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Ultrasonic Relaxation Kinetics on Fast Deuteron Transfer Reaction

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Propylamine has been selected to investigate the isotope effect of a fast deuteron transfer reaction by ultrasonic relaxation method. Ultrasonic absorption coefficients of propylamine in heavy water (D_2O) at 25 °C in the concentration range from 0.0107 to 0.6300 mol dm^{-3} have been measured by pulse and resonance methods over the frequency range from 0.8 to 220 MHz. A Debye-type single relaxation absorption has been observed in the solution. From the dependence of the ultrasonic relaxation parameters on the concentration and solution pH, the source of the observed relaxation has been attributed to a perturbation of the chemical equilibrium associated with the deuteron transfer reaction. The rate and equilibrium constants have been determined by the measurement of the deuteroxyl ion concentration dependence of the relaxation frequency. Also the standard volume change of the reaction has been determined from the concentration dependence of the maximum absorption per wavelength and the adiabatic compressibility has been calculated from the density and the sound velocity in the solution. These results have then been compared with those obtained for propylamine in light water (H_2O). The forward rate constant is greater and the reverse rate constant is smaller in D_2O than in H_2O. The standard volume change for deuteron transfer is greater than that for proton transfer reaction, and the adiabatic compressibility shows a similar trend. These data support an argument that there exists a stronger hydrogen bond in D_2O than in H_2O. The difference of the stability in the intermediate states, $R-ND_3^+\cdots OD^-$ and $R-NH_3^+\cdots OH^-$, has also been considered from the results of the isotope effects.

Introduction

It is well-known that chemical reactions are affected by the structure of the solvent, especially when the solvent itself participates in the reaction. In our previous studies[1−3] on proton transfer reaction by the ultrasonic relaxation method, it was found that some additives in light water cause the change in water structure, and the proton transfer reaction rates depend on the extent of solvent structural change. We have desired to gain insight into the dynamic properties in heavy water for two reasons. First, such studies may reveal the structural difference between heavy and light water from the comparison of the rate constants of a diffusion-controlled reaction. This is because both heavy and light water participate in deuteron and proton transfer reactions, respectively, and heavy water is considered to be substantially more structured than light water at room temperature.[4] The second goal is to obtain information on the stability of an intermediate of the reaction because hydrolysis of amines proceeds through the intermediate which may be the key to the elucidation of the detailed reaction mechanism. A study of isotope effects should provide a powerful means to examine the structure of the intermediate. To evaluate the solvent effects on the hydrolysis, propylamine was chosen as solute in heavy water and the ultrasonic study was carried out on this system. The results are discussed, in this report, by comparing with those in light water.

Experimental Section

Chemicals. The purest grade propylamine and heavy water (more than 99.75%), as well as sodium hydroxide, were purchased from Wako Pure Chemical Ltd. They were used as received.

Measurements. A pulse method was utilized to measure the absorption coefficients in the frequency range from 15 to 220 MHz using 5 and 20 MHz fundamental x-cut quartz crystals. A resonance method was used to obtain the absorption coefficients in the range from 0.8 to 7 MHz. The details of these apparatuses were described elsewhere.[5,6] Sound velocity was obtained by the resonator at around 3 MHz. Values of pH and density in solutions were measured by a glass electrode (HM-60s, Toa Denpa) and a vibrating density meter (DMA 60/602 Anton Paar), respectively. Water bath (Eyela Uni Ace Bath

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TABLE 1: Ultrasonic Parameters for Propylamine in D_2O at 25 °C

C_o (mol dm^{-3})	pH	f_r (MHz)	A (10^{-15} s^2 m^{-1})	B (10^{-15} s^2 m^{-1})	v (m s^{-1})	ρ (kg dm^{-3})
0.0107	11.54	15.8 ± 1.6	63 ± 6	27.1 ± 0.3	1400.52	1.1030
0.0323	11.81	24.1 ± 1.4	89 ± 6	26.1 ± 0.3	1401.77	1.1020
0.0582	11.94	32.9 ± 4.4	79 ± 9	28.4 ± 1.6	1405.23	1.1019
0.1005	12.09	39.6 ± 0.9	102 ± 2	25.8 ± 0.2	1408.76	1.1011
0.2030	12.20	47.7 ± 1.6	114 ± 4	24.3 ± 0.5	1415.58	1.0995
0.3002	12.33	62.9 ± 1.3	111 ± 2	22.6 ± 0.4	1422.20	1.0973
0.3956	12.42	62.4 ± 1.9	112 ± 3	27.1 ± 0.6	1429.86	1.0961
0.6300	12.47	68.3 ± 1.1	116 ± 1	27.6 ± 0.4	1440.58	1.0922

