integral in a collision and s is the spin of the central metal. For strong exchange ($J^2s(s+1)T_1\tau_{\mathrm{c}} \gg 1$), $P=1$ and thus, $k_{\mathrm{ex}}=f_{\mathrm{s}}k_{\mathrm{diff}}$. For weak exchange ($J^2s(s+1)T_1\tau_{\mathrm{c}} \ll 1$),

$$P = (2/3)J^2s(s+1)T_1\tau_{\mathrm{c}}. \tag{4}$$

According to the Stokes–Einstein–Smoluchowski equation,[8)] the bimolecular diffusion constant for collision is given by

$$k_{\mathrm{diff}} = \frac{2000RT}{3\eta}\frac{(r_{\mathrm{A}}+r_{\mathrm{B}})^2}{r_{\mathrm{A}}r_{\mathrm{B}}}, \tag{5}$$

where r_{A} and r_{B} denote the effective hydrodynamic radius of radical and complex, respectively. η (Pa s) is the viscosity coefficient of the medium. According to Plachy and Kivelson,[9)] the collision time τ_{c} can be given by Eq. 6:

$$\tau_{\mathrm{c}} = \frac{2\pi\eta\lambda^2}{kT}\frac{r_{\mathrm{A}}r_{\mathrm{B}}}{(r_{\mathrm{A}}+r_{\mathrm{B}})}, \tag{6}$$

$$\lambda = (\rho_0/\rho)^{1/3}\lambda_0, \tag{7}$$

where λ and ρ are the jump length and the liquid density, respectively. λ_0 and ρ_0 represent them at the freezing point. By combining Eqs. 2, 4, 5, 6, and 7, we obtain Eq. 8.

$$\frac{k_{\mathrm{diff}}}{k_{\mathrm{ex}}} = \frac{3kT(r_{\mathrm{A}}+r_{\mathrm{B}})}{4s(s+1)T_1\pi\lambda_0^2\rho_0^{2/3}r_{\mathrm{A}}r_{\mathrm{B}}J^2f_{\mathrm{s}}}\frac{\rho^{2/3}}{\eta}. \tag{8}$$

Results and Discussion

Spin Exchange between Nitroxide and Tetrahedral Complex. It is recognized that cobalt(II) chloride and bromide form the tetrahedral complexes ([$CoCl_2(ROH)_2$] and [$CoBr_2(ROH)_2$]) in alcohols: $\lambda_{\max}$=about 660 nm.[3)] Figure 1 shows the dependence of the cobalt complex concentration on the EPR signals of nitroxide radical. The linewidth ΔH for the EPR signal of nitroxide radical increased linearly with the concentration of complexes, in accordance with Eq. 1. From the line-broadening in EPR spectra, the spin-exchange rate constants k_{ex} were estimated by means of Eq. 1, and are given in Table 1. The k_{ex} values are in the range of 10^8—$10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and decrease with increasing pressure. As expected from Eq. 5, the pressure effect can be interpreted in terms of viscosity dependence of k_{ex}, suggesting that diffusion-controlled processes are involved. From the pressure effect on k_{ex}, the activation volumes $\Delta V^{\ddagger}_{\mathrm{ex}}$ at 1 bar were estimated according to the following equations, and are given in Table 2:

$$\ln k_{\mathrm{ex}} = ap^2 + bp + c, \tag{9}$$

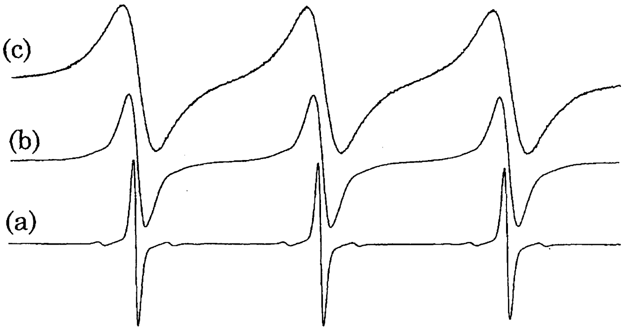

Fig. 1. EPR spectra of TANONE in chloroform; (a) 5×10^{-4} M TANONE, (b) 5×10^{-4} M TANONE and 0.5×10^{-2} M [$CoBr_2(C_3H_7OH)_2$], (c) 5×10^{-4} M TANONE and 1.7×10^{-2} M [$CoBr_2(C_3H_7OH)_2$].

