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ESR Studies at High Pressures. III.[1] Spin-Exchange Reactions of Some Nitroxide Radicals in Acetone and Hexane

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Pressure effects on the rate of spin–spin exchange of some nitroxide radicals in acetone and hexane at 298.2 K have been studied by means of a high-pressure ESR technique. It was found that this exchange reaction is diffusion-controlled. The rate of the spin exchange is related to that of diffusion, the probability of the spin exchange, $P=f(J, \tau_1)$, and steric factor f_s. The values of P and hence τ_1 were estimated as a function of pressure. A method for evaluating the steric factor and the exchange integral is proposed.

It has been recognized over the past half a century that kinetic studies at high pressures are informative for characterizing reaction processes in condensed systems. When investigations at high pressures are undertaken, we often face some difficulties that should be surpassed. For high-pressure NMR and ESR experiments in particular, sophisticated techniques are required. At present, high pressure/high temperature NMR probse have been designed, and this has enabled us to know detailed information about the dynamic structure of liquids.[2] On the contrary, only a few high-pressure ESR studies have been done; among them, papers concerning the effects of pressure on spectral linewidth[3,4] and hyperfine splittings[5] besides chemical equilibria[6,7] and reaction rates[8] have been put forward.

In previous papers,[1,9] we have reported the pressure effects on the rate of spin–spin exchange of 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxyl (TANONE) in various solvents. The rate constant for the spin-exchange process was found to be strongly correlated to solvent viscosity η, indicating that a diffusion-controlled process is involved. Since viscosity variation with temperature inevitably involves unfavorable energetic problems, the viscosity was changed by applying pressure p. It was found that in aprotic solvents except acetone, the activation volumes for the spin-exchange process ($\Delta V_{ex}^{\neq}$) coincided well with the apparent activation volumes for diffusive processes ($\Delta V_{diff}^{\neq}$).

In the present work, we used acetone and hexane as low viscosity solvents to utilize available η–p data together with compressibility data. In order to obtain further information about the effect of pressure on the rate of the spin–spin exchange, we investigated the spin-exchange reaction of three kinds of nitroxides: 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxyl (TANONE), 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO), and di-*t*-butyl nitroxide (DTBN) in acetone and hexane.

Experimental

TANONE, TEMPO, and DTBN were purchased from Wako Pure Chemicals Co., Ltd., and used without further purification. Reagent grade acetone and hexane were used after distillation. The instrumentation of a high-pressure ESR cell has already been described elsewhere.[9] A sample solution was deaerated by bubbling nitrogen and was transferred into the cell under nitrogen atmosphere. After a required pressure had been attained, the stop valve on the cell was closed and then cell was separated from the pump system. By doing that, troublesome instrumentations[6-8] have been overcome.

ESR signals were monitored by using a JEOL JES-FE3XG ESR spectrometer with a 100 kHz field modulator. The peak-to-peak width of the central signal was measured at 298.2 K within a precision of ±1.5%.

Theoretical Background

The rate constant of spin-exchange reaction k_{ex} is related to the line broadening of an ESR signal by Eq. 1.[10]

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

where ΔH and ΔH_0 are the linewidth in the presence and absence of spin exchange, respectively; A is a constant characteristic of each radical, and is equal to $2.28\times 10^8\ \mathrm{mT^{-1}\ s^{-1}}$ for the Lorentzian type of ESR signals of nitroxides.[10] Since no activation energy will be needed for the exchange process, the exchange rate constant can be given by the rate constant for a diffusive process k_{diff} multiplied by P:

$$k_{ex} = Pk_{diff}, \tag{2}$$

where P is the probability of spin exchange upon "collision". The probability (P) is related to the exchange integral J and collision time τ_1 by Eq. 3,[10]

$$P = J^2\tau_1^2/(1 + J^2\tau_1^2). \tag{3}$$

The term collision is used here in the sense that a pair of reacting molecules are encountering in a solvent cage. According to the Stokes–Einstein–Smoluchowski equation, k_{diff} for spherical molecules in a medium-in-continuum of bulk viscosity η is given by:

