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ESR Studies at High-Pressure. IV.[1) Spin-Exchange Reactions of Various Types of Nitroxides in Some Low-Viscosity Solvents

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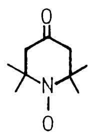
The rate constants (k_{ex}) for the spin exchange of various types of nitroxides were determined from the concentration dependence of the ESR line-broadening. The exchange integral (J) and the steric factor (f_s) for the spin exchange were estimated from the pressure dependence of k_{ex}. The estimated J-values are about 10^{11} s^{-1} and are almost independent of the radical species. For nitroxides having -OH or -NH$_2$ in acetone and nitroxides having long-chain in acetone and toluene, the f_s-values are about 0.3, while for other nitroxides in hexane and pentane, the f_s-values are about 0.5. The results are discussed in terms of the solute–solvent interaction as well as the steric effect.

The spin exchange is an interconversion of the spin states of paramagnetic species upon collison. Studying the spin exchange is informative for binary collisions in solution.[2) Kivelson[3) theoretically treated the dependence of the collision efficiency for spin exchange on the exchange integral (J) and the collision time (τ_1). The exchange integral in the spin exchange affords useful information concerning processes which involve a rearrangement of the spins and the weak overlap of electron orbitals, e.g., quenching of the triplet state and the outer-sphere electron transfer reactions.

The rate constants (k_{ex}) can be determined not only from the decay of the electron spin echo signals, but also from the ESR line-broadening, which can be measured with the help of a routine ESR spectrometer. In previous studies[1) we determined the rate of the spin exchange of a few nitroxides from the line broadening in acetone and hexane, whose viscosities were changed by applying some pressures (p). We pointed out that the exchange integral (J) and steric factor (f_s) for the spin exchange of nitroxide radicals can be estimated from the pressure dependence of the rate constants in low-viscosity solvents.

The present work was initiated in order to obtain further information concerning the collision rates, the steric hindrance, and the exchange integral by using various types of nitroxides.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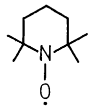
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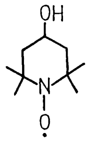
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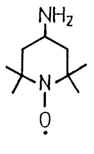
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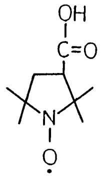
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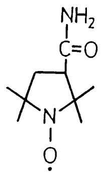
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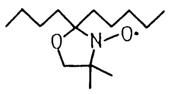
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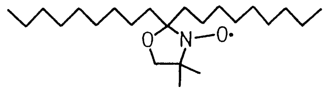

10-DOXYL

Experimental

The following nitroxide radicals were purchased from Aldrich Chemical Company, Inc., and were used without further purification. The solvents were of guaranteed grade and were used after purification in the usual manner. The high-pressure technique and procedures for ESR measurements were almost the same as those described elsewhere.[4) ESR signals were recorded on a JEOL JES-FE3XG ESR spectrometer with a 100 kHz field modulator. Sample solutions (10^{-3}—10^{-2} mol dm^{-3}) were deoxygenated by bubbling nitrogen. The peak-to-peak width of the central signal of the nitroxides was measured at 298 K within a precision of ±1.5%.

Results

The second-order rate constant (k_{ex}) for the spin exchange of various nitroxide radicals was calculated in terms of the concentration dependence of line broadening by the following equation:[2)

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

where ΔH and ΔH_0 are the linewidths in the presence and absence of the spin exchange, respectively. For nitroxide radicals, A can be set to 2.28×10^8 mT^{-1} s^{-1};[2) C is the radical concentration. The rate constants (k_{ex}) at various pressures and in various solvents are given in

Table 1. Rate Constants for the Spin Exchange of Nitroxide Radicals at Various Pressures and at 298 K

