252 © 1990 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 63, 252—254 (1990) [Vol. 63, No. 1

ESR Studies at High Pressure. II. Spin Exchange of 2,2,6,6-Tetramethyl-4-oxo-1-piperidinyloxyl in Protic and Aprotic Solvents

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(Received July 13, 1989)

Synopsis. The activation volumes for the spin exchange of 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxyl (Tanone) in protic and aprotic solvents were determined from the pressure dependence of the rate constants, and were compared with those for the diffusive process. It was concluded that the rate process for the spin exchange in aprotic solvents is a diffusion-controlled one, and in protic solvents an encounter complex as intermediate is formed. The average reaction volume for the complex formation in protic solvents was estimated to be -3.6 cm^3 mol^{-1}.

In our recent work,[1)] we have examined the pressure effects on the spin-exchange rate of Tanone radicals in solutions. It has been found that the activation volumes ($\Delta V_{\text{obsd}}^{\neq}$) for the spin exchange are virtually the same as those for the diffusive process ($\Delta V_{\text{diff}}^{\neq}$) in aprotic solvents (toluene and nitrobenzene), while a substantial difference between them is found in protic solvents (water, methanol, and 2-propanol), and specific solvation has been suggested for the latter case. The present work aims to confirm whether such specific solvation is characteristic of protic solvents.

Experimental

Tanone was purchased from Wako Pure Chemicals and was used without purification. Ethanol, 2-methyl-1-propanol, benzene, and *o*-xylene are of guaranteed grade and were purified in the usual manner.

The high-pressure vessel for the ESR measurements is the same as that described elsewhere.[1)] The solution was deoxygenated by nitrogen bubbling. ESR signals were recorded by an X-band spectrometer with a 100-kHz field modulator. The peak-to-peak width of the central component of the hyperfine structure (hfs) of the Tanone radicals was measured at room temperature. Owing to remarkable line-broadening, the estimation of the intrinsic linewidth of each component of the hfs was unsuccessful in alcohols higher than 2-methyl-1-propanol. The accuracy of measurements was ±1.5%.

Results and Discussion

Spin Exchange in Alcohols. The second-order rate constants k_{obsd} for the spin exchange of the Tanone radicals in solutions were estimated from the linewidth of ESR spectra using the following equation.[2)]

$$k_{\text{obsd}} = A(\Delta H - \Delta H_0)/C, \qquad (1)$$

where ΔH/mT and ΔH_0/mT are linewidths in the presence and absence of the spin exchange, respectively. A-value for the spin exchange of nitroxide radicals is known to be 2.28×10^8 mT^{-1} s^{-1} and C denotes the radical concentration. The values of k_{obsd} obtained at 1 bar in ethanol, 2-methyl-1-propanol, benzene, and *o*-xylene are given in Table 1, together with those in other solvents.[1)]

Spin exchange takes place via collisions among paramagnetic species. In alcohols, specific solvation to the nitroxide radicals is considered to be operating.[3)] Therefore, for association reactions which involve the specific solvent–solute interactions, it would be better to start with a generalized expression:[4)]

$$R + R \underset{}{\overset{K_1}{\rightleftharpoons}} (R,R) \xrightarrow{k_2} RR,$$

where (R,R) represents an encounter complex in which the radicals are separated by one or two solvent molecules, and RR represents a collisional complex upon the formation of which the spin exchange takes place invariably. Then the apparent second-order rate constant k_{obsd} of the spin exchange can be expressed by

$$k_{\text{obsd}} = K_1 k_2. \qquad (2)$$

According to the treatments of Eigen[5)] and Fuoss,[6)] the association constant, K_1 /dm^3 mol^{-1}, for the formation

Table 1. Rate Constants (k_{obsd}/s^{-1}), Activation Volumes ($\Delta V_{\text{obsd}}^{\neq}$/cm^3 mol^{-1}) for Spin Exchange, and Apparent Activation Volumes ($\Delta V_{\text{diff}}^{\neq}$/cm^3 mol^{-1}) for the Diffusive Process

