

動的 NMR에 의한 α -Chlorobenzyl Ethyl Ether의 이온解離速度에 관한 研究

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A Study on the Ionic Dissociation Rate of α -Chlorobenzyl Ethyl Ether by Dynamic NMR Spectroscopy

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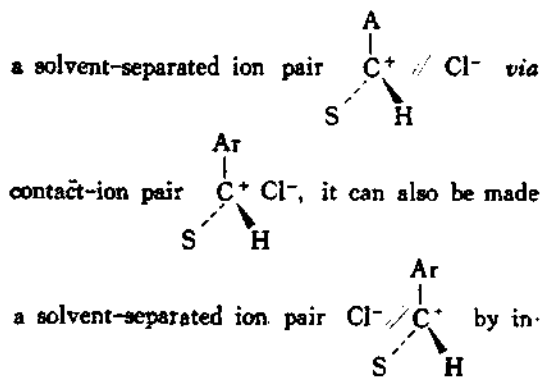
要約. 動的核磁氣共鳴法에 의하여 toluene-d₈ 및 carbon tetrachloride 溶媒속에서의 α -chlorobenzyl ethyl ether의 이온解離速度를測定하였다. 먼저, 動的NMR spectra를 얻고 J_{AB} , T_2 , $\Delta\nu_{AB}$ 값 등을 이용하여 computer simulation에 의한 理論spectra를 얻었는데 實測spectra와 매우 잘一致하였으며, 이로부터 解離速度定數 k 를 얻고 이 k 의 Eyring plot에 의하여 기울기와 切片의 길이를 알고 이로부터 動力學的 parameter를 얻었다. 이온解離의 難易度는 溶媒의 極性에 依存하였으며 活性化 enthalpy는 toluene-d₈ 溶媒中에서 4.7 kcal/mole 이었고 carbon tetrachloride 溶媒中에서 10.7 kcal/mole 이었다. 活性化 entropy는 toluene-d₈ 溶媒中에서 -35.8 e. u. 이었고 carbon tetrachloride 溶媒中에서 -14.4 e. u. 이었다. S_N1 mechanism의 初期段階로 볼 수 있는 이 이온解離는 ΔH^* 값이 작아도 非極性 非陽性溶媒中에서 이온解離가 容易함을 알았으며 작은 ΔH^* 에 比하여 ΔS^* 는 陰의 큰 값을 가졌음은 注目할 必要가 있다.

ABSTRACT. Ionic dissociation rates of α -chlorobenzyl ethyl ether in each solvent of toluene-d₈ and carbon tetrachloride were measured by the method of dynamic NMR spectroscopy. The spin system of these ¹H NMR spectra was ABX₃. The theoretical spectrum was calculated by computer simulation of dynamic NMR spectra, which agreed very well with observed spectra. From this computer simulation, the ionic dissociation rate constant k was obtained, and by Eyring plot with it, slope and intercept length was gained, from which kinetic parameters were calculated. The easiness of ionic dissociation depended upon solvent polarity. Activation enthalpy was 4.7 kcal/mole in toluene-d₈, 10.7 kcal/mole in carbon tetrachloride, and activation entropy was -35.8 e. u. in toluene-d₈, -14.4 e. u. in carbon tetrachloride. It was understood that though the ΔH^* value was small, this ionic dissociation had an easier procession in nonpolar solvents with increasing temperatures. Considering that the ionic dissociation could be thought as the first step of S_N1 mechanism, attention might be paid to the results that the value of ΔS^* had a large negative value in comparison with a small ΔH^* .

1. INTRODUCTION

Recently, with the development of large-high-speed computers, the dynamic NMR spectroscopic method has come to be applied in the studies of rotation, inversion and rearrangement of molecules, and in various studies of the exchange process rate. There had chiefly been a number of studies in the exchange systems about intramolecular rotation; but lately, the rate of molecular ionization, or of ionic rearrangement reaction has also been studied. One example is the ionic dissociation rate measurement of α -chlorodibenzyl sulfide by Ōki and Arai^{1,2}.