Solvent	Radical	$10^{-9}\,k_{\mathrm{ex}}{}^{\mathrm{a)}}/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ $(10^{-9}\,k_{\mathrm{diff}})^{\mathrm{b)}}$					
		p/MPa					
		0.1	9.8	19.6	34.3	49.0	63.7
Acetone	TANONE[c]	8.07	7.79	7.44	7.04	6.69	6.38
	TEMPO[c]	7.78	7.41	7.03	6.56	6.21	5.85
	TANOL	6.42	6.10	5.84	5.49	5.08	4.79
	Amino-TEMPO	5.82	5.49	5.18	4.74	4.43	4.14
	Carboxy-PROXYL	5.73	5.35	5.10	4.71	4.42	4.09
	Carbamoyl-PROXYL	5.78	5.47	5.25	4.86	4.61	4.29
	5-DOXYL	5.47	5.20	4.92	4.68	4.40	4.28
	10-DOXYL	4.14	3.95	3.74	3.48	3.26	3.08
		(23.2)	(21.7)	(20.3)	(18.6)	(17.1)	(15.9)
Hexane	TANONE[c]	11.5	10.8	10.3	9.28	8.54	7.92
	TEMPO	10.3	9.80	9.15	8.22	7.58	7.08
	TANOL	10.7	10.2	9.43	8.62	7.69	6.97
	Amino-TEMPO	8.94	8.33	7.93	7.18	6.59	5.98
		(22.3)	(20.1)	(18.3)	(16.1)	(14.3)	(13.0)
Hexane/Ethanol[d]	TANOL	5.57	5.06	4.89	4.40	3.92	3.65
Pentane	TANONE	13.6	12.5	11.9	10.9	9.91	9.23
	TEMPO	10.9	10.4	9.63	8.63	7.90	7.16
	TANOL	12.3	11.5	10.8	9.85	8.96	8.36
	Amino-TEMPO	11.8	11.3	10.5	9.55	8.99	8.02
		(30.1)	(27.5)	(25.2)	(22.4)	(20.0)	(18.1)
Toluene	10-DOXYL	1.86	1.70	1.61	1.44	1.35	1.23
		(11.9)	(11.1)	(10.4)	(9.36)	(8.50)	(7.75)

a) The reproducibilities of the rate constants were within ±5%. b) The rate constants calculated by Eq. 4 are given in parentheses. c) Cited from Ref. 1. d) Hexane/Ethanol=9/1 (v/v).

Table 2. Activation Volumes, Steric Factors, and Exchange Integrals at 0.1 MPa for the Spin Exchange of Nitroxide Radicals

Solvent	Radical	$\Delta V_{\mathrm{ex}}^{\neq}$ / $\mathrm{cm^3\,mol^{-1}}$	$\Delta\Delta V^{\neq\mathrm{a)}}$ / $\mathrm{cm^3\,mol^{-1}}$	$10^{10}r$ / m	f_{s}	$10^{-10}\,J$ / $\mathrm{s^{-1}}$
Acetone	TANONE[b]	8.7	−7.1	3.9	0.48	6.9
	TEMPO[b]	10.7	−5.1	3.7	0.41	9.5
	TANOL	8.1	−7.7	4.0	0.33	9.2(7.7)[c]
	Amino-TEMPO	12.6	−3.2	4.0	0.27	14(11)[c]
	Carboxy-PROXYL	12.3	−3.5	4.0	0.27	13(10)[c]
	Carbamoyl-PROXYL	10.6	−5.2	4.0	0.30	9.3(7.0)[c]
	5-DOXYL	10.7	−5.1	4.8	0.31	6.1
	10-DOXYL	11.1	−4.7	6.4	0.21	6.1
Hexane	TANONE[b]	12.1	−11.1		0.68	5.3
	TEMPO	14.3	−8.9		0.60	5.8
	TANOL	13.3	−9.9		0.59	6.4
	Amino-TEMPO	11.5	−11.7		0.51	5.6
Hexane/Ethanol[d]	TANOL	14.5	−8.7		0.31	6.1
Pentane	TANONE	12.7	−5.4		0.56	11
	TEMPO	9.2	−8.9		0.42	15
	TANOL	13.0	−5.1		0.50	11
	Amino-TEMPO	9.9	−8.2		0.50	10
Toluene	10-DOXYL	16.6	0.8		0.16	—

a) $\Delta V_{\mathrm{ex}}^{\neq}-\Delta V_{\mathrm{diff}}^{\neq}$. b) Cited from Ref. 1. c) Recalculated J-Value. d) Hexane/Ethanol=9/1 (v/v).

