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Studies on the Proton Magnetic Resonance Spectra of Aliphatic Systems. IX.[1] Complex Shift and Equilibrium Constant of Association between Excess Amount of Aliphatic Alcohol and Tris(dipivalomethanato)europium

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From the two step equilibria of the complex formation between the shift reagent $Eu(DPM)_3$ and a large excess of aliphatic alcohol, the two complex shifts Δ_1, Δ_2 and equilibrium constants K_1, K_2 are estimated. Δ_1 and K_1 are comparable with Δ_c and K_c obtained in an equimolar condition, and the magnitudes of K_2 are included within the errors of K_1. The infinite concentration shift Δ_{ic} obtained in the presence of a large excess of the donor is also comparable with Δ_1. These results suggest the role of the solvent molecule occupying an overwhelming majority in the sample solution, where the molecular interaction is a time-averaging 1:1 donor-acceptor collision in the nuclear magnetic resonance time scale.

Keywords——shift reagent; complex shift; equilibrium constant; infinite concentration shift; aliphatic alcohol

Introduction

In the previous report,[1] the details of the 1:1 complex formation between the shift reagent $Eu(DPM)_3$ and aliphatic alcohol were examined under the condition of $Eu(DPM)_3 \gtrsim ROH$. We extended here our discussion of this complex formation in the presence of a large excess of aliphatic alcohol, and examined the possibility of the simultaneous formation of the 1:2 complex. This possibility has been already supported for the association between the shift reagent $Eu(FOD)_3$ and aliphatic ketone[3] under similar experimental condition of this work. In this work, we expected the contribution of the 1:2 complex in the presence of a large excess of the donor, but the evidence of this complex formation could not be realized. In addition, the so-called infinite concentration shift Δ_{ic} estimated from the linear relation between the successive dilution shift and total concentration term $C_t^{-2/3}$ was approved to the 1:1 complex shift Δ_1.[1]

Experimental

Aliphatic alcohols used in this work were of the J.I.S. grade. They were dried over Linde molecular sieves 4A for some days before use. The shift reagent $Eu(DPM)_3$ purchased from Dojin Chemical Laboratories was sublimed under the reduced pressure and stored over silica gel in a desiccator. Sample preparations were carried out in a dry box. All nuclear magnetic resonance (NMR) spectra were recorded on a Hitachi R-20A type spectrometer at 35°. Line positions are reported relative to the internal reference Me_4Si with an accuracy of ±1.0 Hz. The details of the experimental condition are mentioned in the figures and tables.

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1) Part VIII: Y. Sasaki, H. Fujiwara, H. Kawai, and Y. Okazaki, *Chem. Pharm. Bull.* (Tokyo), **26**, 1066 (1978).

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3) *a)* B.L. Shapiro and N.D. Johnson, Jr., *J. Am. Chem. Soc.*, **94**, 8185 (1972); *b)* J. Reuben, *ibid.*, **95**, 3534 (1973); *c)* M.D. Johnson, Jr., B.L. Shapiro, M.J. Shapiro, T.W. Proulx, A.D. Godwin, and H.L. Pearce, *ibid.*, **97**, 542 (1975).

Results and Discussion

Estimation of Complex Shift and Equilibrium Constant

In this work, the simultaneous formation of 1: 1 and 1: 2 complex between acceptor A and donor B was taken into account as shown in Eq. 1 and 2;

$$A + B \rightleftarrows AB \tag{1}$$

$$AB + B \rightleftarrows AB_2 \tag{2}$$

When the activity coefficients are approximated to 1, equilibrium constants K_1 and K_2 are expressed as Eq. 3, where C_A, C_B, C_{AB} and C_{AB_2} are equilibrium concentration of each species, and C_A° and C_B° are the total concentrations (*cf.* Eq. 4).

$$\begin{aligned} K_1 &= C_{AB}/C_AC_B \\ K_2 &= C_{AB_2}/C_{AB}C_B \end{aligned} \tag{3}$$

$$\begin{aligned} C_A^\circ &= C_A + C_{AB} + C_{AB_2} \\ C_B^\circ &= C_B + C_{AB} + 2C_{AB_2} \end{aligned} \tag{4}$$