In this process the fact that ionic dissociation of a molecule results in racemization, which also brings an equivalence of diastereotopic protons to the molecule, was applied. In other words, if an organic halogen compound becomes



version in the solvent. Ion pairs are racemized for each other. Accordingly it can even be said that the proton exchange of $AB \rightleftharpoons BA$ is always occurring in stabilized molecules. According to the above experiment, it has been confirmed that: (1) The greater the polarity of the general solvent, the faster the rate of ionic dissociation; and (2) the ionic dissociation of the compound results in both cation and chloride ion forms. The formula³ applied to obtain the kinetic parameter was

$$k_c = \frac{\pi}{2} \sqrt{6(J_{AB})^2 + (\Delta\nu_{AB})^2}$$

The value demanded for exchange of diastereotopic protons in the solvent at coalescence temperature, ΔG_c^* could be obtained by applying k_c to the following formula

$$\Delta G_c^* = 4.75 T_c (10.319 + \log T_c / k_c)$$

and the value of ΔG_c^* in carbon tetrachloride at 80°C was 17.8 kcal/mole (up). We are interested in this ionic dissociation because it can be thought as the first stage of the S_N1 type reaction process.

Studies on the perfect line-shape analysis of NMR spectra of the spin coupled system have been multiplying in recent years; and in this case chemical exchange rate is comparatively slow, about $10^{-1} \sim 10^3 \text{ sec}^{-1}$. Then NMR signals show a characteristic change, and by analysing this line-shape of the changed signals, we can obtain a kinetic process rate constant.

After that, we can also obtain activation parameters of chemical exchange from the constant. In this case, the activation energy E_a lies in the range of 7~30 kcal/mole. Recently, in other experiments with more complicated systems, some theoretical spectra could be obtained, from which we can also obtain activation parameters. The parameters give us some useful data for the study of dynamic molecular mechanism.

As the carbonium ion can be stabilized not only by sulfur but also by oxygen, this study tried to investigate the ionic dissociation rate of α -chlorobenzyl ethyl ether that has an oxygen in the β position of chloride substituent.

2. EXPERIMENT

Synthesis of α -Chlorobenzyl Ethyl Ether.

⁵⁻¹⁷ When 37.5 grams of benzaldehyde and 0.75

* k is rate constant, J is coupling constant and $\Delta\nu$ is chemical shift difference. Subscript c is an abbreviation of coalescence, those that follow are the same as this.