Table 1. Rate Constants for the Spin Exchange of Nitroxide with Tetrahedral Cobalt Complexes

Radicals	Complexes	Solvent	$10^{-8}k_{ex}/M^{-1}s^{-1}$					
		P/bar	1	98	196	343	490	637
TANONE	$[CoCl_2(C_3H_7OH)_2]$	1-Propanol	14.2	13.3	12.2	11.1	10.2	9.00
	$[CoCl_2(C_4H_9OH)_2]$	1-Butanol	9.49	8.85	8.46	6.63	6.39	5.79
	$[CoCl_2((CH_3)_2CHCH_2OH)_2]$	2-Methyl-1-propanol	9.76	8.62	8.25	9.76	5.81	5.23
	$[CoCl_2(C_5H_{11}OH)_2]$	1-Pentanol	7.52	7.01	6.93	6.43	5.60	4.94
	$[CoBr_2(C_3H_7OH)_2]$	1-Propanol	17.5	16.3	14.8	13.9	12.4	11.4
	$[Co(NCO)_4]^{2-}$	Chloroform	3.17	3.12	3.08	3.00	2.71	2.83
10-DOXYL	$[CoCl_2(C_3H_7OH)_2]$	1-Propanol	4.22	4.08	4.08	3.99	3.90	3.83

Table 2. Activation Volumes for the Spin Exchange of Nitroxide with Tetrahedral Cobalt Complexes

Radicals	Complexes	Solvent	$\varkappa_T RT$	$10^{10}r_{Complex}$	$\Delta V^{\ddagger}_{diff}$	$\Delta V^{\ddagger}_{ex}$	$\Delta\Delta V^{\ddagger}$ [a]	$10^{-20}J^2f_s$
				m	$cm^3 mol^{-1}$	$cm^3 mol^{-1}$	$cm^3 mol^{-1}$	s^{-1}
TANONE	$[CoCl_2(C_3H_7OH)_2]$	1-Propanol	2.2	6.1	16.4	15.1	−1.3	—f_s=0.43
	$[CoCl_2(C_4H_9OH)_2]$	1-Butanol	1.7	6.3	20.7	24.4	3.7	—f_s=0.35
	$[CoCl_2((CH_3)_2CHCH_2OH)_2]$	2-Methyl-1-propanol	2.4	6.6	20.4	25.0	4.6	—f_s=0.45
	$[CoCl_2(C_5H_{11}OH)_2]$	1-Pentanol	2.0	6.6	9.5	4.4	−5.1	—f_s=0.45
	$[CoBr_2(C_3H_7OH)_2]$	1-Propanol	2.2	6.2	16.4	16.6	0.2	—f_s=0.52
	$[Co(NCO)_4]^{2-}$	Chloroform	2.3	5.8	9.9	1.1	−8.9	1.8
10-DOXYL	$[CoCl_2(C_3H_7OH)_2]$	1-Propanol	2.2	6.1	16.4	1.3	−15.1	13(0.93)[b]

a) $\Delta\Delta V^{\ddagger}=\Delta V^{\ddagger}_{ex}-\Delta V^{\ddagger}_{diff}$. b) Calculated J^2f_s-value.

$$\Delta V^{\ddagger}_{ex} = -RT(\partial \ln k_{ex}/\partial p)_T - \varkappa_T RT \tag{10}$$

where the notations have their usual meanings. $\varkappa_T$ is the isothermal compressibility of the medium.[10)] Using available η–p data,[10)] the activation volumes $\Delta V^{\ddagger}_{diff}$ for the diffusive process have been calculated from Eq. 11.

$$\begin{aligned}\Delta V^{\ddagger}_{diff} &= -RT(\partial \ln k_{diff}/\partial p)_T - \varkappa_T RT \\ &= RT(\partial \ln \eta/\partial p)_T - \varkappa_T RT\end{aligned} \tag{11}$$

When the diffusive process alone is operating for the spin-exchange reaction, $\Delta V^{\ddagger}_{ex}$ is to be equivalent to $\Delta V^{\ddagger}_{diff}$, as expected from Eqs. 2, 10, and 11. However, the small difference between $\Delta V^{\ddagger}_{ex}$ and $\Delta V^{\ddagger}_{diff}$ was observed for the spin exchange between TANONE and $[CoCl_2(ROH)_2]$ in alcohols. For the nitroxide radicals in alcohol, specific solvation, such as hydrogen bonds, is considered to be operative. When specific solute–solvent interaction is involved, an encounter complex in which solute molecules are separated by one or two solvent molecules may be formed as intermediate of the association reaction. Previously, we reported that the formation of the encounter complex gives the small $\Delta\Delta V^{\ddagger}$ values, indicating the existence of the encounter complex.[11)] After the formation of encounter complex, the solvent molecules trapped in the encounter complex are released, and a collision complex, in which spin exchange takes place, is formed. On one hand, the large difference ($\Delta\Delta V^{\ddagger}$) was observed for the spin exchanges of the TANONE–$[Co(NCO)_4]^{2-}$ and 10-DOXYL–$[CoCl_2(C_3H_7OH)_2]$ systems, strongly suggesting that the spin exchanges are weak.

