ESR Studies of Solvent and Pressure Effects on Spin Exchange of Nitroxide Radicals in Solution

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(Received April 12, 1988)

The rate constants of spin exchange for 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxyl (Tanone) in various solvents at high pressures were estimated from the line-broadening in ESR spectra. The rate constants of the spin exchange were in the range of 10^9—10^{10} M^{-1} s^{-1} and were compared with the calculated ones on the basis of the Smoluchowski-Stokes-Einstein equation. A significant disagreement between them was observed as the solvent viscosity decreased. The activation volumes estimated from the pressure dependence of the rate constant for the spin exchange were slightly smaller than those for diffusive processes. These findings suggest that the rate process for the spin exchange is virtually a diffusion-controlled one. An interpretation of activation volumes for diffusive process of spin exchange is given.

Recently, the usefulness of the examination of kinetic pressure effects has become recognized in mechanistic studies on the chemical reactions taking place near the diffusion-controlled limit. In particular, such studies have been made actively in the field of photochemistry. Interesting reports on the dynamic measurements of transient fluorescence for some exciplex-formation systems have been put forward,[1-3] and the mechanism of the exciplex-formation reaction has been explained in terms of diffusion-controlled encounters. The physical meaning of the activation volume which is formally obtained from the pressure dependence on the diffusion-controlled rate constants, however, has not yet been well established.

The rate constants of the spin exchange can be easily estimated from the line-broadening of ESR-spectra of radicals.[4] The spin exchange reaction can be regarded as a simplified model of a complex chemical reaction. Up to the present, few ESR studies at high pressures have been done, mainly due to the technical difficulty.

Plachy and Schaafsma[5] used a vessel containing a microwave helix and the field-modulation coils for the measurement of ESR signals at high pressures, and such a vessel can withstand pressures of several thousand atmospheres. It, however, is unsuitable for ESR measurements in polar solvents. Böddeker et al.[6] designed a high-pressure glass cell which could be pressurized to 405 bar.

In the present report, a study on the spin exchange reaction in the solvents of various polarities was carried out at various pressures using a newly designed high-pressure cell for ESR measurements. From the pressure dependence on the rate constant of the spin exchange the activation volumes were estimated, and the results were discussed on the basis of the volume change associated with diffusive processes.

Experimental

Materials. 2,2,6,6-Tetramethyl-4-oxo-1-piperidinyloxyl (Tanone) was purchased from Wako Pure Chemicals, and used without further purification. Toluene, acetone, 2-propanol, methanol, and nitrobenzene are of guaranteed grade and were purified in the usual manner.

High-Pressure ESR Cell. The high-pressure vessel, which is made of copper-beryllium alloy and equipped with a stop valve, is shown in Fig. 1. The sample cell for ESR measurements was composed of a Pyrex glass capillary and its top was bound to the high-pressure vessel by epoxy resin. The glass parts, which were hand-made in our laboratory, were sealed at an open end, annealed, and washed with the 5% aqueous hydrogen fluoride solution at room temperature. In preliminary tests, the cell was designed to be repeatedly pressurized up to 588 bar, however, it was broken at 883 bar as an example (1 bar=0.1 MPa).

Procedures. Pressures were generated by means of a plunger pump, and the pressure was measured by a Haise Bourdon gauge. The sample solution was purged by bubbling nitrogen for ca. 30 min and charged into the pressure cell under a nitrogen atmosphere. After a required pressure

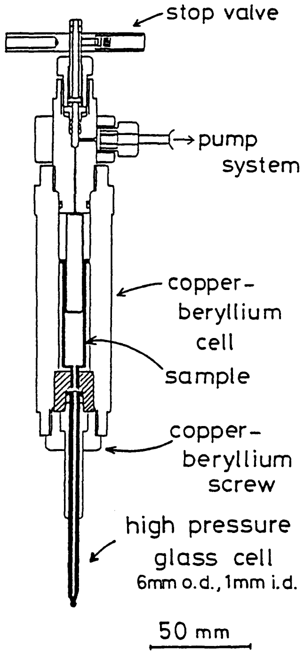

Fig. 1. High pressure cell for use in standard ESR spectrometer.
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was established the stop valve was closed, and the pressure vessel separated from the pump system and placed in the ESR cavity.