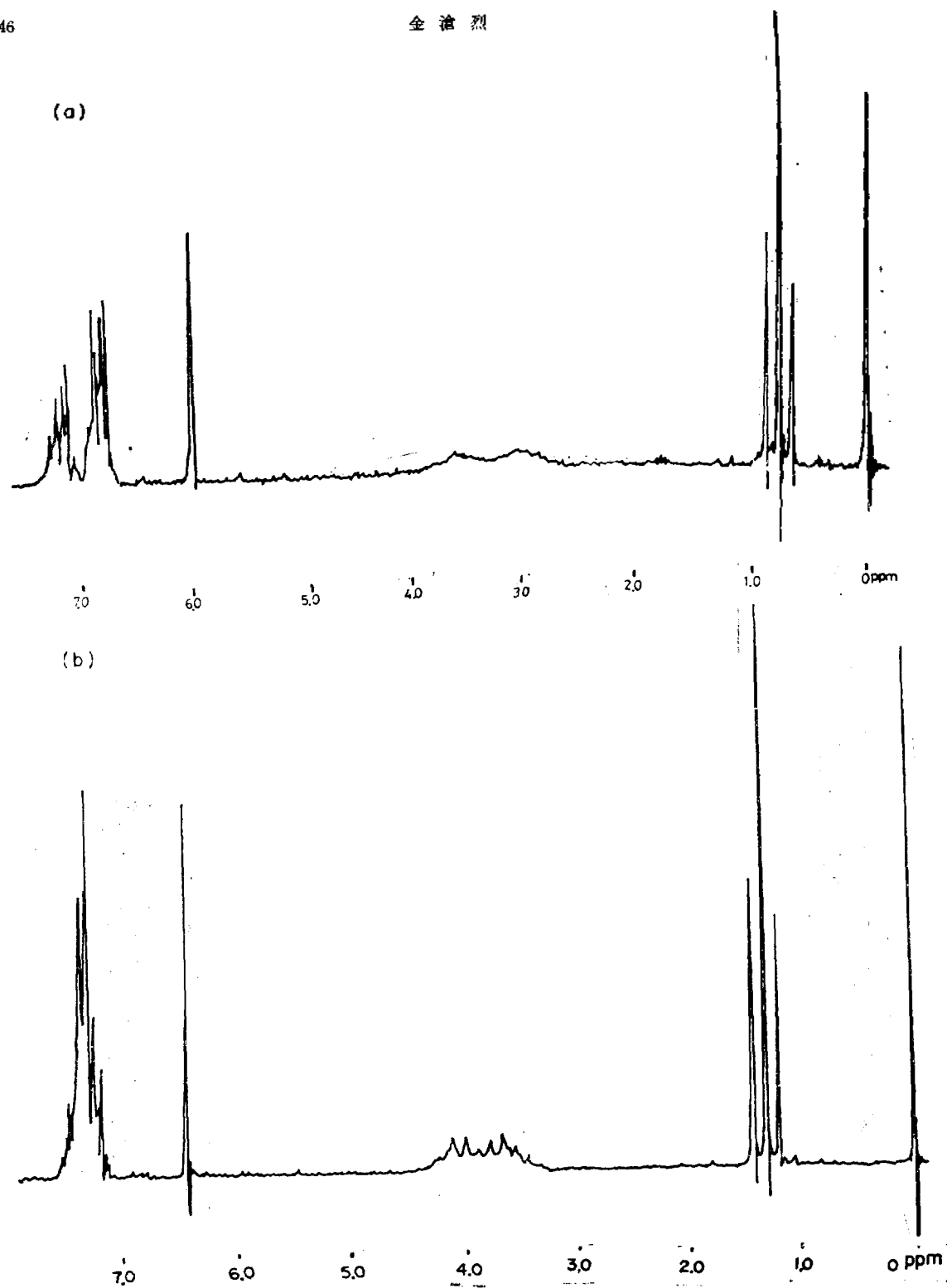


Fig. 1. The ^1H NMR spectra of α -chlorobenzyl ethyl ether at 34°C : (a) in toluene- d_6 , (b) in carbon tetrachloride.

Table 1. ^1H NMR spectral data (δ) of α -chlorobenzyl ethyl ether at 34 °C.

Solvent	Reference	C_6H_5-	$-\text{CHCl}-$	$-\text{CH}_2-$	$-\text{CH}_3$
Toluene- d_8	HMDS**	6.77(<i>m</i>)	5.98(<i>s</i>)	3.03~3.70(<i>m</i>)	0.77(<i>t</i>)
Carbontetrachloride	TMS	7.30(<i>m</i>)	6.43(<i>s</i>)	3.67~4.14(<i>m</i>)	1.30(<i>t</i>)

*Toluene- d_8 : $\text{C}_6\text{D}_5\text{-CD}_3$; **HMDS: Hexamethyldisiloxane, *m*: multiplet, *s*: singlet, *t*: triplet.

grams of ammonium chloride were added to 49 grams of ethyl alcohol in a reaction flask, and were agitated in order to react, the benzaldehyde diethyl acetal was obtained by distillation of the contents. Two molar times of acetyl chloride and as a catalyst small quantity of thionyl chloride were added to the benzaldehyde diethyl acetal and they were agitated. Then excess acetyl chloride, residual products and incomplete reactants were removed from the products by a suction pump, and α -chlorobenzyl ethyl ether was finally obtained by vacuum distillation.

Its density at 0 °C was 0.968 g/ml, Fig. 1 demonstrates the ^1H NMR spectra of α -chlorobenzyl ethyl ether at 34 °C and Table 1 its spectral data.

The Measurement of ^1H NMR Spectra. The α -chlorobenzyl ethyl ether was very unstable in the air and so it immediately decomposed, getting white smoke because of the reaction with water. So the sampling was proceeded using a drying box, or nitrogen gas atmosphere.