We have expected that screening of the cobalt atom by organic molecules leads to a significant decrease in the rate constants of spin exchange. The k_{ex} value seems to decrease with increasing bulkiness of alkyl group of alcohols (Table 1). However, this can not be simply explained in terms of the screening effects. Equation 5 predicts that the exchange rate constant decreases with increasing solvent viscosity. The ratio of exchange rate k_{ex}(in 1-propanol)/k_{ex}(in 1-pentanol)=1.9 is compared with that of solvent viscosity η(1-pentanol)/η(1-propanol)=2.0. This supports the idea that the retardation of the exchange rate is ascribed to an increase in the solvent viscosity. In this case, the screening effects are not operating effectively.

Another equation is obtained by the combination of Eqs. 2 and 5:

$$k_{ex}\eta \propto P. \tag{12}$$

We reported that the probability P for weak exchange in susceptible to η, and $k_{ex}\eta$ increases with η. On the other hand, for strong exchange, $P \approx 1$ holds, and $k_{ex}\eta$ is independent of η.[1)] In Fig. 2, $k_{ex}\eta$ is plotted against η for the spin exchange between TANONE and tetrahedral complexes. The $k_{ex}\eta$ value for the spin exchange between TANONE and $[CoCl_2(ROH)_2]$ is found to be independent of η. It is to be noted that the spin exchange of $[CoCl_2(ROH)_2]$ shows the aspect of strong exchange. The role of chlorine ligands for spin exchange is important. The presence of a chlorine ligand may provide the strong exchange. The high efficiency due to the chlorine atom for spin exchange can be accounted for by a superexchange mechanism involving spin transfer from metal ion to ligand.[13)] The unpaired spin on the ligand is usually interpreted as being in a 2p orbit on a chlorine atom. When a chloride ion and NO group chance to be in contact, the spin exchange may occur. The similar results were obtained for the spin exchange of $[CoBr_2(C_3H_7OH)_2]$

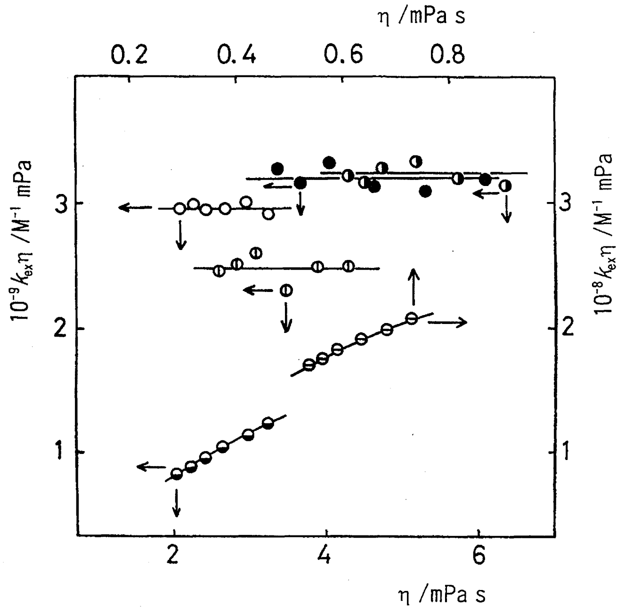

Fig. 2. Relationship between $k_{ex}\eta$ and η for spin exchange of TANONE with tetrahedral complexes: (○) TANONE–[$CoCl_2(C_3H_7OH)_2$] system, (⦶) TANONE–[$CoCl_2(C_4H_9OH)_2$] system, (●) TANONE–[$CoCl_2((CH_3)_2CHCH_2OH)_2$] system, (◑) TANONE–[$CoCl_2(C_5H_{11}OH)_2$] system, (⊖) TANONE–[$Co(NCO)_4$]$^{2-}$ system, and (◒) 10-DOXYL–[$CoCl_2(C_3H_7OH)_2$] system.

complex having bromine ligands. To clarify the situation, we have examined the spin exchange of TANONE with tetrahedral [$Co(NCO)_4$]$^{2-}$ complex, in which no chloride ion is contained in the first coordination sphere. As can be seen in Table 2 and Fig. 2, the large difference between $\Delta V^{\ddagger}_{ex}$ and $\Delta V^{\ddagger}_{diff}$ is observed, and $k_{ex}\eta$ increases obviously with increasing η for the spin exchange of [$Co(NCO)_4$]$^{2-}$. These findings correspond to the case of weak exchange. In this case, steric restriction screened by NCO ligands undergoes weak exchange.