$$k_{diff} = 8000RT/3\eta. \tag{4}$$

In real solution, the shape, mutual orientation and solvation of reacting molecules would affect k_{ex}. Hereafter such composite effects will be called comprehensively the steric factor f_s. Then, Eq. 2 can be modified as:

$$k_{ex} = Pf_s k_{diff}. \qquad (5)$$

According to Plachy and Kivelson,[11] the collision time τ_1 can be given by Eq. 6

$$\tau_1 = \pi b\lambda^2\eta/kT, \qquad (6)$$

where b is the effective hydrodynamic radius of a molecule moving in a liquid, and $\lambda=\lambda(p, T)$ is the jump length which may be, according to the hole theory, inversely proportional to the cube root of the liquid density.[11] Thus, the following relationship will approximately hold.

$$\lambda_p{}^3 = \lambda_0{}^3\rho_0/\rho_p, \qquad (7)$$

where λ_0 and ρ_0 denotes the jump length and the (liquid) density at the freezing point under atmospheric pressure, respectively and λ_p and ρ_p represent them at pressure p and 298.2 K. By combining Eqs. 3, 5, 6, and 7, and eliminating P and λ_p, we finally obtain Eq. 8 which enables us to estimate the steric factor f_s and exchange integral J:

$$k_{diff}/k_{ex} = 1/f_s + (k^2T^2/J^2\pi^2\lambda_0{}^4\rho_0{}^{4/3}b^2f_s)(\rho_p{}^{4/3}/\eta^2). \qquad (8)$$

Another equation that will be useful for our discussion is obtained by the combination of Eqs 4 and 5:

$$k_{ex}\eta \propto P. \qquad (9)$$

Results

Figure 1 shows that ΔH increases linearly with the radical concentration at each pressure (correlation coefficient $r \geqslant 0.9985$) in accordance with Eq. 1. From the linewidth of the central peak of the triplet signals, the spin-exchange rate constants k_{ex} at various pressures were estimated by means of Eq. 1, and are given in Table 1. From the pressure dependence of k_{ex}, the activation volumes $\Delta V_{ex}^{\neq}$ at 1 bar for the spin exchange have been estimated. These are given in Table 2. Using available η-p data[12] the apparent activation volumes for diffusion $\Delta V_{diff}^{\neq}$ extrapolated to 1 bar have been calculated to be 15.8 cm^3 mol^{-1} in acetone and 23.2 cm^3 mol^{-1} in hexane. The differences between $\Delta V_{ex}^{\neq}$ and $\Delta V_{diff}^{\neq}$ are about -5 and -11 cm^3 mol^{-1} in acetone and hexane, solvents of low viscosity, but are near zero in toluene, benzene, and *o*-xylene. The physical meaning of the activation volume for a diffusive process has already been discussed.[9]

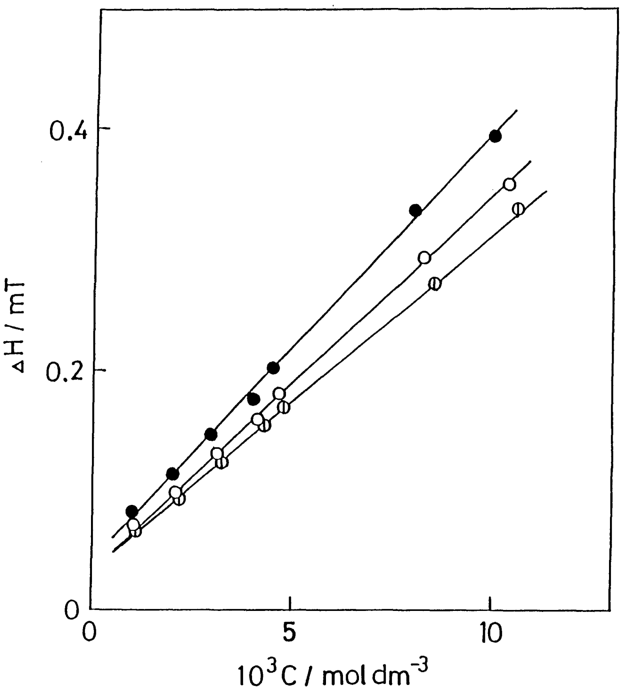

Fig. 1. Concentration dependence of ESR linewidth for TANONE radical in acetone at 1 (●), 343 (○), and 637 (◐) bar.