ESR measurements were performed using a home-made X-band spectrometer with a 100-kHz field modulation. The peak-to-peak width of the central component of the hyperfine structure of the nitroxide radical was measured. The accuracy of the linewidth thus obtained was ±1.5%.

Results

Spin Exchange at High Pressures. The second-order rate constant k_e for the spin exchange process has been estimated easily from the dependence of line-broadening on the concentration of radicals.[4]

$$k_e = A(\Delta H - \Delta H_0)/C, \tag{1}$$

where ΔH_0/mT and ΔH/mT are linewidths in the absence and presence of spin exchange, respectively. C is a radical concentration. A is a constant and its value for the spin exchange of nitroxide radicals has been given to be 2.28×10^8 mT^{-1} s^{-1}.[4] The linear relationships between the linewidths ΔH and the concentrations of the Tanone radical in toluene at different pressures are shown in Fig. 2. This linear relationship shows that the spin exchange makes the major contribution to line-broadening in the concentration range from 10^{-3} to 10^{-2} M (1M=1 mol dm^{-3}) at high pressures as well as at 1 bar. Thus the rate constants k_e for the spin exchange of the Tanone radicals could be estimated by Eq. 1 in various solvents and those values are listed in Table 1.

In Fig. 3, the rate constants of the spin exchange are plotted against the applied pressures. Each plot is seen to be almost linear in the pressure range up to 588 bar. It is noted that the slope is positive in water due to the viscosity decrease with increase of pressure in this pressure range at 288 K (Table 1).

The second-order rate constant of the diffusive processes is given by the Smoluchowski expression,[7] namely

$$\begin{aligned} k_{\text{diff}} &= 4\pi aD \\ &= (8000\,RT)(3\eta)^{-1}/\text{M}^{-1}\,\text{s}^{-1}, \end{aligned} \tag{2}$$

where a is the sum of the radii of the diffusive molecules, D is the sum of the Stokes-Einstein diffusion

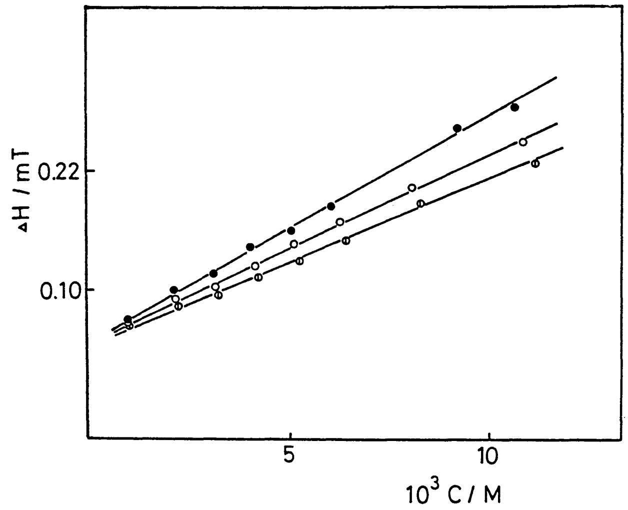

Fig. 2. Concentration dependence of ESR linewidth for Tanone radical in toluene at 1 (●), 294 (○), and 588 (⦶) bars.

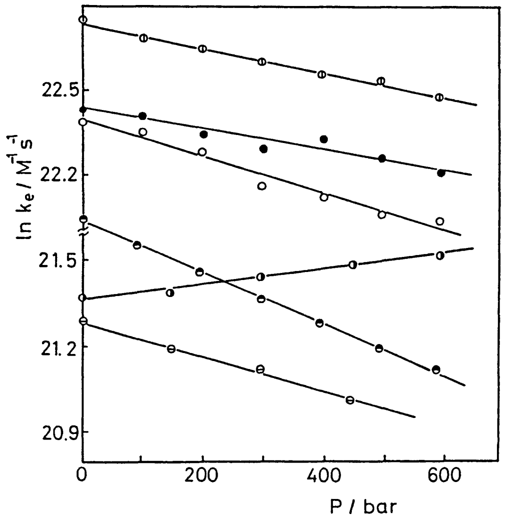

Fig. 3. Pressure effects on the spin exchange reaction between Tanone radicals; (⦶) in acetone, (●) in methanol, (○) in toluene, (◓) in 2-propanol, (◑) in water, (⊖) in nitrobenzene.