The steric circumstance around the $\rangle$N–O· group of 10-DOXYL radical having long-chain is severe. We reported that the spin exchange between 10-DOXYL radicals is weak due to steric reasons.[1] For the spin exchange between 10-DOXYL and [$CoCl_2(C_3H_7OH)_2$], the large difference $\Delta V^{\ddagger}_{ex}-\Delta V^{\ddagger}_{diff}$ and viscosity dependence of $k_{ex}\eta$ were observed (Table 2 and Fig. 2). The same trend is observed for the spin exchange between TANONE and [$Co(NCO)_4$]$^{2-}$ and these are different from the spin exchange between TANONE and [$CoCl_2(ROH)_2$]. This observation for 10-DOXYL and [$CoCl_2(C_3H_7OH)_2$] points to weak exchange, caused by the steric hindrance around the $\rangle$N–O· group.

In weak exchange, Eq. 8 shows that a plot of k_{diff}/k_{ex} against $\rho^{2/3}\eta^{-1}$ gives a straight line with the slope $3kT(r_A+r_B)/4s(s+1)T_1\pi\lambda_0^2\rho_0^{2/3}r_Ar_BJ^2f_s$ and passes through the origin. Representative plots are shown in Fig. 3. From the slope of the plots, the J^2f_s values can be estimated. It is difficult to estimate numerical values of r and λ_0 exactly. The radius (r= 0.32 nm) of di-*t*-butylnitroxide (DTBN), estimated by Plachy and Kivelson,[9] was used as the standard,

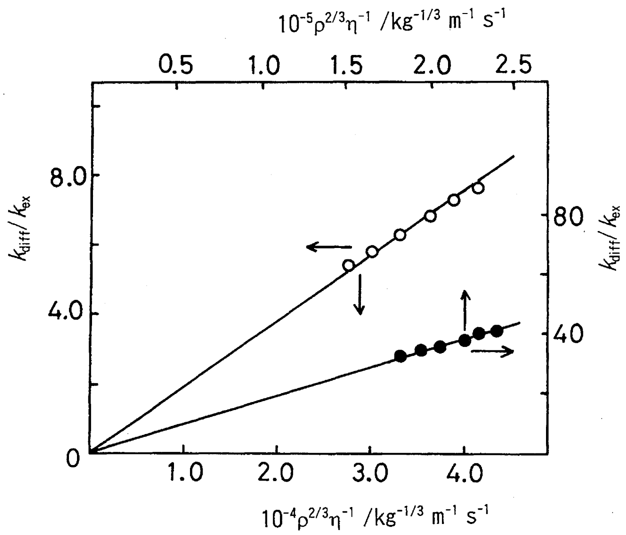

Fig. 3. Plots of k_{diff}/k_{ex} against $\rho^{2/3}\eta^{-1}$ for spin exchanges of tetrahedral complexes: (○) the 10-DOXYL and [$CoCl_2(C_3H_7OH)_2$] system and (●) the TANONE and [$Co(NCO)_4$]$^{2-}$ system.

and r and λ_0 values were estimated by referring the size of their Corey–Pauling–Koltum models (CPK): r= 0.39 nm for TANONE and 0.64 nm for 10-DOXYL. λ_0= 0.51 nm for 1-propanol and 0.57 nm for chloroform. The r values of cobalt complexes are given in Table 2. The ρ_0 values are available as follows: ρ_0= 0.974 g cm^{-3} for 1-propanol and 1.644 g cm^{-3} for chloroform.[10,14] After these numerical values were substituted into Eq. 8, the J^2f_s values were estimated to be 1.3×10^{21} s^{-2} for the 10-DOXYL–[$CoCl_2(C_3H_7OH)_2$] system, and 1.8×10^{20} s^{-2} for the TANONE–[$Co(NCO)_4$]$^{2-}$ system. A discussion on the J^2f_s values is given below.