Discussion

Pressure Dependence of the Probability *P*. It is seen in Table 1 that k_{ex}-values clearly decrease inversely to the applied pressure and that they are smaller in toluene than in acetone and hexane. The above findings may simply

Table 1. Rate Constants for the Spin Exchange of Nitroxide Radicals at Various Pressures and at 298.2 K

Compd	Solvent	$10^{-9}\,k_{ex}$/mol^{-1} dm^3 s^{-1} ($10^{-9}\,k_{diff}$/mol^{-1} dm^3 s^{-1})[a]								
		p/bar								
		1	98	196	294	343	392	490	588	637
TANONE	Toluene[b]	5.27	5.08	4.74	4.22		4.06	3.81	3.74	
	Benzene[b]	5.31	4.73	4.57		4.04		3.43		
	o-Xylene[b]	4.17	3.94	3.69	3.21		3.28	3.10	2.71	
	Acetone	8.07	7.79	7.44		7.04		6.69		6.38
	Acetone	(23.2)	(21.7)	(20.3)		(18.6)		(17.1)		(15.9)
	Hexane	11.5	10.8	10.3		9.28		8.54		7.92
	Hexane	(22.3)	(20.1)	(18.3)		(16.1)		(14.3)		(13.0)
DTBN	Acetone	9.44	8.98	8.65		8.27		7.85		7.41
TEMPO	Acetone	7.78	7.41	7.03		6.56		6.21		5.85

a) The rate constants calculated by Eq. 4 are given in parentheses. b) Cited from Refs. 1 and 9.

Table 2. Activation Volumes and Exchange Integrals at 1 bar for the Spin-Exchange Reactions of Nitroxides

Compd	Solvent	$\Delta V_{ex}^{\neq}$	$\Delta\Delta V^{\neq}$ a)	f_s	$10^{-10} J$
		$cm^3 mol^{-1}$	$cm^3 mol^{-1}$		s^{-1}
TANONE	Acetone	8.7	−7.1	0.48	6.9
	Hexane	12.1	−11.1	0.68	5.3
	Toluene b)	13.7	−0.5		
	Benzene b)	18.4	0.7		
	o-Xylene b)	15.3	−0.2		
TEMPO	Acetone	10.7	−5.1	0.41	9.5
DTBN	Acetone	7.4	−8.4	0.56	8.4

a) $\Delta V_{ex}^{\neq} - \Delta V_{diff}^{\neq}$. b) Cited from Refs. 1 and 9.

Table 3. Collision Time (in s) and Probability for the Spin Exchange of Nitroxides at Various Pressures at 298.2 K

Pressure	TANONE in acetone		DTBN in acetone		TEMPO in acetone		TANONE in hexane	
bar	$10^{11}\tau_1$	P	$10^{11}\tau_1$	P	$10^{11}\tau_1$	P	$10^{11}\tau_1$	P
1	2.35	0.72	1.93	0.71	2.23	0.81	3.39	0.76
98	2.50	0.75	2.05	0.74	2.37	0.83	3.69	0.79
196	2.65	0.78	2.17	0.76	2.51	0.84	4.03	0.83
343	2.87	0.80	2.36	0.79	2.73	0.86	4.36	0.85
490	3.09	0.82	2.54	0.82	2.94	0.89	4.68	0.88
637	3.30	0.84	2.71	0.83	3.13	0.90	5.01	0.90