The concentration of α -chlorobenzyl ethyl ether in each solvent in the NMR sample tube was about 10 percent by volume. As an external standard, HMDS in a capillary tube was put in the toluene- d_8 solution in the sample tube. And 0.5 volume percent of TMS as internal reference was added in the carbon tetrachloride solution. The NMR spectrometer was HITACHI R-20B with temperature variation accessory. The scanning was proceeded over 600 Hertz and 300 Hertz. Toluene- d_8 in the ampoule (the French Office of Atomic Energy) was used as received.

GR carbon tetrachloride (Wako Chemical Co.) was used after drying over synthetic zeolite 48 hours. At low temperatures, cooled nitrogen gas stream was sent to the spinner in the mean time of NMR operation in order to protect the spinner from freezing by dint of water in the air. The cooling of nitrogen gas was done by exchanging the heat with liquified nitrogen gas.

The measured temperature in the case of toluene- d_8 solution ranged from -56 °C to 40 °C, and from -40 °C to 40 °C in the case of carbon tetrachloride. The temperature check of the measuring process was achieved by Van Geet's temperature calibration method¹⁸. In this method, the chemical shift difference ($\Delta\nu$) of each of the two peaks of methanol at low temperatures, and of ethylene glycol in high temperatures, was measured. The temperature was calculated by the following equations:

$$T = 478.6 - 1.906|\Delta\nu|, \text{ (for methanol)}$$

$$T = 466.0 - 1.694|\Delta\nu|, \text{ (for ethylene glycol)}$$

The error of temperatures in this method was ± 0.5 °C. $\Delta\nu_{AB}$ was calculated by following equation

$$\Delta\nu_{AB} = \sqrt{a(2J_{AB} + a)}$$

where ' J_{AB} ' was the coupling constant and ' a ' the distance between two J_{AB} 's in Hertz unit.

Computer Simulation of NMR Spectra. The computer programming that was partly modified for the sake of theoretical NMR spectra was owed to "General NMR Line-Shape Program with Symmetry and Magnetic Equivalence Factoring" by Binsch¹⁹, making use of the

Density Matrix Method. The computer used was one of the large size computers, HITAC 8800/8700 at the computer centre of the University of Tokyo, of which the plotter was a Watanabe Guage KK.

Spin-spin relaxation time was calculated by the equation:

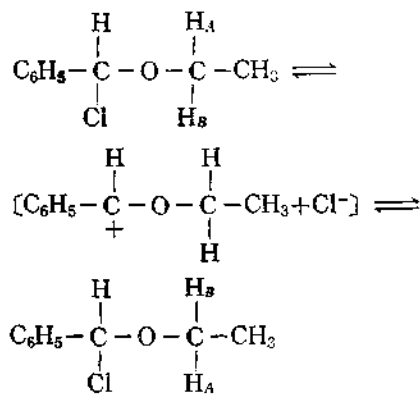
$$T_2 = 1/W_{1/2}^{20}$$

where $W_{1/2}$ was a half-value width of a sharp signal that had no exchange.

Chemical shift difference depended upon the temperature change, so $\Delta\nu$ could easily be estimated at optional temperatures. The procedure was as follows: After the protons clearly represented AB part of ABX_3 signals at the proper temperature, their spectra were measured again at lower temperature, and examined the drift which relied on these temperatures. Finally, chemical shift differences were estimated by extrapolation of these tendencies at optional temperature, and thereafter $\Delta\nu$ could be used in the computer simulation of spectra.

3. RESULTS AND DISCUSSION

It is believed that the α -chlorobenzyl ethyl ether maintains the following equilibrium in nonpolar aprotic solvent:



but these molecules exist as the mixtures of

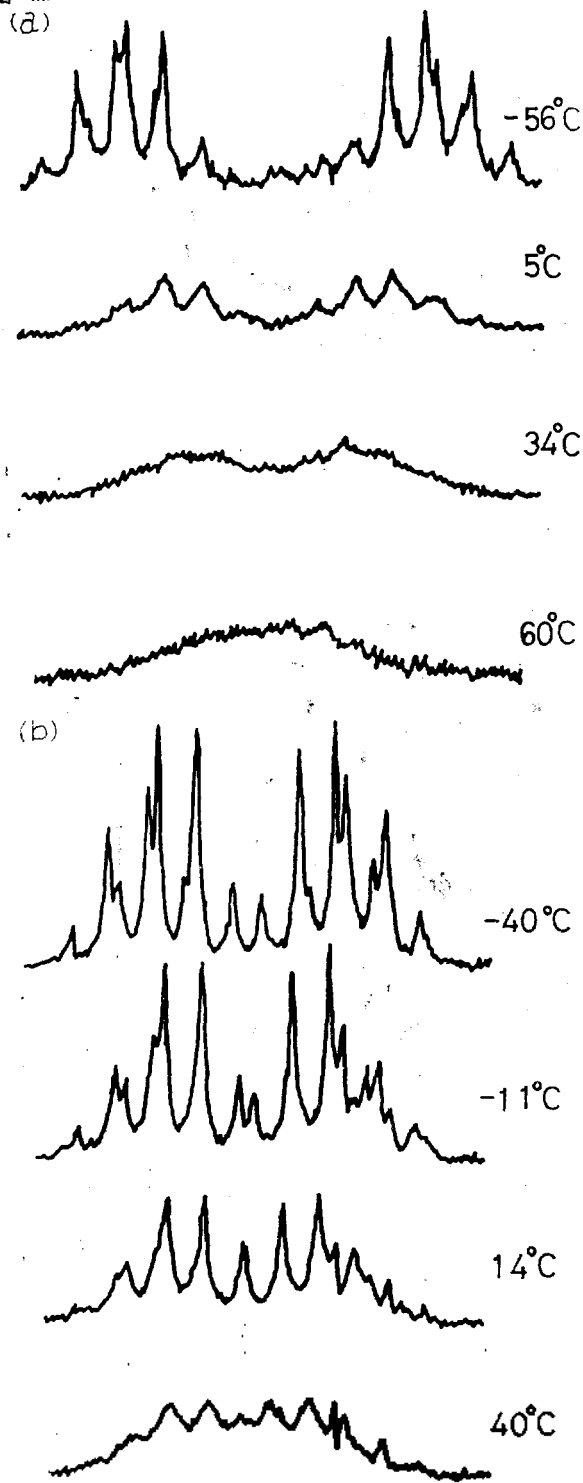


Fig. 2. The NMR spectra of A and B protons ($-\text{OCH}_2-$) according to temperature changes. (a) Solvent: toluene- d_6 , reference: HMDS; (b) solvent: carbon tetrachloride, reference: TMS.

their various conformers, and the chemical shift that can be seen in the NMR spectra is measured as the average of various conformers. Under these circumstances it is considered that the chemical shift difference of AB protons changes in accordance with the changing temperature.

The NMR spectrum of α -chlorobenzyl ethyl ether was a complicated ABX_3 spin system, and the spectra of AB protons which had the spin-coupling by $-CHCl-$ and $-CH_3$ at various temperatures, can be seen in Fig. 2.

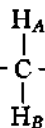
In the spectra, AB proton parts show the extreme changes, while C_6H_5- , $-CHCl-$, and the $-CH_3$ parts as demonstrated, show little change.

The 16 splitting patterns of AB protons are shown in Fig. 3.

In the solvent toluene- d_8 at $-56^\circ C$, 16 sharp peaks are broadening more and more with increasing temperatures, and also the spectra in carbon tetrachloride has the same tendency as that of toluene- d_8 .

To analyse the line-shaped spectrum, it is necessary to apply the chemical shift difference, coupling constant and T_2 . The coupling constant of AB protons J_{AB} equals 7.2 Hertz and there was no temperature dependency as we expected, but chemical shifts were paramagnetically shifted with increasing temperatures.

The Hertz values in Fig. 4 ν_A , ν_B and ν_X are



each chemical shifts of $-O-C-$ and $-CH_3$.

NMR spectrum was measured in toluene- d_8 .

Each of the ABX_3^* proton peaks were shifted to a low magnetic field, bit by bit, with increasing temperatures. and ν_B showed the most intense tendency and ν_X showed little shifting.