Spin Exchange of Nitroxide with Octahedral Complex. A change in the structure of the complex may reflect on the effectiveness for spin exchange. The cobalt and nickel ions are incorporated into cyclam, and the geometry of the host–guest complexes is hexacoordinated.[5] The steric restriction around the paramagnetic metal in the cyclam complex is most severe for the present spin-exchange reaction. It is instructive to examine the role of chlorine ligands through the spin exchange of the cyclam complex. The rate constants observed for spin-exchange reaction of nitroxides with octahedral complexes (acetylacetonate and cyclam complexes) are given in Table 3. Using the data in Table 3, $\Delta V^{\ddagger}_{ex}$ and $\Delta\Delta V^{\ddagger}$ (= $\Delta V^{\ddagger}_{ex}-\Delta V^{\ddagger}_{diff}$) were calculated, and the values are listed in Table 4. When the data in Tables 3 and 4 are inspected, we notice some interesting points: (1) the $\Delta\Delta V^{\ddagger}$ values are divided roughly into two groups: $\Delta\Delta V^{\ddagger}\fallingdotseq 0$ and $\Delta\Delta V^{\ddagger}\fallingdotseq -10$ cm^3 mol^{-1}. These correspond to the cases of strong and weak exchanges, as exemplified by the spin exchanges of nitroxides.[2] (2) The activation volumes indicate that the spin exchanges of TANONE with acetylacetonate complexes are weak exchange. (3) The framework of DTBN is smaller than that of TANONE. The entrance of nitroxide radical into the coordination sphere is expected to increase the efficiency of spin exchange. However, the exchange rate

Table 3. Rate Constants for the Spin Exchange of Nitroxides with Octahedral Complexes

Radicals	Complexes	Solvent	$10^{-8}k_{\mathrm{ex}}/\mathrm{M^{-1}\,s^{-1}}$					
		P/bar	1	98	196	343	490	637
TANONE	$[\mathrm{Co(acac)_2(C_5H_5N)_2}]$[a)]	1-Propanol[b)]	3.06	3.03	3.00	2.97	2.94	2.87
TANONE	$[\mathrm{Co(acac)_2(C_5H_5N)_2}]$	Chloroform[c)]	1.88	1.87	1.87	1.86	1.83	1.79
DTBN	$[\mathrm{Co(acac)_2(C_5H_5N)_2}]$	Chloroform[c)]	1.15	1.19	1.12	1.10	1.08	1.05
TANONE	$[\mathrm{Ni(acac)_2(C_5H_5N)_2}]$	1-Propanol[b)]	6.54	6.45	6.43	6.19	5.91	5.71
TANONE	$[\mathrm{Ni(acac)_2(C_5H_5N)_2}]$	Chloroform[c)]	5.03	5.00	4.97	4.96	4.92	4.89
TANONE	$[\mathrm{Ni(acac)_2(C_6H_5NH_2)_2}]$	Chloroform[d)]	7.22	7.14	7.04	6.99	6.90	6.67
DTBN	$[\mathrm{Ni(acac)_2(C_5H_5N)_2}]$	Chloroform[c)]	2.46	2.40	2.37	2.22	2.10	2.07
TANONE	$[\mathrm{CoCl_2(cyclam)}]$	1-Propanol	15.3	14.6	12.8	12.5	10.8	9.92
TANONE	$[\mathrm{NiCl_2(cyclam)}]$	Chloroform	34.6	33.1	31.2	30.1	28.5	25.7
TANONE	$[\mathrm{NiBr_2(cyclam)}]$	Chloroform	42.6	41.9	39.5	35.5	34.3	31.7
TANONE	$[\mathrm{Ni(NCS)_2(cyclam)}]$	$\mathrm{CH_3OH{-}H_2O}$[e)]	25.7	25.2	25.0	24.0	23.2	22.5
TANONE	$[\mathrm{Ni(NCO)_2(cyclam)}]$	$\mathrm{CH_3OH{-}H_2O}$[e)]	22.8	22.5	22.4	21.9	21.3	20.5

a) acac: Acetylacetonate. b) 1-Propanol+3%$\mathrm{C_5H_5N}$. c) $\mathrm{CHCl_3}$+3%$\mathrm{C_5H_5N}$. d) $\mathrm{CHCl_3}$+3%$\mathrm{C_6H_5NH_2}$. e) mol fraction $x = 0.5$.

Table 4. Activation Volumes for the Spin Exchange of Nitroxides with Octahedral Complexes