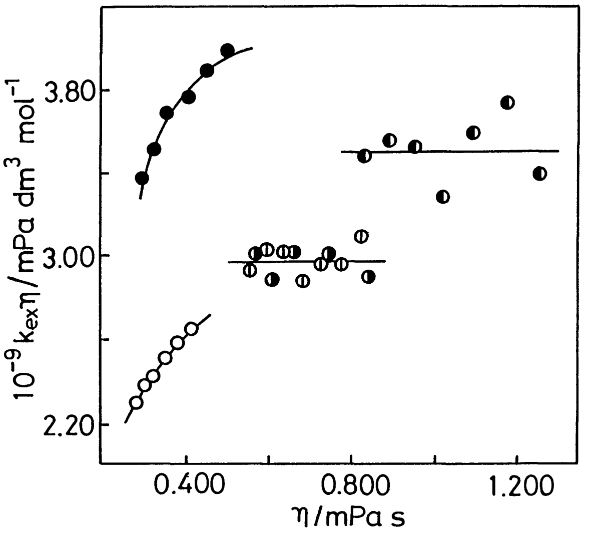

Fig. 2. Relationship between $k_{ex}\eta$ and η for spin exchange of TANONE radical in acetone (○), hexane (●), toluene (⦶), benzene (◑), and *o*-xylene (◐).

be interpreted in terms of viscosity dependence of k_{ex}. As stated in the introductory section, acetone behaves differently from other aprotic solvents of comparatively high viscosity. The reason is as follows. In Fig. 2, $k_{ex}\eta$ is plotted against η. It could safely be said that $k_{ex}\eta$ and hence P is independent of η in toluene, benzene, and *o*-xylene. Judging from Eq. 3, the condition $J^2\tau_1^2 \gg 1$ and hence $P \approx 1$ must hold in this case. In acetone and hexane, $k_{ex}\eta$ increases with viscosity, suggesting that P is susceptible to η. By means of Eqs. 4 and 5, the P-values for spin exchange of some nitroxide radicals in acetone and hexane were calculated as a function of pressure assuming the steric factor (vide infra) is independent of pressure and they are given in Table 3. No significant difference among P-values of the some nitroxide radicals listed in Table 3 was observed. In acetone and hexane, the P-values become progressively larger and approach unity, as the external pressure increases. The pressure dependence of P-value in acetone and hexane is ascribed to that of the collision time τ_1 in agreement with the prediction of Eqs. 3 and 6. The discussion on τ_1 will be made below. In any case, it is obvious that the difference $\Delta V_{ex}^{\neq} - \Delta V_{diff}^{\neq}$ in acetone and hexane is a result of the pressure dependence of the probability in accordance with Eq. 5.

Estimation of the Steric Factor and the Exchange Integral. According to Eq. 8, a plot of k_{diff}/k_{ex} against $\rho_p^{4/3}/\eta^2$ will give a straight line with the slope $(k^2T^2/J^2\pi^2\lambda_0^4\rho_0^{4/3}b^2f_s)$ and the intercept $1/f_s$. The plots are shown in Fig. 3. It follows that each plot constitutes a straight line, and this strongly suggests that the f_s- and J-values are independent of pressure or viscosity. It is difficult to estimate the numerical value of b and λ_0 exactly. Plachy and Kivelson[11] measured the diffusion coefficient of DTBN in pentane and estimated the radius b as 0.32 nm. Here, this value was used as the standard of estimating the b-values (TANONE and TEMPO) and λ_0 (acetone and hexane) referring the size of their CPK models. The estimated b-values are 0.39 nm for TANONE and 0.37 nm for TEMPO, and λ_0=0.50 nm for acetone and λ_0=0.59 nm for hexane. The liquid density extrapolated to its freezing point ρ_0 was estimated as 0.920 g cm^{-3} for acetone[12] and 0.757 g cm^{-3} for hexane.[13] After these numerical values were substituted in Eq. 8, f_s-