From Eq. 3 and 4, Eq. 5 is obtained;

$$C_B^3 + C_B^2(2C_A^\circ - C_B^\circ + 1/K_2) + C_B(C_A^\circ/K_2 - C_B^\circ/K_2 + 1/K_1K_2) - C_B^\circ/K_1K_2 = 0 \tag{5}$$

Then, we are able to express C_A, C_{AB} and C_{AB_2} by C_B, K_1 and K_2 as below.

$$\begin{aligned} C_A &= [2C_A^\circ - (C_B^\circ - C_B)]/(2 + K_1C_B) \\ C_{AB} &= K_1C_AC_B = K_1C_B[2C_A^\circ - (C_B^\circ - C_B)]/(2 + K_1C_B) \\ C_{AB_2} &= K_2C_{AB}C_B = K_1K_2C_B^2[2C_A^\circ - (C_B^\circ - C_B)]/(2 + K_1C_B) \end{aligned} \tag{6}$$

When 1: 1 and 1: 2 complexes coexist at equilibrium, the calculated shift $\Delta_{\text{calc.}}$ is expressed by Eq. 7, where $\Delta_{\text{calc.}}$, Δ_1 and Δ_2 are defined as follows (*cf.* Eq. 8).

$$\Delta_{\text{calc.}} = (C_{AB}/C_B^\circ)\Delta_1 + (2C_{AB_2}/C_B^\circ)\Delta_2 \tag{7}$$

$$\begin{aligned} \Delta_{\text{calc.}} &= \delta_{\text{calc.}} - \delta_B \\ \Delta_1 &= \delta_{AB} - \delta_B \\ \Delta_2 &= \delta_{AB_2} - \delta_B \end{aligned} \tag{8}$$

TABLE I. Complex Shifts (Δ_1, Δ_2) and Equilibrium Constants (K_1, K_2) estimated from Simulation Method at 35° in CCl_4

		Δ (ppm)[a)			K_1(M^{-1})[b)	K_2(M^{-1})[c)
		α	β	γ		
iso-C_4H_9OH	(I)	24.5		9.4	705	5
	(II)	21.3		9.0		
s-C_4H_9OH	(I)		15.0	9.5	540	2
	(II)		13.2	8.2		
t-C_4H_9OH	(I)		16.3		387	4
	(II)		16.0			
neo-$C_5H_{11}OH$	(I)			8.8	326	1
	(II)			8.0		

(I)=Δ_1, (II)=Δ_2; C_A°=~0.003—0.02 M, C_B°=~0.03—0.2 M.

a) Error being within ±5%.

b) Error being within ±20%.

c) Error being within ±30%.

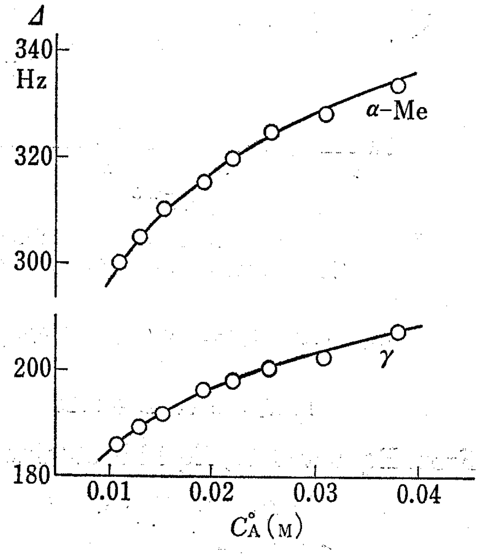

Fig. 1. Comparisons between $\Delta_{\text{calc.}}$ and $\Delta_{\text{obs.}}$ of s-C_4H_9OH at 35° in CCl_4

——=calculated curves.

○ =experimental points of C_A°/C_B°=0.37.