Fig. 5 is also the chemical shift variations of X_3 protons; CH_3 protons.

ABX_3 protons depending upon temperature changes in carbon tetrachloride. Here too, chemical shifts were paramagnetically shifted with increasing temperatures and ν_B showed the greatest tendency but ν_X showed little change.

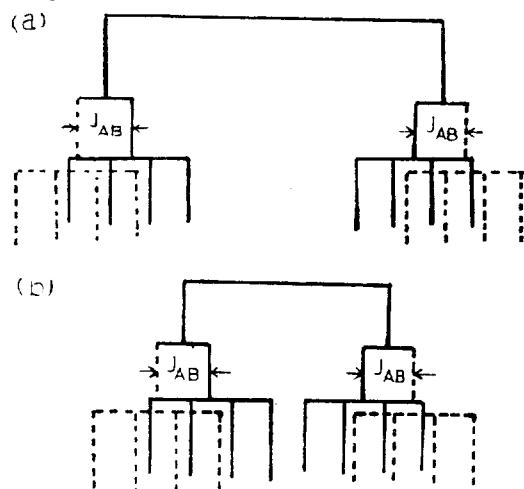


Fig. 3. The 16 splitting patterns of AB protons that had spin couplings with $-CH-$ and $-CH_3$: (a) toluene- d_8 , (b) carbon tetrachloride.

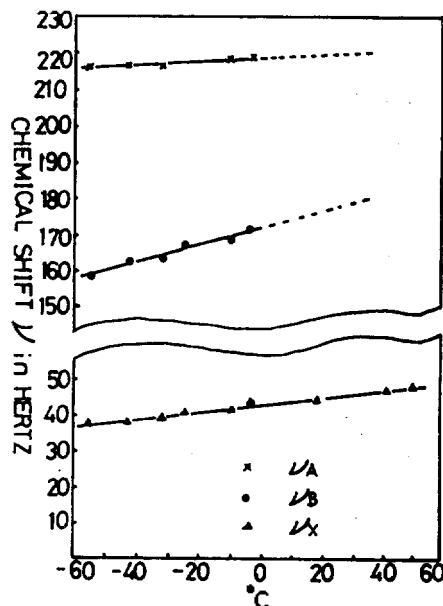


Fig. 4. The relationship of chemical shifts vs. temperatures in toluene- d_8 solution.

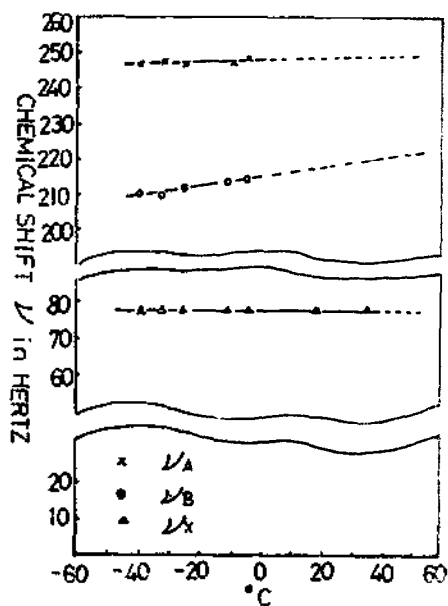


Fig. 5. The relationship of chemical shifts vs. temperatures in carbon tetrachloride solution.

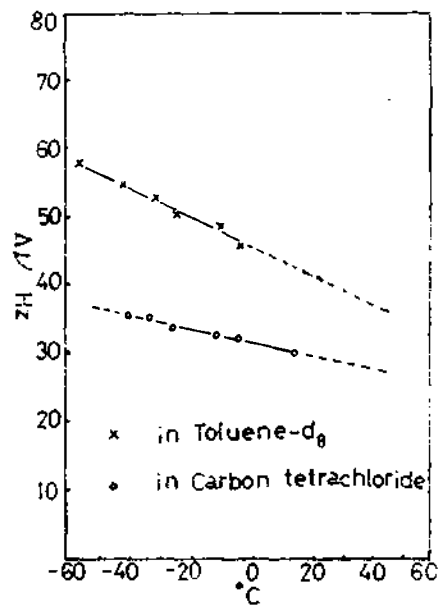


Fig. 6. The relationship of chemical shift difference vs. temperature.