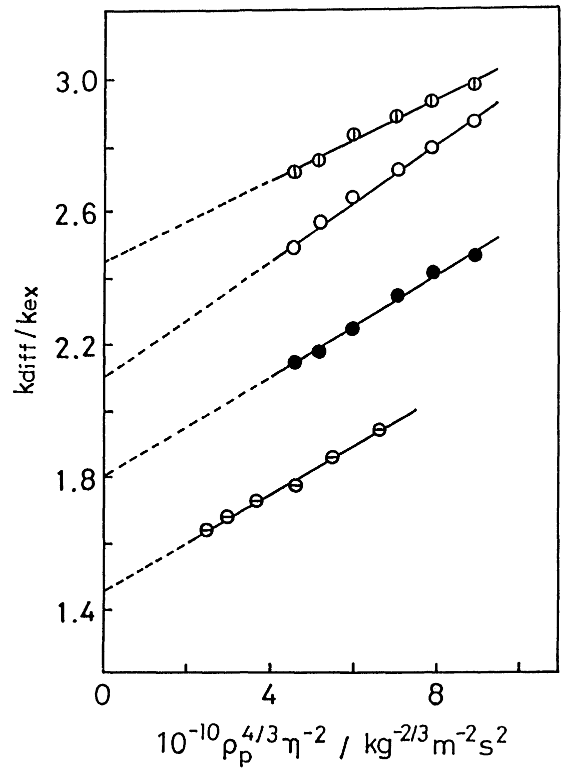

Fig. 3. Plots of $k_{\mathrm{diff}}/k_{\mathrm{ex}}$ against $\rho_p^{4/3}\eta^{-2}$ for spin exchange: TANONE (○) in acetone, TEMPO (⦶) in acetone, DTBN (●) in acetone, TANONE (⊖) in hexane.

and J-values for the spin exchange of the nitroxide radicals were calculated from the slope of the linear plot of Eq. 8, and they are given in Table 2. The f_s-values of some nitroxide radicals listed in Table 2 are about 0.5 and the J-values are of the order of 10^{10} s^{-1}.

According to Kivelson,[14] J should be a rapidly varying function of the radical–radical separation r, but approximately be regarded as constant if $r \leqslant r_c$, and zero if $r > r_c$, where r_c is a critical distance. The straight line of the above plot indicates the constancy of J. This means that the radicals are remaining within a distance r_c to each other during the collision time.

The J- and f_s-values seem to depend somewhat on the nature of radical species (Table 2). Studies are under way using various types of nitroxides. As the numerical values agree fairly well with the reported J-value for DTBN in pentane (J=6×10^{10} s^{-1}),[11] these values could be regarded as reasonable. It is notable that the exchange integral which is a very important quantity for radical–radical reactions can be simply estimated.

Estimation of Collision Time. The jump length at pressure p and at 298.2 K can be estimated by means of Eq. 7, using available ρ–p data.[12] If the numerical values of b, ρ_p, and ρ_0 are substituted into Eqs. 6 and 7, one obtains the collision time τ_1. They are listed in Table 3. The viscosity η raises while the jump length λ decreases with increasing pressure. We can see that the product $\lambda^2\eta$ increases proportionately with pressure resulting in the net increase in τ_1. The collision times τ_1 for the spin exchange of the nitroxide radicals in acetone and hexane are of the order of 10^{-11} s (Table 3). These values are nearly equal to the rotational correlation time (τ_{rot}=1.7×10^{-11} s TANONE in acetone) estimated from the following equation:[15]

$$\tau_{\mathrm{rot}} = 4\pi\eta b^3/3kT. \tag{10}$$

This suggests that the collision time in acetone and hexane is deeply correlated to the rotational correlation time, which is responsible for $P < 1$. Meanwhile for toluene, if the numerical values of b, λ, and η (b=0.39 nm TANONE, λ=0.86 nm, η=0.556 mPa s at 1 bar and λ_p= 0.84 nm, η_p=0.853 mPa s at 637 bar) are substituted in Eq. 6, we have τ_1=1.22×10^{-10} and 1.79×10^{-10} s at 1 and 637 bar, respectively. With these values and J= 6.9×10^{10} s^{-1}, $J^2\tau_1^2$ becomes 71 and 153 at 1 and 637 bar, respectively, in agreement with our foregoing prediction from Fig. 2.

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