Table 1. From the pressure effects on k_{ex}, the activation volumes ($\Delta V_{\mathrm{ex}}^{\neq}$) at 0.1 MPa were estimated according to the following equations and are given in Table 2:

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

and

$$\Delta V_{\mathrm{ex}}^{\neq} = -RT(\partial \ln k_{\mathrm{ex}}/\partial p)_T - \kappa_T RT. \tag{3}$$

Here, the notations have their usual meanings. The term $\kappa_T RT$ amounts to 2.9 $\mathrm{cm^3\,mol^{-1}}$ for acetone, 3.7 $\mathrm{cm^3\,mol^{-1}}$ for hexane, and 4.5 $\mathrm{cm^3\,mol^{-1}}$ for pentane at 298 K.[5] According to the Smolukowski equation,[6] the second-order rate constant for a diffusion-controlled reaction is given by

$$k_{\mathrm{diff}} = 8000RT/3\eta \qquad (4)$$

where η is the viscosity coefficient of the medium. The apparent activation volumes ($\Delta V_{\mathrm{diff}}^{\neq}$), determined from the available η-p data,[5] are 15.8 cm^3 mol^{-1} for acetone, 23.2 cm^3 mol^{-1} for hexane, and 18.1 cm^3 mol^{-1} for pentane.

Discussion

Pressure Effects. Table 1 shows that the k_{ex} values are in the range of 10^9—10^{10} dm^3 mol^{-1} s^{-1} and decrease with increasing applied pressure. The pressure effect can be explained simply in terms of the dependence of k_{ex} on the viscosity of the solvent, suggesting that diffusion-controlled processes are involved. The observed $\Delta V_{\mathrm{ex}}^{\neq}$-values are smaller than the $\Delta V_{\mathrm{diff}}^{\neq}$-values and the difference ($\Delta\Delta V^{\neq}(=\Delta V_{\mathrm{ex}}^{\neq}-\Delta V_{\mathrm{diff}}^{\neq})$) is -3—-12 cm^3 mol^{-1} (Table 2).

It has been shown[1] that k_{ex} is related to k_{diff} by

$$k_{\mathrm{ex}} = P_{\mathrm{r}} f_{\mathrm{s}} k_{\mathrm{diff}}, \qquad (5)$$

where f_{s} denotes the steric factor, and P_{r} is the probability of a spin exchange upon collision, and is given by

$$P_{\mathrm{r}} = J^2\tau_1{}^2/(1 + J^2\tau_1{}^2), \qquad (6)$$

where J and τ_1 denote the exchange integral and the collision time, respectively. $\Delta\Delta V^{\neq}$ can thus be given by

$$\Delta\Delta V^{\neq} = \Delta V_{\mathrm{ex}}^{\neq} - \Delta V_{\mathrm{diff}}^{\neq} = -RT(\partial \ln P_{\mathrm{r}}/\partial p)_T. \qquad (7)$$

In previous paper,[1] we showed that the values of f_{s} and J can be estimated by using

$$k_{\mathrm{diff}}/k_{\mathrm{ex}} = f_{\mathrm{s}}^{-1} + (k^2T^2/J^2\pi^2\lambda_0{}^4\rho_0{}^{4/3}r^2f_{\mathrm{s}})(\rho_p{}^{4/3}/\eta^2), \qquad (8)$$

where r is the effective hydrodynamic radius of a radical, λ_0 is the jump length, and ρ_0 represents the liquid density at the freezing point under atmospheric pressure. The estimated λ_0 and ρ_0-values are as follows: λ_0=0.50 nm and ρ_0=0.769 g cm^{-3} for pentane,[5] λ_0=0.50 nm and ρ_0= 0.920 g cm^{-3} for acetone,[5] and λ_0=0.59 nm and ρ_0=0.757 g cm^{-3} for hexane.[5] Plachy and Kivelson[7] measured the translational diffusion constant of di-*t*-butyl nitroxide (DTBN) and estimated the radius (r) as 0.32 nm. The r-values of the various nitroxide radicals were estimated with the help of Corey–Pauling–Koltun models (CPK) using the size of DTBN as a standard. Representative plots of Eq. 8 are shown in Fig. 1. From the plot, the f_{s} and J values were estimated and are given in Table 2. The estimated J-values are of the order 10^{10}—10^{11} s^{-1} and are in agreement with the J-value (6×10^{10} s^{-1}) for DTBN in pentane reported by Plachy and Kivelson.[7] The J-values in pentane seem to be somewhat large compared to those in acetone and hexane. The exchange integral is, roughly speaking, proportional to the square of the overlap integral (S),[2]