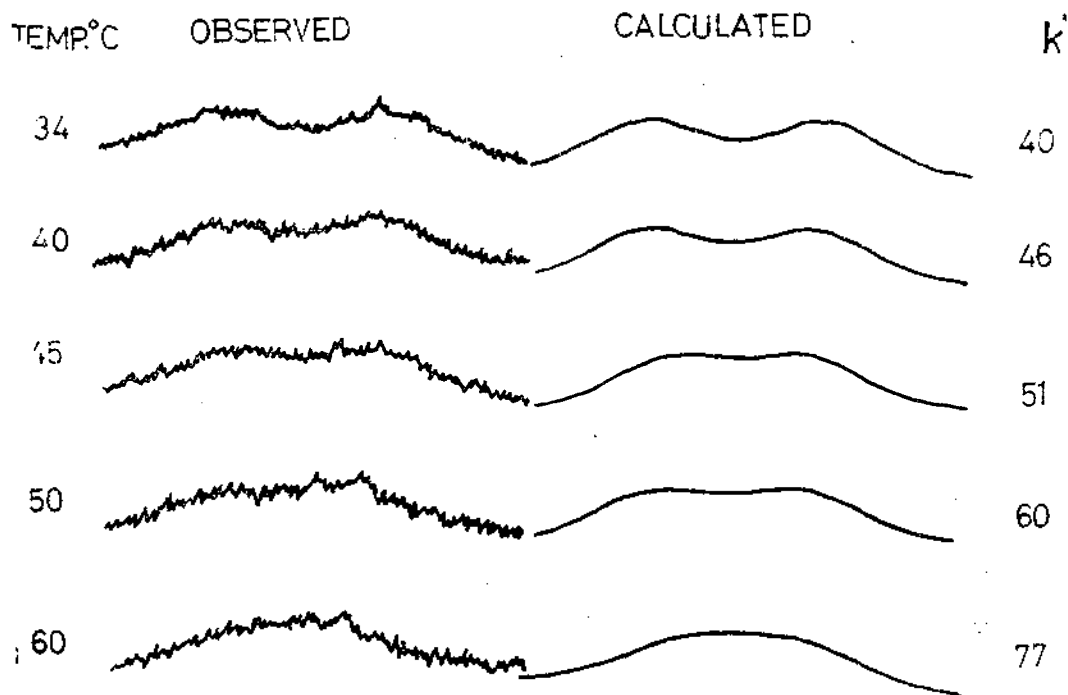


Fig. 7. The computer simulation results of the observed spectra in toluene- d_8 .