Solvent	$10^{-9}\,k_{\text{obsd}}$	$\Delta V_{\text{obsd}}^{\neq}$	$\Delta V_{\text{diff}}^{\neq}$	ΔV_1 ($\Delta V_{\text{obsd}}^{\neq} - \Delta V_{\text{diff}}^{\neq}$)
Benzene	5.31±0.34	18.4±1.0	17.7	0.7
Toluene[a)]	5.27±0.09	13.7±0.9	14.2	−0.5
o-Xylene	4.17±0.16	15.3±1.2	15.5	−0.2
Nitrobenzene[a)]	1.77±0.11	13.3±0.7	14.1	−0.8
Water[a)]	1.91±0.10	−7.6±0.4	−2.5	−5.1
Methanol[a)]	5.52±0.21	6.7±1.1	8.8	−2.1
Ethanol	3.51±0.09	9.5±0.6	13.8	−4.3
2-Propanol[a)]	2.83±0.11	15.4±0.9	19.5	−4.1
2-Methyl-1-propanol	1.89±0.05	19.6±0.4	22.0	−2.4

a) Cited from Ref. 1.

of the encounter complex can be approximately given by Eq. 3.

$$K_1 = 4\pi L a^3/3000, \qquad (3)$$

where L is the Avogadro number and a/m is the effective distance of the closest approach of the radicals in the encounter complex. Let us assume that the Tanone radicals are separated by one solvent molecule in the encounter complex. Using the effective radii 4.2×10^{-10} m for the Tanone radical,[7] 2.3×10^{-10} m for ethanol,[8] and 1.4×10^{-10} m for water,[8] the equilibrium constants K_1 are calculated to be 5.5 M^{-1} (ethanol) and 3.5 M^{-1} (water). With the K_1- and k_{obsd}-values in Table 1, the rate constants k_2 of the release of the solvent molecule trapped in the encounter complex are estimated to be 6.4×10^{8} s^{-1} (ethanol) and 5.4×10^{8} s^{-1} (water). These values may be compared with the value of 3×10^{8} s^{-1} for the exchange reaction of water molecules on the Cd^{2+} ions.[9]

The rate constant k_2 may be regarded as a measure of the interaction between solvent and solute. In this sense, the interaction between water and Tanone seems to be stronger than that between ethanol and Tanone. The situation, however, is not so simple, because the easiness of the release also depends on the interaction between the surrounding and releasing solvents. More direct information about the solvent-solute interaction in our case is accessible from the ESR nitrogen hyperfine coupling constant (hfcc). The hfcc value varies from a_N=1.59 mT in water to 1.49 mT in ethanol. This fact indicates that the specific solvation of water to the radical is more strongly operating than that of ethanol, which is in line with the above calculation.

Pressure Effects. The pressure dependence on the rate constants of the spin exchange in ethanol, 2-methyl-1-propanol, benzene, and *o*-xylene is shown in Fig. 1. It is seen that the rate constant of the spin exchange decreases as the applied pressure increases.

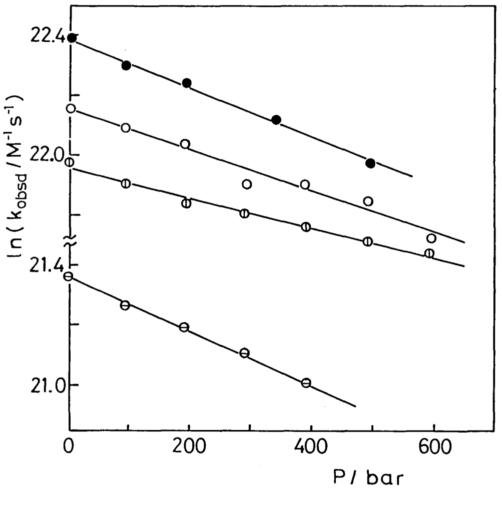

Fig. 1. Pressure dependence of the rate constants of the spin exchange; (●) in benzene, (○) in *o*-xylene, (◐) in ethanol, (⊖) in 2-methyl-1-propanol.

The apparent activation volume ($\Delta V_{obsd}^{\ddagger}$) can be estimated by using the following equation:

$$\Delta V_{obsd}^{\ddagger} = -RT(\partial \ln k_{obsd}/\partial p)_T + \Delta n^{\ddagger}\kappa_T RT, \qquad (4)$$

where $\Delta n^{\ddagger}$ is the difference in the number of species between the activated complex and reactants, and κ_T the isothermal compressibility of the medium.[10] The values of $\Delta V_{obsd}^{\ddagger}$ are given in Table 1.