$$J \propto |S|^2, \qquad (9)$$

The overlap integral decreases rapidly as the distance between the radical species increases. Therefore, the J-value can be regarded as being a measure of the distance between a pair or radicals in a solvent cage. It is noted that the J-values in pentane are about twice as large as in hexane. The reason for this perhaps comes from the numerical choice for λ_0 and r, which greatly affects the J-value. A discussion concerning the f_{s}-values of the spin exchange is given in detail below.

Nitroxides Having -OH or -NH$_2$ Group. It is to be noted that the nitroxide radicals having an -OH or -NH$_2$ group give small f_{s}-values in acetone, while their f_{s}-values are about 0.5 in hexane and pentane. The values of TANONE and TEMPO are also about 0.5 in acetone. This suggests that specific solvation takes place between acetone and the -OH or -NH$_2$ group. A specific solute–solvent interaction between nitroxides and hydrocarbons, such as hexane and pentane, is unlikely. In order to clarify the situation, we added a small amount of ethanol to hexane (1 : 9 v/v) and examined the spin–spin exchange rate of TANOL. The rate constant as well as the f_{s}-value for TANOL in the mixed solvent is substantially decreased compared with those in pure hexane and pentane.

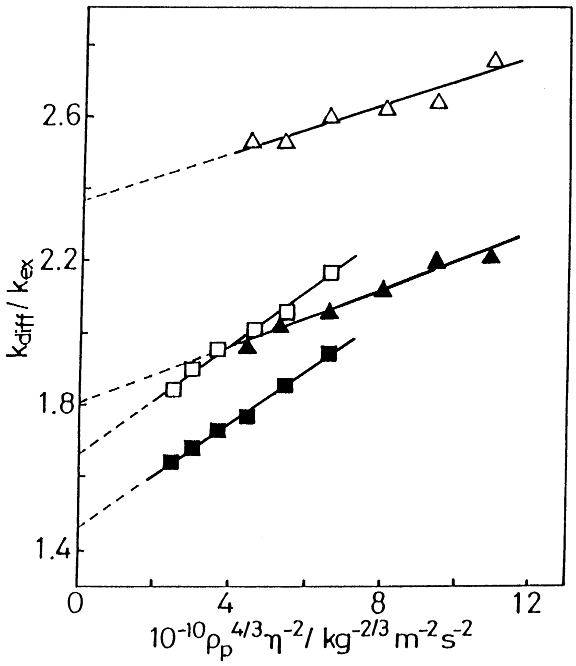
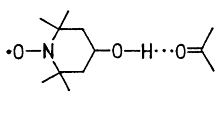


Fig. 1. Plots of $k_{\mathrm{diff}}/k_{\mathrm{ex}}$ against $\rho_p{}^{4/3}\eta^{-2}$: TANONE (■) and TEMPO (□) in hexane, TANONE (▲) and TEMPO (△) in pentane.

The following types of hydrogen bonds are possible for TANOL and Amino-TEMPO in acetone. Based on the assumption of these structures, the rotational rate of the radicals in solution may become slower.[8] The above structures give rise to a change in the hydrodynamically equivalent radii (r-value) of the radicals and the rotational rate is proportional to $1/r^3$ (see below). Thus, we estimated the r-values involving the length of the hydrogen bond to be r=0.48 nm for TANOL and Carboxy-PROXYL (structure **A**), and r=0.53 nm for Amino-TEMPO and Carbamoyl-PROXYL (structure **B**). By using the above hydrodynamic radii, the J-values for TANOL, Carboxy-PROXYL, Amino-TEMPO, and Carbamoyl-PROXYL in acetone were recalculated and are given in Table 2. It can be seen that the recalculated J-values decreased, so as to be comparable with the values of TANONE and TEMPO in acetone.