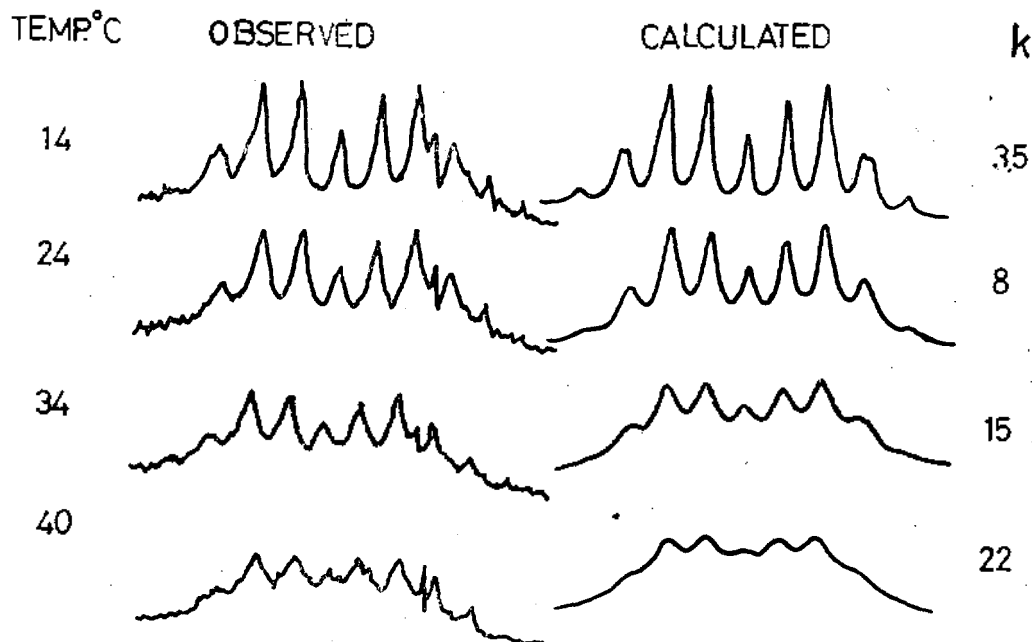


Fig. 8. The computer simulation results of the observed spectra in carbon tetrachloride.

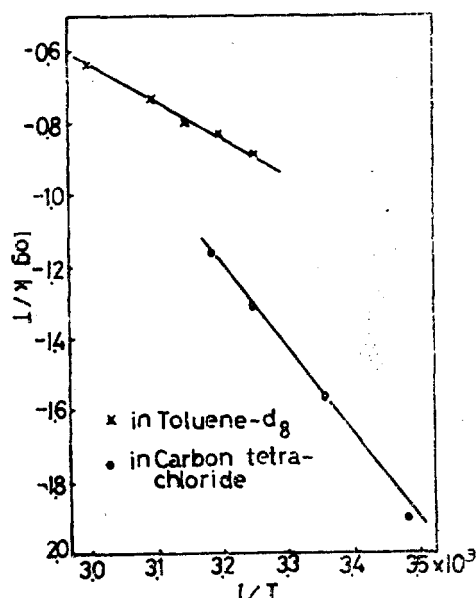


Fig. 9. The relationship of $\log k/T$ vs. $1/T$.

Fig. 6 is the relationship of chemical shift difference ($\Delta\nu$) versus temperature. Here we can see that the chemical shift difference $\Delta\nu_{AB}$ of protons A and B is decreasing with increasing

Table 2. Kinetic parameters about ionic dissociation of α -chlorobenzyl ethyl ether.

Solvent	ΔH^*	ΔS^*
Toluene-d ₈	4.7 kcal/mole	-35.8 e. u.
Carbon tetrachloride	10.7 kcal/mole	-14.4 e. u.

temperatures. This is because $\Delta\nu$ is observed as a means of variant possible conformers. In Fig. 6 $\Delta\nu_{AB}$ is decreasing both in toluene-d₈ and in carbon tetrachloride with increasing temperatures.

From the computer simulation, we obtained rate constant k in each solvent at various temperatures. With the k , Eyring plot is shown in Fig. 9. From the results of Eyring plot, the following dynamic parameters were calculated.

The small value of ΔH^* and large negative value of ΔS^* were considered to demonstrate that the solvent molecular participation was great during the transition state. We have to pay attention to the large negative value of ΔS^*

in comparison with small ΔH^\ddagger . Also the fact that ΔH^\ddagger in toluene- d_8 is smaller than that in carbon tetrachloride, means that the easiness of ionic dissociation is dependent upon the solvent polarity. The kinetic parameters also support the fact.

4. CONCLUSIONS

(1). The $-CH_2-$ part in NMR spectra of α -chlorobenzyl ethyl ether is AB proton system. This splitting pattern is an ABX_3 type, and so, at low temperatures 16 peaks can be seen clearly.

(2) The chemical shift difference of proton A and B ($\Delta\nu_{AB}$) is bigger in toluene- d_8 than in carbon tetrachloride.

(3) The chemical shifts of proton A and B are paramagnetically shifted with increase in temperature.

(4) The calculated spectra agrees very well with the observed spectra.

(5) The easiness of ionic dissociation in an organic solvent depends upon solvent polarity, and the kinetic parameters support this.

(6) The fact that the activation entropy has a large negative value means that participation of solvent molecules is great and, thus, must be given special attention.

(7) The study of ionic dissociation is very important. It can be said that the ionic dissociation is the first step in the S_N1 mechanism, and one can gain the necessary kinetic parameters by dynamic NMR spectroscopy.

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