The second-order rate constant for diffusion-controlled reactions may be expressed in terms of a Smoluchowski–Stokes–Einstein type equation as

$$k_{diff} \propto RT/\eta, \qquad (5)$$

where η is the viscosity coefficient of the medium. Hence the apparent activation volume ($\Delta V_{diff}^{\ddagger}$) for a diffusive process is given by

$$RT(\partial \ln k_{diff}/\partial p)_T = -RT(\partial \ln \eta/\partial p)_T = -\Delta V_{diff}^{\ddagger} - \kappa_T RT. \qquad (6)$$

In the preceding paper,[1] we have discussed the physical meanings of $\Delta V_{diff}^{\ddagger}$ which can be formally obtained by Eq. 6. Using the available η-P data,[10] $\Delta V_{diff}^{\ddagger}$ in a variety of solvents were estimated and they are given in Table 1. In Fig. 2, $\Delta V_{obsd}^{\ddagger}$ is plotted against $\Delta V_{diff}^{\ddagger}$, and some interesting features can be found as follows: (1) The plots are divided into two groups, i.e. aprotic and protic solvent groups. (2) Each falls on a straight line having the slope of unity. (3) The line originating from the former group passes through the origin, but the line of the latter group is shifted downward by about 4 cm^3 mol^{-1}. The above findings show obviously that in aprotic solvents, the essential feature of the spin exchange process is nothing but a diffusive one, and no concept of the encounter complex need be introduced. On the other hand, the downward shift seems to indicate the existence of the encounter complex.

Liphard and Jost[11] reported that the reaction volume of the encounter complex formation is -3.1 cm^3 mol^{-1} for the reaction of Alizalin Yellow GG with OH^- in water. They explained the small

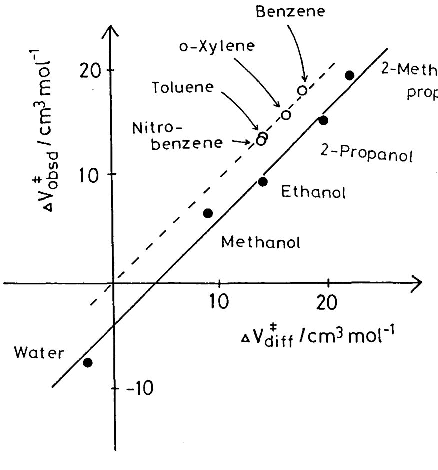

Fig. 2. Relationship between $\Delta V_{obsd}^{\ddagger}$ and $\Delta V_{diff}^{\ddagger}$.

negative value as due to the contraction of the complex along $R_1 \cdots H_2O \cdots R_2$ axis. The volume contraction of $-1.4\ \text{cm}^3\ \text{mol}^{-1}$ for the association reaction of Pyronine G in aqueous solutions is reported by Ohling.[12] These values are near to the shift in our case. Hence it can be safely said that the downward shift is due to the formation of association complexes between Tanone and protic solvents. In this case, the volume change corresponding to Eq. 2 is given by

$$V_{\text{obsd}}^{\ddagger} = \Delta V_1 + \Delta V_2^{\ddagger}, \tag{7}$$

where ΔV_1 denotes the volume change accompanied by the formation of the encounter complex, and $\Delta V_2^{\ddagger}$ the activation volume for the second step. In this step, the sandwiched solvent molecule between the radicals in the encounter complex must be pushed out in order to contact the paired radicals to each other. Therefore, $\Delta V_2^{\ddagger}$ is to be equivalent to $\Delta V_{\text{diff}}^{\ddagger}$. For details, the preceding paper should be referred to.[1] The values of ΔV_1 can be estimated by substracting $\Delta V_{\text{diff}}^{\ddagger}$ from $\Delta V_{\text{obsd}}^{\ddagger}$, and they are given in Table 1. In agreement with the above statement, ΔV_1 is near zero in aprotic solvents, and the average value of ΔV_1 is $-3.6\ \text{cm}^3\ \text{mol}^{-1}$ in protic solvents.

In short, it is deduced that for the spin-exchange reaction the diffusive process alone is operating in aprotic solvents, while in protic solvents, some stabilization is operating through the encounter complex formation, followed by the diffusive process. These are in line with our previous suggestion.

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