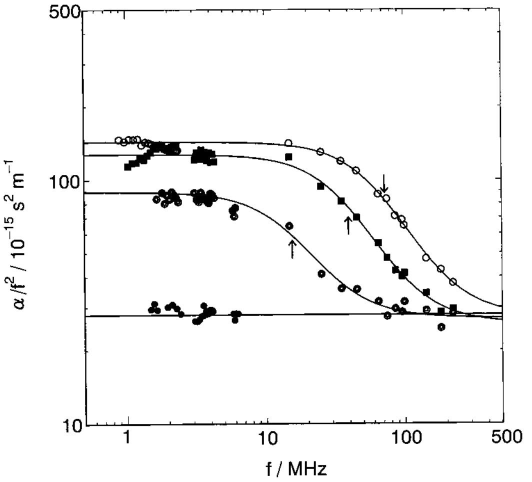

Figure 1. Representative ultrasonic relaxation absorption spectra for propylamine in D_2O: (●) pure D_2O; (◎) 0.0107 mol dm^{-3}; (■) 0.1005 mol dm^{-3}; (○) 0.6300 mol dm^{-3}. The arrows show the location of the relaxation frequency.

NCB-2200) and circulating water (Lauda, RM20) were used to maintain the measurement temperature at 25 °C.

Sample solutions were prepared by weighing. They were prepared at least one day before the measurements and were stored under nitrogen gas atmosphere to avoid contamination by carbon dioxide as much as possible. The solution pH was adjusted to the desired value, if necessary, by an addition of concentrated solution of NaOH in D_2O.

Results and Discussion

The concentration of propylamine is much smaller than that of the solvent, D_2O, in the present research work. When heavy water is used as solvent, the amino hydrogen atoms of propylamine are spontaneously exchanged with deuterium.[7] Therefore, most of the amino groups are deuterated.

Figure 1 shows representative ultrasonic absorption spectra of propylamine in D_2O. As shown in this figure, a clear relaxational absorption is observed in the concentration range from 0.0107 to 0.6300 mol dm^{-3}. That is, the absorption coefficients divided by the square of the frequency, α/f^2, are dependent on the frequency over the frequency range of the measurements. The frequency dependence has been tested by Debye-type relaxation equation as follows:

$$\alpha/f^2 = A/[1 + (f/f_r)^2] + B \qquad (1)$$

where f_r is the relaxation frequency, A is the amplitude of the ultrasonic absorption, and B is the background absorption. The ultrasonic parameters f_r, A, and B were determined by a nonlinear least-mean-squares method and they are tabulated in Table 1 along with the solution pH and the sound velocity. The solid curves shown in Figure 1 are the calculated values using eq 1. Excellent agreement can be seen between the experimental and calculated values. These results suggest that the Debye-type single relaxation process is observed in these solutions. Figure 2 shows the ultrasonic absorption spectra for 0.0582 mol dm^{-3} propylamine in D_2O at different pH's, in which the higher pH solution is prepared by adding the concentrated NaOH solution. As is seen, the observed relaxation process is highly sensitive to the solution pH, which phenomenon has been found in aqueous solutions of amines and is characteristic for a proton transfer reaction. The propylamine concentration dependence of the relaxation frequency in D_2O and in H_2O (the latter data were those reported previously.[3]) is presented in Figure 3. The relaxation frequency in D_2O shifts to lower frequency range, when compared with that in H_2O. However, a very similar trend of monotonic increase is observed although the magnitudes are dependent on the solvents. In D_2O, the relationships between the concentration and the amplitude, A, or the background

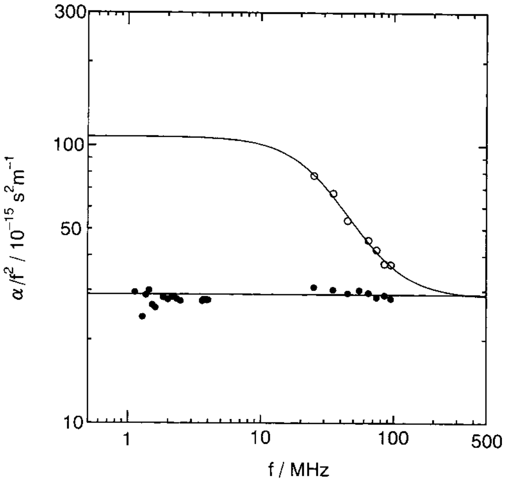

Figure 2. Ultrasonic absorption spectra for 0.0582 mol dm^{-3} propylamine in D_2O: (○) pH 11.94; (●) pH 13.47.