Radicals	Complexes	Solvent	$10^{10}r_{\mathrm{Complex}}$	$\Delta V^{\ddagger}_{\mathrm{ex}}$	$\Delta\Delta V^{\ddagger}$	$10^{-20}J^2f_{\mathrm{s}}$
			m	$\mathrm{cm^3\,mol^{-1}}$	$\mathrm{cm^3\,mol^{-1}}$	$\mathrm{s^{-1}}$
TANONE	$[\mathrm{Co(acac)_2(C_5H_5N)_2}]$	1-Propanol	8.0	−0.2	−16.6	8.6 (0.72)[c)]
TANONE	$[\mathrm{Co(acac)_2(C_5H_5N)_2}]$	Chloroform	8.0	−0.7	−10.6	4.6
DTBN	$[\mathrm{Co(acac)_2(C_5H_5N)_2}]$	Chloroform	8.0	−0.2	−10.1	6.0
TANONE	$[\mathrm{Ni(acac)_2(C_5H_5N)_2}]$	1-Propanol	8.0	3.2	−13.2	1.7 (0.14)[c)]
TANONE	$[\mathrm{Ni(acac)_2(C_5H_5N)_2}]$	Chloroform	8.0	−1.2	−11.1	0.92
TANONE	$[\mathrm{Ni(acac)_2(C_6H_5NH_2)_2}]$	Chloroform	8.0	0.5	−9.4	1.5
DTBN	$[\mathrm{Ni(acac)_2(C_5H_5N)_2}]$	Chloroform	8.0	0.3	−9.6	0.93
TANONE	$[\mathrm{CoCl_2(cyclam)}]$	1-Propanol		15.7	−0.7	— $f_{\mathrm{s}} = 0.47$
TANONE	$[\mathrm{NiCl_2(cyclam)}]$	Chloroform		10.6	0.6	— $f_{\mathrm{s}} = 0.28$
TANONE	$[\mathrm{NiBr_2(cyclam)}]$	Chloroform		10.4	0.4	— $f_{\mathrm{s}} = 0.34$
TANONE	$[\mathrm{Ni(NCS)_2(cyclam)}]$	$\mathrm{CH_3OH{-}H_2O}$[a)]	6.2	0.9	−4.3	13[b)]
TANONE	$[\mathrm{Ni(NCO)_2(cyclam)}]$	$\mathrm{CH_3OH{-}H_2O}$[a)]	5.8	0.1	−5.1	12[b)]

a) $\Delta V^{\ddagger}_{\mathrm{diff}} = 5.2\ \mathrm{cm^3\,mol^{-1}}$ (mole fraction $x = 0.5$).[14)] b) $\rho_0 = 0.97\ \mathrm{g\,cm^{-3}}$.[15)] c) Calculated J^2f_{s}-value.

of DTBN with acetylacetonate complexes is small compared with that of TANONE, though the reason is not clear. The spin exchange of DTBN is also weak. (4) The exchange rate of nickel-acetylacetonate complexes having the pyridine ligand is smaller than that having the aniline ligand. Similar results have been reported by Skubnevskaya and Molin.[3)] They suggested that this decrease reflects a transition from strong to weak. The activation volume observed, however, indicates that the spin exchange of the aniline complex, as well as the pyridine complex, is weak. In aniline, the spin density is delocalized through the π-bonds of the aromatic ring. Unlike aniline, pyridine is a σ electron ligand in complex with $[\mathrm{Ni(acac)_2}]$, and the spin density attenuates as the distance from the metal increases.[3,6)] This accounts for the difference in the rate constants of spin exchange. (5) For the spin exchange of cyclam complexes containing $\mathrm{Br^-}$ and $\mathrm{Cl^-}$ ligands, the $\Delta V^{\ddagger}_{\mathrm{ex}}$ values are comparable to the $\Delta V^{\ddagger}_{\mathrm{diff}}$ ones. This is some evidence in favor of strong exchange. (6) The spin-exchange rate of nickel-cyclam complex involving the $\mathrm{Cl^-}$ ligand is smaller than that involving $\mathrm{Br^-}$.

Figure 4 shows the representative plots of $k_{\mathrm{ex}}\eta$ against η for the spin exchanges of octahedral complexes with TANONE. As discussed above, the viscosity dependence of $k_{\mathrm{ex}}\eta$ makes it possible to segregate cases of strong and weak spin exchange. For $[\mathrm{Ni(NCS)_2(cyclam)}]$ and $[\mathrm{Ni(NCO)_2(cyclam)}]$ complexes, the $k_{\mathrm{ex}}\eta$ value increases obviously with η, as shown in Fig. 4. This suggests that the spin exchange is weak, though the difference $\Delta V^{\ddagger}_{\mathrm{ex}} - \Delta V^{\ddagger}_{\mathrm{diff}}$ is somewhat small. The $\Delta V^{\ddagger}_{\mathrm{diff}}$ value predicted for most solvents is of the order of 12—25 $\mathrm{cm^3\,mol^{-1}}$.[2)] However, the $\Delta V^{\ddagger}_{\mathrm{diff}}$ value (5.2 $\mathrm{cm^3\,mol^{-1}}$) for a mixture of $\mathrm{CH_3OH{-}H_2O}$ is very small. This may lead to the small $|\Delta V^{\ddagger}_{\mathrm{ex}} - \Delta V^{\ddagger}_{\mathrm{diff}}|$ value in the $\mathrm{CH_3OH{-}H_2O}$ mixture. On the other hand, the spin exchange of the cyclam complex containing $\mathrm{Br^-}$ and $\mathrm{Cl^-}$ is strong. Though the degrees of shielding of the paramagnetic metal in cyclam complexes are most severe, the presence of halide ion in the first coordination sphere provides strong spin exchange through the superexchange interaction, in analogy with the case of the tetrahedral complex. The spin exchange may be achieved by contacts of the N–O group with the coordinated halide ion. The difference between the spin-exchange rates of complexes containing the $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ ligands can be interpreted as follows. Owen