Table 1. Rate Constants (k_e) for Spin Exchange of Tanone Radicals and Diffusion-Controlled Rate Constants (k_{diff}) in Various Solvents at Different Pressures

Solvent	T	1 bar			588 bar		
		η[a]	$10^{-9}k_{\text{diff}}$	$10^{-9}k_e$	η[a]	$10^{-9}k_{\text{diff}}$	$10^{-9}k_e$
	K	mPa·s	M^{-1} s^{-1}	M^{-1} s^{-1}	mPa·s	M^{-1} s^{-1}	M^{-1} s^{-1}
Toluene	296	0.570	11.6	5.27±0.09	0.848	7.74	3.74±0.07
Nitrobenzene	293	2.01	3.24	1.77±0.11	2.65[b]	2.45[b]	1.35±0.07[b]
Acetone	303	0.285	23.6	7.61±0.22	0.409	16.4	5.81±0.27
2-Propanol	298	2.07	3.19	2.83±0.11	3.34	1.98	1.87±0.06
Methanol	298	0.556	11.9	5.52±0.21	0.718	9.24	4.42±0.16
Water	288	1.40	4.57	1.91±0.10	1.35	4.74	2.21±0.07

a) The viscosities for toluene, 2-propanol, and methanol were estimated from the data at 30 and 75 °C according to $\ln\eta = A + B/T$, and the viscosity of water at 15 °C was estimated from the data at 0, 10.3, and 30 °C. The viscosity of nitrobenzene is the data at 30 °C. b) At 441 bar.

coefficients, and η/Pa·s is the viscosity coefficient of the medium. By this equation and using available data[8] for viscosity, k_{diff}-values were estimated and are given in Table 1.

Discussion

Spin Exchange of Tanone Radicals. As seen in Table 1, the rate constants k_e for the spin exchange in various solvents almost reach the diffusion-controlled limit k_{diff}. As far as our data are concerned, no correlation between the k_e-value and the dielectric constant ε of solvent is observed. This could be accepted when we recall that Tanone is not a polar species. The rate of the spin exchange, however, is invariably retarded by the increase in the solvent viscosity, as predicted by Eq. 2. The rate constant is plotted as a function of inverse viscosity in Fig. 4, where two remarkable features are seen. One is that k_e deviates more and more from that predicted for the diffusive process (Eq. 2) as the solvent viscosity decreases. Another is that the plots of k_e against inverse viscosity seem to fall roughly on a same curve irrespective of solvent, temperature, and pressure. These findings strongly indicate that the spin exchange is controlled by the diffusive processes. At a solvent viscosity $\eta>0.3$ mPa·s the discrepancy between the rate constants of the diffusion collisions calculated according to Eq. 2 and those obtained from the spin exchange amounts to about two-fold, which may be attributed to the discrepancy between the measured diffusion coefficient D[9,10] and the calculated one. At low viscosity $\eta<0.3$ mPa·s the large deviation may be due to transition into the region of weak exchange[4] as well as above.

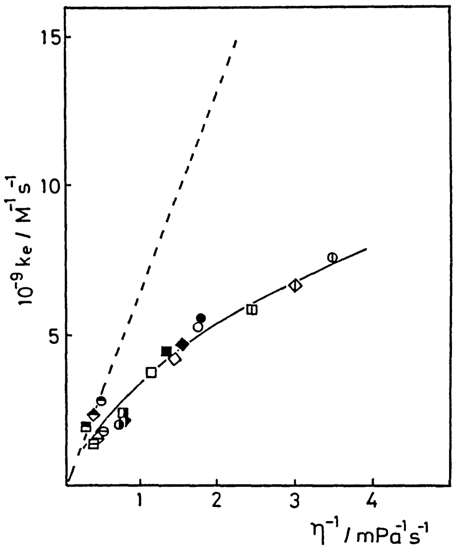

Fig. 4. Plots of k_e against η^{-1} in various solvents, and at various temperatures and pressures; ○ at 1 bar, ◇ at 288 bar, □ at 588 bar. Dashed line; calculated from Eq. 2. The key is shown in Fig. 3.