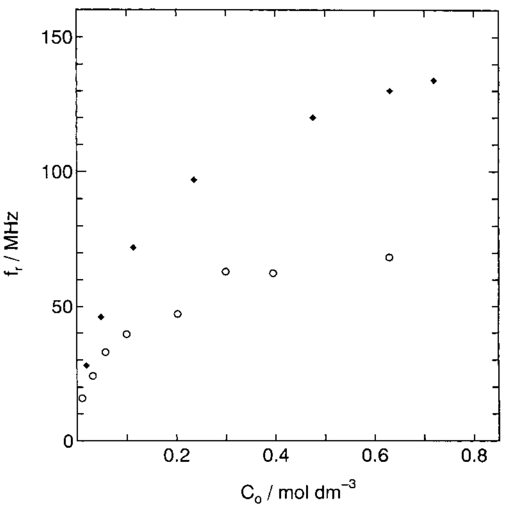

Figure 3. Plots of relaxation frequency against concentration of propylamine in D_2O (○) and in H_2O (◆).

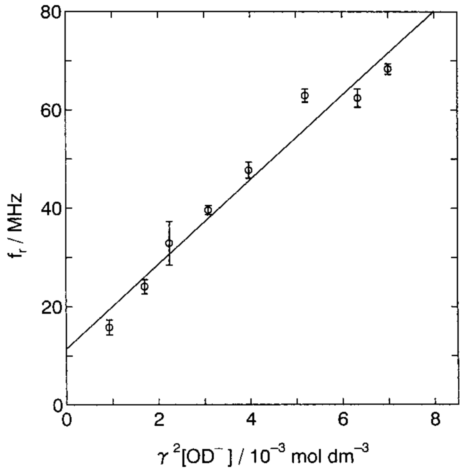

Figure 4. Plots of relaxation frequency against $\gamma^2[\mathrm{OD}^-]$ for propylamine in D_2O.

absorption, B, also show similar trends to those in H_2O. From the similar concentration dependences of the ultrasonic parameters, and the sensitive pH dependence of the absorption, the source of the observed relaxation in D_2O is predicted to be associated with hydrolysis of amine. It is a deuteron transfer reaction shown as follows:

$$\mathrm{R\text{-}ND_3^+ + OD^-} \underset{\text{step I}}{\underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}}} \mathrm{R\text{-}ND_3^+\cdots OD^-} \underset{\text{step II}}{\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}}} \mathrm{R\text{-}ND_2 + D_2O} \quad (2)$$

where k_{ij} is the rate constant at each step. In general, the relationship between the relaxation frequency and the reactant concentrations is derived from the coupled reactions (step I and step II). However, an analysis based on the assumption that only step I is associated with the observed relaxation process was used because the analysis through the coupling reaction mechanisms gave unreasonable rate and equilibrium constants.[3,8] It is considered that step II may proceed too fast to affect step I. Therefore, the relationship between the relaxation frequency and the reactant concentrations is derived as eq 3 and simplified to eq 3′:

$$\tau^{-1} = 2\pi f_r = k_{12}\gamma^2([\mathrm{R\text{-}ND_3^+}] + [\mathrm{OD^-}]) + k_{21} \quad (3)$$

$$= 2k_{12}\gamma^2[\mathrm{OD^-}] + k_{21} \quad (3')$$

where γ is the activity coefficient calculated from the Davis equation.[9] Figure 4 shows the plots of f_r vs $\gamma^2[\mathrm{OD}^-]$. Here, the concentration of deuteroxyl ions, $[\mathrm{OD}^-]$, is calculated according to the pH meter reading using the formula:[10−13]

$$\mathrm{pD}_{\text{in } D_2O} = \mathrm{pH}_{\text{meter reading in } D_2O} + 0.41 \quad (4)$$

The ionization constant pK_w equals 14.955 for D_2O at 25 °C.[14a] The good linear relationship shown in Figure 4 confirms that the source of the relaxational absorption is due to the deuteron transfer reaction associated with the hydrolysis of the deuterated propylamine. The rate constants, k_{12} and k_{21}, were determined from the slope and intercept of the plots using a least-mean-squares method and they are listed in Table 2 along with those of propylamine in H_2O for comparison. The forward rate constant is reasonable as the diffusion-controlled reaction.