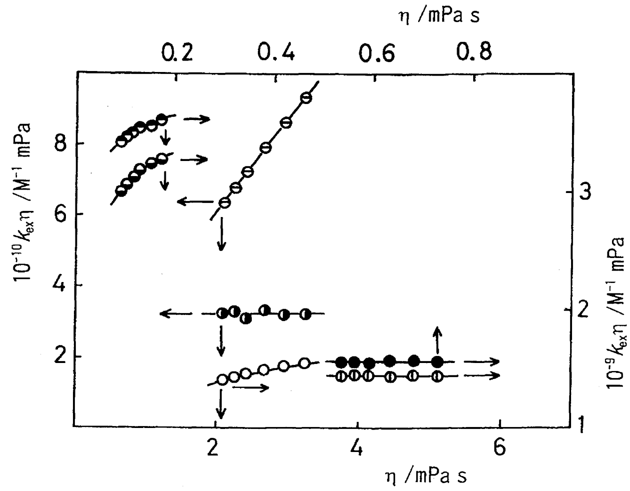

Fig. 4. Relationship between $k_{ex}\eta$ and η for spin exchange of TANONE with octahedral complexes: (⊖) [Co(acac)$_2$(C$_5$H$_5$N)$_2$] in 1-propanol, (○) [Ni(acac)$_2$(C$_5$H$_5$N)$_2$] in 1-propanol, (◑) [CoCl$_2$(cyclam)] in 1-propanol, (●) [NiCl$_2$(cyclam)] in chloroform, (⦶) [NiBr$_2$(cyclam)] in chloroform, (◓) [Ni(NCS)$_2$(cyclam)] in CH$_3$OH–H$_2$O, and (◒) [Ni(NCO)$_2$(cyclam)] in CH$_3$OH–H$_2$O.

and Thornley[13] suggested that it is easier for electrons to be pulled into the central ion as the electronegativity of the ligand decreases. Spin transfer may increase as one moves from Cl$^-$ to Br$^-$, which is responsible for the difference in the exchange rates. In any case, the presence of the halide ligand is deeply correlated to the collision efficiency for spin exchange.

The J^2f_s values can be estimated according to Eq. 8. The representative plots for the spin exchange of the octahedral complexes with TANONE and DTBN are shown in Fig. 5.

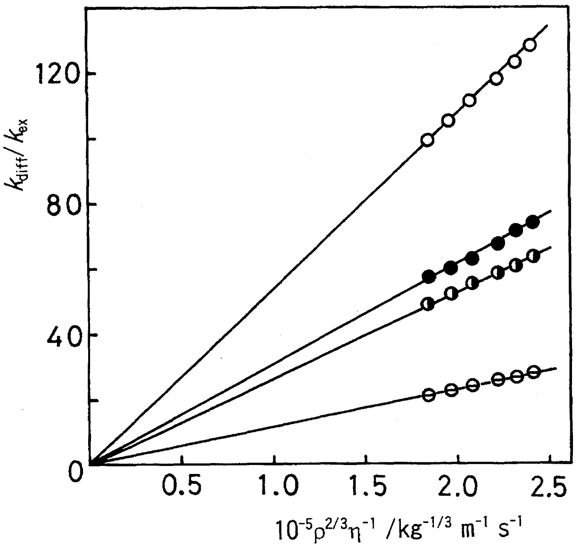

Fig. 5. Plots of k_{diff}/k_{ex} against $\rho^{2/3}\eta^{-1}$ for spin exchanges of octahedral complexes in chloroform: (○) DTBN–[Co(acac)$_2$(C$_5$H$_5$N)$_2$] system, (●) TANONE–[Co(acac)$_2$(C$_5$H$_5$N)$_2$] system, (◑) DTBN–[Ni(acac)$_2$(C$_5$H$_5$N)$_2$] system, and (⊖) TANONE–[Ni(acac)$_2$(C$_5$H$_5$N)$_2$] system.

From the linear relation, the J^2f_s values were estimated and are given in Table 4. The estimated J^2f_s values are of the order of 10^{20} s^{-2}. The J^2f_s values for the octahedral complexes are comparable to those for the tetrahedral complexes.