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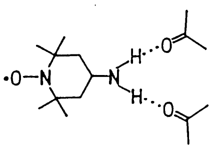

B

It is instructive to compare the collision time (τ_l) with rotational correlation time (τ_R). The correlation time (τ_R) for the isotropic rotation of a molecule may be approximated by the following Debye equation:[9]

$$\tau_R = 4\pi\eta r^3/3kT. \tag{10}$$

The collision time (τ_l) is given by Eq. 10,[7]

$$\tau_l = \pi r\lambda^2\eta/kT, \tag{11}$$

where $\lambda=\lambda(p,T)$ is the jump length; λ is 0.53 nm for acetone and 0.86 nm for toluene at 0.1 MPa.[1,5] From Eqs. 10 and 11, the rotational and collision times of TANONE, TANOL, Amino-TEMPO, and PROXYL were estimated, and are given in Table 3. Though the above estimations of τ_R and τ_l are approximate, the following points are noticeable: (1) In toluene, the τ_l-value of TANONE is obviously large compared to τ_R, indicating that the rotational rate ($1/\tau_R$) is evidently fast compared to the rate ($1/\tau_l$) that a pair of reacting molecules diffuse out of a solvent cage. (2) In acetone, the τ_l-values are small due to low-viscosity of the medium. The small τ_l-values and the retardation in the rotational rates of TANOL, Amino-TEMPO, Carboxy-PROXYL, and Carbamoyl-PROXYL in acetone are deeply correlated to the collision efficiency for the spin exchange, which is responsible for the small f_s-value.

Nitroxide Having Long-Chain. The nitroxide radicals having a long-chain give small f_s-values in acetone and toluene. There is no significant difference among the J-values. In toluene the condition $J^2\tau_l^2\gg1$ of Eq. 6 must hold, due to the large τ_l-value and, hence, $P_r\sim1$ (see below). Thus, the f_s-value for 10-DOXYL in toluene cannot be estimated according to Eq. 8. It was estimated as follow: Substituting the numerical values of λ, η, and r into Eq. 11, the τ_l-values were calculated to be $\tau_l=2.0\times10^{-10}$ s at 0.1 MPa and $\tau_l=2.9\times10^{-10}$ s at 63.7 MPa in toluene. Therefore, with $J=6.1\times10^{10}$ s^{-1} (DOXYL in acetone) and these values, the probability P_r for the spin exchange in toluene becomes 0.993 at 0.1 MPa and 0.997 at 63.7 MPa, both nearly equal to unity. This indicates that $\Delta\Delta V^{\neq}\fallingdotseq0$ (see Eq. 7) is in agreement with our observation. The f_s-value of 10-DOXYL in toluene was calculated using Eq. 5 to be 0.16. This value can be compared to that in acetone. It is likely that the low value of f_s for long-chain nitroxides is caused by the steric circumstance around the >N–O· group. As predicted from Eq. 10, the rotational rate in solution may be retarded due to the long chain (Table 3). The small f_s-values for long-chain nitroxides are therefore ascribed to both the steric hindrance upon collision and retardation in the rotational rate.

Table 3. Calculated Collision and Rotational Correlation Times of Various Nitroxide Radicals

Radical	Solvent	r	$10^{11}\tau_l$	$10^{11}\tau_R$
		nm	s	s
TANONE	Toluene	0.39	12	3.4
	Acetone	0.39	2.4	1.7
TANOL	Acetone	0.48[a)]	2.9	3.2
Amino-TEMPO	Acetone	0.53[a)]	3.2	4.3
Carboxy-PROXYL	Acetone	0.48[a)]	2.9	3.2
Carbamoyl-PROXYL	Acetone	0.53[a)]	3.2	4.3
5-DOXYL	Acetone	0.48	2.9	3.2
10-DOXYL	Toluene	0.64	20	15
	Acetone	0.64	3.9	7.6

a) Reestimated value of r.

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