Comparison of $\Delta V^{\neq}_{\mathrm{obs}}$ with $\Delta V^{\neq}_{\mathrm{diff}}$. The solid lines in Fig. 3 represent the following linear regression equation.

$$\ln k_e = ap + b \tag{3}$$

The activation volumes $\Delta V^{\neq}_{\mathrm{obs}}$ at 1 bar were estimated as

$$RT(\partial \ln k_e/\partial p)_T = aRT = -\Delta V^{\neq}_{\mathrm{obs}} + \Delta n^{\neq}\, \kappa_T RT \tag{4}$$

where $\Delta V^{\neq}_{\mathrm{obs}}$ is the partial molar volume change that occurs when a molecule passes from an initial state into a transition state, $\Delta n^{\neq}$ ($=-1$ in the present case) is the difference in number of species between the activated and initial states, and κ_T is the isothermal compressibility of the solvent. The values of $\kappa_T RT$ at 1 bar were calculated from available data.[8] The values of $\Delta V^{\neq}_{\mathrm{obs}}$ are given in the third column of Table 2. The apparent activation volume for this process $\Delta V^{\neq}_{\mathrm{diff}}$ can be calculated by

$$RT(\partial \ln k_{\mathrm{diff}}/\partial p)_T = -RT(\partial \ln\eta/\partial p)_T = -\Delta V^{\neq}_{\mathrm{diff}} - \kappa_T RT \tag{5}$$

The calculated values $\Delta V^{\neq}_{\mathrm{obs}}$ are given in the fourth column of Table 2.

It is interesting to examine how $\Delta V^{\neq}_{\mathrm{obs}}$ relates to $\Delta V^{\neq}_{\mathrm{diff}}$. The observed activation volumes $\Delta V^{\neq}_{\mathrm{obs}}$ were in the range from -7.6 to 15.4 cm^3 mol^{-1} and no systematic solvent dependency was observed (Table 2). On the other hand, the values of $\Delta V^{\neq}_{\mathrm{obs}}-\Delta V^{\neq}_{\mathrm{diff}}$ in Table 2 are small and all negative. The present values of $\Delta V^{\neq}_{\mathrm{obs}}-\Delta V^{\neq}_{\mathrm{diff}}$ seem to be classified with regard to viscosity of solvent and difference in solvation; $\Delta V^{\neq}_{\mathrm{obs}}-\Delta V^{\neq}_{\mathrm{diff}}\approx 0$ cm^3 mol^{-1} in aprotic solvents, -4.6 cm^3 mol^{-1} in acetone, a solvent of low viscosity, and ca. -4 cm^3 mol^{-1} in protic solvents. $\Delta V^{\neq}_{\mathrm{obs}}$ in aprotic solvents (toluene and nitrobenzene) are almost equal to $\Delta V^{\neq}_{\mathrm{diff}}$, indicating that the spin exchange in such solvents is governed by diffusion of the Tanone radicals. The relatively large difference between $\Delta V^{\neq}_{\mathrm{obs}}$ and $\Delta V^{\neq}_{\mathrm{diff}}$ was found in protic solvents (methanol, 2-propanol, and water). When we examined the relationship between $\Delta V^{\neq}_{\mathrm{obs}}$ and $\Delta V^{\neq}_{\mathrm{diff}}$ in protic solvents, a plot of $\Delta V^{\neq}_{\mathrm{obs}}$ against $\Delta V^{\neq}_{\mathrm{diff}}$ was found to be almost linear; a slope of 1.0 ± 0.1 and intercept of -4.2 ± 1.1. For reactions governed by a diffusive process, the slope and intercept are expected to be ca. 1 and ca. 0, respectively. An appar-

Table 2. Activation Volumes (cm^3 mol^{-1}) for Spin Exchange of Tanone Radicals in Various Solvents

Solvent	T/K	$\Delta V^{\neq}_{\mathrm{obs}}$	$\Delta V^{\neq}_{\mathrm{diff}}$	$\Delta V^{\neq}_{\mathrm{obs}}-\Delta V^{\neq}_{\mathrm{diff}}$
Toluene	296	13.7±0.9	14.2	−0.5
Nitrobenzene	293	13.3±0.7	14.1	−0.8
Acetone	303	7.7±0.4	12.3	−4.6
2-Propanol	298	15.4±0.9	19.5	−4.1
Methanol	298	6.7±1.1	8.8	−2.1
Water	288	−7.6±0.4	−2.5	−5.1

ent disagreement between the intercept obtained in protic solvents and that expected for the diffusion-controlled reactions was found and this finding may be ascribed to specific solvation of alcohols to nitroxide radicals. In fact, the observations of large hyperfine coupling constants and g-values of nitroxide radical in protic solvents compared with those in aprotic solvents have been reported.[11] The present value (−4.6 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$) in acetone is probably to be attributed to weak exchange.[4]

Value of the Activation Volume for Diffusive Processes. Although $\Delta V^{\neq}_{\mathrm{diff}}$ is formally obtainted from the pressure dependence of viscosity (Eq. 2), no clear-cut interpretation of its physical meanings has been put forward so far. In this section, we would like to try to explain the physical meanings of the activation volume of the diffusion process and to estimate its value.