When the spin exchange in alcohols involves the formation of an encounter complex, the apparent rate constant k_{ex} observed for the spin exchange can be expressed by[11]

$$k_{ex} = K_1 k_{ex}^{spin}, \tag{13}$$

$$K_1 = \frac{4\pi L a^3}{3000}. \tag{14}$$

The association constant K_1 for the formation of the encounter complex can be approximately given by Eq. 14.[16] L is the Avogadro number. The rate constant k_{ex}^{spin} denotes the formation rate of a collision complex, in which the spin exchange takes place. Assuming that nitroxide and the metal complex are separated by one solvent molecule, a is the effective distance of the closest approach between nitroxide and the metal complex. Though an approximation and the numerical choice for the effective radii greatly affect the K_1 value, we tentatively estimated the K_1 values in 1-propanol. Using the effective radii r= 0.39 nm for TANONE,[1] r= 0.61 nm for 10-DOXYL,[1] r= 0.80 nm for [Co(acac)$_2$(C$_5$H$_5$N)$_2$], r= 0.61 nm for [CoCl$_2$(C$_3$H$_7$OH)$_2$], and 2r= 0.51 nm for 1-propanol, one can calculate the equilibrium constants K_1 in 1-propanol to be 14 M^{-1} for the 10-DOXYL–[CoCl$_2$(C$_3$H$_7$OH)$_2$] system and 12 M^{-1} for the TANONE–[Co(acac)$_2$(C$_5$H$_5$N)$_2$] system. Using the k_{ex}^{spin} values estimated from Eq. 13 and the K_1-values, we calculated the J^2f_s values for the spin exchange in 1-propanol according to Eq. 8. These are given in Tables 2 and 4. It can be seen that the calculated J^2f_s valves are decreased substantially. As expected from Eqs. 2 and 4, the k_{ex} value is proportional to the J^2f_s value. The apparent spin exchange rate in the process accompanying the encounter-complex formation overestimates the efficiency of exchange.

As suggested above, when halide ligands are not involved in the first coordination sphere, the spin exchange of nitroxide with the complex is weak, and shielding of the paramagnetic metal by organic molecules is effective for the spin exchange. However, shielding of the paramagnetic metal in the complex having halide ligands is not effective due to the superexchange interaction, regardless of the complex structure. In this case, the spin exchange is strong, and $p \approx 1$ must hold ($J^2s(s+1)T_1\tau_c \gg 1$, Eq. 4). From Eq. 2, the f_s values can be calculated, and these are given in Tables 3 and 4. The steric factor f_s is introduced into the exchange rate constant to take into account the mutual orientations of colliding two particles. The f_s values (0.3—0.5) estimated above are compared with those for the spin exchange of nitroxide radicals,[1] which is responsible for the similarity of the collision efficiency.

The J^2f_s values in Tables 3 and 4 reflect the efficiency of the spin exchange. It can be safely considered that the small f_s-value for the spin exchange of nitroxide with complexes having no halide ligands is caused by the steric hindrance. We reported the small f_s value

(0.16) for the spin exchange of 10-DOXYL radicals having the steric circumstance around the $\rangle$N–O· group. If the numerical value f_s = 0.16 is substituted into the $J^2 f_s$ values, we can estimate the value to be $J = 2.4 \times 10^{10}$ s^{-1} for 10-DOXYL–[CoCl$_2$(C$_3$H$_7$OH)$_2$] in 1-propanol, 3.4×10^{10} s^{-1} for TANONE–[Co(NCO)$_4$]$^{2-}$ in chloroform, 2.1×10^{10} s^{-1} for TANONE–[Co(acac)$_2$(C$_5$H$_5$N)$_2$] in 1-propanol, 5.4×10^{10} s^{-1} for TANONE–[Co(acac)$_2$(C$_5$H$_5$N)$_2$] in chloroform, and 6.1×10^{10} s^{-1} for DTBN–[Co(acac)$_2$(C$_5$H$_5$N)$_2$] in chloroform. The exchange integrals for a radical-complex collision is somewhat smaller than for a radical–radical collision (J = 5—10×10^{10} s^{-1}).[1] The J value can be regarded as being a measure of the distance between the colliding particles in a solvent cage. If one judges from the shielding of a paramagnetic metal, the above estimation could be regarded as reasonable. The $J^2 f_s$ values of nickel complexes seem to be somewhat small compared to those of cobalt complexes. Since the ionic radius of nickel is smaller than that of cobalt, it is likely that the nickel complex causes larger screening effects, which gives the small f_s-value.

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