Table 2 also lists the dissociation constant, K_b, which is estimated from the deuteroxyl ion concentration and the analytical concentration of propylamine, C_o, using the relationship

$$K_b = \gamma^2[\mathrm{OD^-}]^2/(C_o - [\mathrm{OD^-}]) \quad (5)$$

The relationship between K_b in D_2O and that in H_2O is proposed as[10]

$$pK_b(\text{in } D_2O) \doteqdot 1.02\ pK_b(\text{in } H_2O) + 0.42 \quad (6)$$

This gives $K_b = 1.8 \times 10^{-4}$ mol dm^{-3} in D_2O which is considered to be in satisfactory agreement with that in Table 2.

From the equilibrium constant for step I in eq 2, K_{21}, defined as $K_{21} = k_{21}/k_{12}$, and the dissociation constant, K_b, the equilibrium constant for step II, K_{32} can be calculated using the relationship

$$1/K_b = 1/K_{21} + 1/K_{21}K_{32} \quad (7)$$

The obtained K_{32} value for propylamine in D_2O is listed in Table 2 along with that in H_2O for comparison.

Another useful parameter for elucidating the source of the relaxation is the maximum absorption per wavelength, μ_{max}, which is calculated with the use of the relaxation frequency, f_r, the amplitude of the ultrasonic absorption, A, and the sound velocity, v. This quantity is related to the standard volume change of the reaction, ΔV.

$$\mu_{max} = 0.5Af_r\, v = \pi\rho v^2\Gamma(\Delta V)^2/2RT \quad (8)$$

where ρ is the solution density and Γ is the concentration term given by following equation:

$$\Gamma = (1/[\mathrm{OD^-}] + 1/[\mathrm{R\text{-}ND_3^+}] + 1/[\mathrm{R\text{-}ND_3^+\cdots OD^-}])^{-1} \quad (9)$$

The contribution of the activity coefficient to Γ is considered to be negligible.[15] The calculated ΔV value is listed in Table 2. It appears somewhat greater than that in H_2O.

From the solution density and sound velocity, it is possible to estimate the adiabatic compressibility, β_s, using Laplace's equation as

$$\beta_s = -(1/V)(\partial V/\partial P)_s = 1/\rho v^2 \quad (10)$$

The dependence of β_s on the concentration of propylamine in D_2O and in H_2O is shown in Figure 5. It is seen that the values in D_2O are greater than those in H_2O.

Ultrasonic studies to obtain kinetic and thermodynamic properties for fast reactions in D_2O have seldom been carried out to our knowledge.[16] It is interesting to note the differences between the rate constants, the standard volume change of the reactions, and the adiabatic compressibility in D_2O and in H_2O.

First, a slightly greater forward rate constant for the diffusion-controlled reaction is obtained in D_2O (Table 2). This result is not explained by the solution viscosity because the viscosity coefficient for D_2O is greater than that for H_2O.[17] Generally, the mobility of the hydrogen ions is higher than that of deuterium ions; the ratio between them is 1.4 at 25 °C.[18] Therefore, one predicts that the rate constant should be smaller for deuteron transfer than for proton transfer. This is indeed observed for many cases of slow proton or deuteron transfers.[19] However, the present result is contrary to this expectation. It is worthwhile to consider a microscopic feature of the reaction. According to Debye, the diffusion-controlled rate constant, k_{12},

TABLE 2: Rate and Thermodynamic Constants for Propylamine in D_2O and in H_2O at 25 °C

	k_{12} (10^{10} mol^{-1} dm^3 s^{-1})	k_{21} (10^7 s^{-1})	K_{21} (10^{-3} mol dm^{-3})	K_{32}	K_b (10^{-4} mol dm^{-3})	ΔV (10^{-6} m^3 mol^{-1})
propylamine in D_2O	2.70 ± 0.14	7.1 ± 1.3	2.6	0.041	1.04 ± 0.07	39.6 ± 3.3
propylamine in H_2O^a	2.1 ± 0.2	13 ± 4	6.2	0.0995	5.6 ± 1.5	33 ± 8

[a] The data quoted from refs 1, 2, and 3.

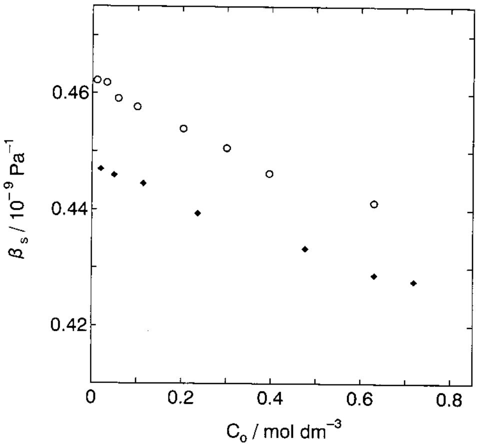

Figure 5. Concentration dependence of adiabatic compressibility for propylamine in D_2O (○) and in H_2O (◆).