$\Delta_{\text{calc.}}$, therefore, is expressed as a function of K_1, K_2, Δ_1 and Δ_2, and these four parameters are determined by simulation so as to give the best fit between $\Delta_{\text{calc.}}$ and $\Delta_{\text{obs.}}$.[4] The results are summarized in Table I, and the four parameters thus determined well reproduced the observed shifts as illustrated in Fig. 1. As shown in Table I, K_1 is comparable with K_c determined in the previous report[1] under the equilibrium of Eq. 1, and the magnitude of K_2 is too small to warrant the contribution of the 1: 2 complex. The observed shift, therefore, may be concluded to reflect only the 1: 1 complex formation in the presence of a large excess of the donor. This difference between the shift reagent Eu(DPM)$_3$ and Eu(FOD)$_3$ in the stoichiometry of the complex formation will be ascribed to the electronegative fluorine atom of the latter.

Concentration Dependence of Induced Shift

In the previous work,[1] the correlations between the successive dilution shift and concentration term $C_B^{-2/3}$ of the base were examined in the solution of an equimolar mixture. In this work, we also confirmed the reliability of this relationship in the presence of a large excess of the donor. Taking into account the molar ratio of acceptor/donor, the linear relations between the successive dilution shift and total concentration term $C_t^{-2/3}$ depicted in Fig. 2 are formulated as Eq. 9.

$$\ln\Delta/x = BC_t^{-2/3} + \ln\Delta_{ic} \qquad (9)$$

where

x = molar ratio of acceptor/donor

B = slope of the linear relation

C_t = total concentration of the solute

Δ_{ic} = the infinite concentration shift

The infinite concentration shift corresponds to the 1: 1 complex shift Δ_1, and Eq. 10 is deduced.

$$\Delta_1 = 1.01\,\Delta_{ic} + 0.32 \qquad (10)$$

The slopes B are related to K_1 as shown in Fig. 3, and Eq. 11 is deduced.

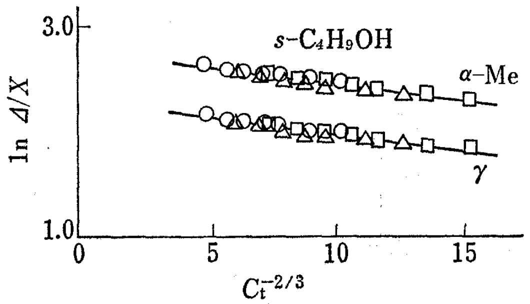

Fig. 2. Correlations between Successive Dilution Shifts of s-C_4H_9OH and $C_t^{-2/3}$ in CCl_4

$C_A^\circ = \sim 0.02$ M; $C_A^\circ/C_B^\circ = 0.45$ (△), 0.52 (○), 0.80 (□).

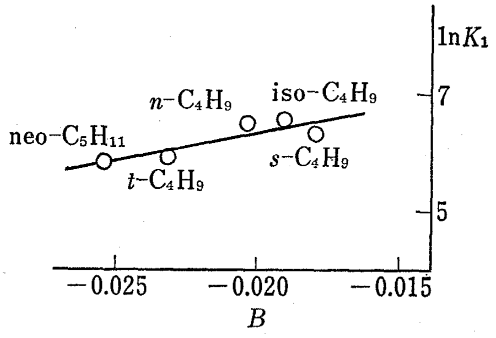

Fig. 3. Correlations between ln K_1 and B in CCl_4

$$\ln K_1 = 96.43\,B + 8.28 \qquad (11)$$

From Eq. 9 and 11, Eq.12 is obtained.

$$\ln\Delta/x = (\ln K_1 - 8.28)\,C_t^{-2/3}/96.43 + \ln\Delta_{ic} \qquad (12)$$

where $K_1 < 3900\ \text{M}^{-1}$.

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4) Root mean square deviations were minimized with a NEAC 2200 Model 500 computer at Osaka University Computer Center utilizing a library program DAVID.

Role of Solvent in the Presence of Large Excess of Donor

In this work, the 1: 1 complex formation is confirmed in the condition of donor$\gg$Eu(DPM)$_3$. This result suggests the important role of the solvent molecule in the process of complex formation, even in the presence of a large excess of the donor. It is evident that acceptor and donor molecules are surrounded by an overwhelming majority of the solvent molecules in the sample solution, and the observed actual effect is ascribed to the time-averaging 1: 1 collision between donor and acceptor allowed in the NMR time scale.1)