According to the theory of rate processes,[12] the flow of a molecule in the liquid phase can be treated as a rate process. The jump of a molecule from its equilibrium site to the neighboring site is described as a passage over a potential energy surface. The number of times that a molecule passes over the barrier per second is given by

$$k=(kT/h)(q^{\neq}/q)\exp(-\varepsilon_0/kT), \qquad (6)$$

where q's are the partition functions and the other notations have their usual meanings. If the passage is to occur, the generation of a hole is necessary, and the excavation of such a hole requires the expenditure of energy. According to this model,[12] the potential energy ε_0 can approximately be related to the viscosity coefficient η of the medium such as

$$\eta=(hL/V)(q/q^{\neq})\exp(\varepsilon_0/kT), \qquad (7)$$

where L is the Avogadro number and V the partial molar volume of the molecule. Combining Eq. 6 with Eq. 7, k is given by

$$k=(RT/V)/\eta. \qquad (8)$$

Thus the number of passages over the barrier is inversely proportional to η. If we tentatively set $\eta=10^{-3}/$ Pa·s (the order of viscosities for most solvents under ordinary conditions), $V=10^{-4}/\mathrm{m}^3\ \mathrm{mol}^{-1}$, and $RT=2.5\times10^3/\mathrm{J\ mol}^{-1}$, then we have $k=2.5\times10^{10}/\mathrm{s}^{-1}$, in a reasonable order of magnitude.

It follows from Eq. 8 that

$$RT(\partial\ \ln\eta/\partial p)_T=\kappa_T RT+\Delta V^{\neq}_{\mathrm{diff}} \qquad (9)$$

This is formally the same as Eq. 5. Thus the process for a particle to move from the initial state to the activated state is deduced to require two kinds of energies. The first term comes from the kinetic energy even for a point particle. On the theoretical basis, this term has been predicted[13,14] and has been verified recently.[15] For most liquids, $\kappa_T RT$ is an order of a few $\mathrm{cm}^3\ \mathrm{mol}^{-1}$.

The second term is considered to be associated with the work to generate a hole as stated above. The volume of this hole is predicted to be a fraction of the molecular volume of the solvent.[12] This could be justified as follows: Let λ be the distance between two equilibrium positions in the direction of motion. The potential energy barrier is assumed to be symmetric. The distance between the initial and the activated state position is $\lambda/2$, thus the ratio of the volume of the molecule to that of the hole may be ca. 8 $(=\lambda^3/(\lambda/2)^3)$. Therefore, the predicted $\Delta V^{\neq}_{\mathrm{diff}}$-value is an order of 12—25 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ since the partial molar volume of most solvents are between 100 and 200 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$. This is in agreement with available data for $\Delta V^{\neq}_{\mathrm{diff}}$ estimated from the pressure dependence of the viscosity.[2,3] It is noted that the reported $\Delta V^{\neq}_{\mathrm{diff}}$-values are almost independent of the size of the diffusing molecules. For instance, the $\Delta V^{\neq}_{\mathrm{diff}}$-values for the termination constants of free radical polymerization of vinyl monomers are between 13 and 21 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$.[16] In this case only work to make a hole for the terminal radical segment to move need be necessary.

Concluding Remarks

We estimated the rate constant for the spin exchange reaction of Tanone at high pressures by means of linewidth measurement. The rate was well correlated to the applied pressure. By comparing the rate constant and the activation volume with those for diffusive processes, the conclusion that the rate of the spin exchange is virtually governed by a diffusive process is given. An interpretation for the activation volume associated with the diffusive process is also given.

This work was supported by a Grant-in-Aid for Encouragement of Young Scientist from the Ministry of Education of Japan (No. 62740259).

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