is given by[20]

$$k_{12} = \sigma N z_A z_B e_0^{\,2}(D_A + D_B)/\epsilon\epsilon_0\kappa T[\exp(z_A z_B e_0^{\,2}/4\pi\epsilon\epsilon_0 r_d \kappa T) - 1] \qquad (11)$$

where σ is a steric factor, N is Avogadro constant, z_i is the algebraic charge of ions, e_0 is the electronic charge, D_i is the diffusion coefficient of the reacting ions, ϵ_0 is the dielectric constant in a vacuum, ϵ is the dielectric constant of the solvent, κ is Boltzmann constant, and r_d is an effective radius for the reaction. Equation 11 is well suited to the interpretation of proton transfer reactions of various amines and amino acids in H_2O.[20-22] To apply the equation to the present system, the dielectric constant available in the literature[14b] is used and the diffusion coefficient for OD^-, D_{OD}, has to be estimated. D_{OD} is considered to be slightly smaller than D_{OH} because of the smaller mobility of deuterium ion in D_2O.[18] Therefore, the value of k_{12} in D_2O should have been smaller than that in H_2O, if the reaction radii were the same in the two solvents. However, a model calculation using eq 11 shows that the very crucial parameter for the rate constant is the reaction radius, r_d. When the steric factor, $\sigma = 0.58$, and the diffusion coefficient for OD^-, $D_{OD} = D_{OH}/1.4$, are assumed, r_d is calculated to be 13×10^{-10} m for $k_{12} = 2.7 \times 10^{10}$ mol^{-1} dm^3 s^{-1}. This reaction radius is much greater than that for proton transfer reaction in H_2O, such as $R\text{-}NH_3^+\cdots OH^-$, 5.0×10^{-10} m, which is calculated under the same conditions using $\sigma = 0.58$.[2,23] Although the calculated reaction radius for the reaction in D_2O seems to be overestimated, it may suggest that the interaction between $R\text{-}ND_3+$ and OD^- provides longer range order than that between $R\text{-}NH_3^+$ and OH^-, and this situation may indicate that the intermediate, $R\text{-}ND_3^+\cdots OD^-$, of the reaction of hydrolysis is formed by a slightly stronger bond when compared with $R\text{-}NH_3^+\cdots OH^-$. Lee et al.[24] have calculated from theory that a stable intermediate between ammonium and hydroxide ions includes three water molecules as $NH_3^+(3H_2O)OH^-$. Therefore, the intermediate shown in eq 2 may also include several D_2O molecules and the reaction radius is estimated to be greater than the characteristic hydrogen-bond length.

The isotope effect for the forward rate constants, $k_{12}^H/k_{12}^D = 0.78$, may be interpreted as follows. The vibrational energy level for the reactants, $R\text{-}ND_3^+$ and OD^-, is considered to be lower than that for $R\text{-}NH_3^+$ and OH^- because the former contain heavier atom. Even if the energy level is lower in D_2O, the rate constants in D_2O is greater than that in H_2O. The rate constant should be controlled by an activation energy and the activation energy for the forward process in D_2O for step I may be smaller than that in H_2O. That is, the vibrational energy of the activated complex may decrease, which causes the rate constant in D_2O to increase.

Next we consider the result for the reverse rate constant. It is smaller in D_2O than in H_2O as seen in Table 2. This means that the intermediate is more stable than in H_2O. The isotope effect for the reverse process is $k_{21}^H/k_{21}^D = 1.83$. This effect is simply interpreted by the stability of the intermediate due to the decrease in the energy level caused by the deuterium. The decrease in the level for the intermediate is greater than the decrease for the activated complex. This may be because multiple D_2O molecules still exist in the intermediate.

There has been no report, to our knowledge, concerning opposite isotope effects for the forward and reverse rate constants of fast reactions in solutions. This kind of isotope effect has also been found in slow reactions of hydrolysis of esters.[25]

Finally, the standard volume change and compressibility results are considered. The volume change estimated in D_2O is slightly greater than that in H_2O. As was discussed above, the intermediates still include some solvent molecules and it is considered that these reactants cause the large volume change of the reaction. The solution compressibility in D_2O is greater than that in H_2O, which means that the hydrogen-bond networks are further reorganized in D_2O. The deuteron transfer reaction is proceeding through these networks (Grotthuss mechanism) and the reaction rate may be then facilitated.

In conclusion, it is found in this study that the diffusion-controlled rate constant for propylamine in heavy water is greater than that in light water and the rate of the departure to individual ions shows the opposite trend. These results have been interpreted in terms of the effective radius for the reaction and the stabilization of the intermediate, respectively.

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