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NUCLEAR MAGNETIC RESONANCE STUDY OF EXCHANGING SYSTEMS. VI.1) ROTATIONAL BARRIER OF FORMANILIDE BY ^{13}C NMR COMPLETE LINE SHAPE ANALYSIS

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The complete line shape analysis of temperature-dependent ^{13}C NMR spectra of formanilide in the system where the populations of the isomers change with temperature was performed by a modified Bloch equation method, and the activation parameters of the restricted rotation around amide bond were determined accurately.

Although there have been a lot of studies carried out on the restricted rotation around the C-N bond in various amides,2) only a few dealing with the rotational barrier in secondary amides have been reported.3,4) This may be because of the small population of the cis isomer (in most secondary amides, the cis isomer does not exist). Furthermore considerable difficulty is encountered in the line shape analysis of the temperature-dependent ^{1}H NMR spectra due to various spin couplings, the quadrupole interaction effect of ^{14}N on the line widths, and the changes in the chemical shifts with temperature by means of the intermolecular hydrogen bonding. On the other hand, the line shape analysis of ^{13}C NMR spectra in the amides can be easily made since the spectral patterns become much simpler with ^{1}H decoupling and in most cases the latter two effects little affect the ^{13}C NMR line shapes.

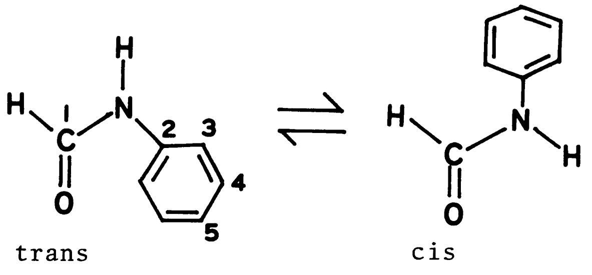

Fig.1. Rotation around amide bond of 1.

In this paper, we report the results of the complete line shape analysis of the ^{13}C NMR spectra to determine the rotational barrier of the C-N bond in secondary amides. Formanilide (1) was chosen because in this compound the cis isomer exsists to a considerable extent. Another aim of this study is to make a complete line shape analysis accurately in the exchanging system where the populations of the isomers change with temperature. Such an analysis had not formerly been tried except with t-butyl formate.5)

^{13}C NMR spectra were measured using a NEVA NV-14 spectrometer operating at 15.087 MHz with a Varian 620/L computer for an FT mode. Usually the spectra were accumulated 1000-1500 times. The concentrations of the samples are 33.3 and 45.8 Wt% in $CDCl_3$ and dioxane-d_8,respectively. The temperature was determined by a calibrated copper-constantan thermocouple. The line shape analysis of the ^{13}C NMR spectra was performed by means of a computer program EXNMR1 using modified Bloch equations.6)

^{13}C NMR spectrum of 1 is shown in Fig.2. Since the rotation around the C-N bond of 1 is sufficiently slow at room temperature, the peaks of both trans and cis isomers appear in the spectrum. The population of the latter in 1 was determined from the spectrum to be 33% in the $CDCl_3$ solution, which is larger than that in N-alkyl formamides, for example, 11% in N-methyl formamide.7) Taking the chemical shifts, the relative intensities of the peaks, and the chemical shift differences between the paired peaks (A: 3.03, B: 0.21, C: 0.62, D: 0.33, E: 1.70 ppm) into account, the signals of the carbonyl and phenyl groups can be assigned as follows:

A: C_1, B: C_2, C: C_4, D: C_5, E: C_3,

the notations being shown as in Fig.1 and 2.

^{13}C NMR spectra of the ortho carbons in the benzene ring of 1 at several temperatures are shown in Fig.3. The line widths of all peaks begin to broaden with increasing temperature, and the signals of the paired peaks begin to coalesce into singlets (Fig.3(c)). At higher temperatures, the singlets become sharper (Fig.3(a)). The population ratio of the trans isomer to the cis changes with temperature: The population of the cis isomer increases when the temperature is raised (33% at 32.5 °C and 43% at 125.4°C c=33.3 Wt% in $CDCl_3$). Even when the population difference is about 1%, the spectra show apparently different line shapes, especially in the case of sharper peaks at slower rotation. When the rotation is enough slow on the NMR

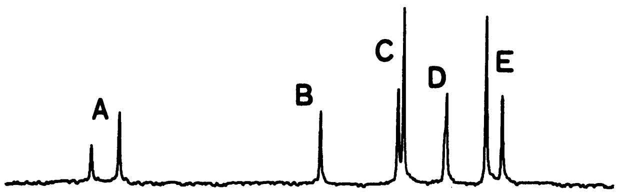

Fig.2. ^{13}C spectrum of 1 in $CDCl_3$ at 32.5°C.

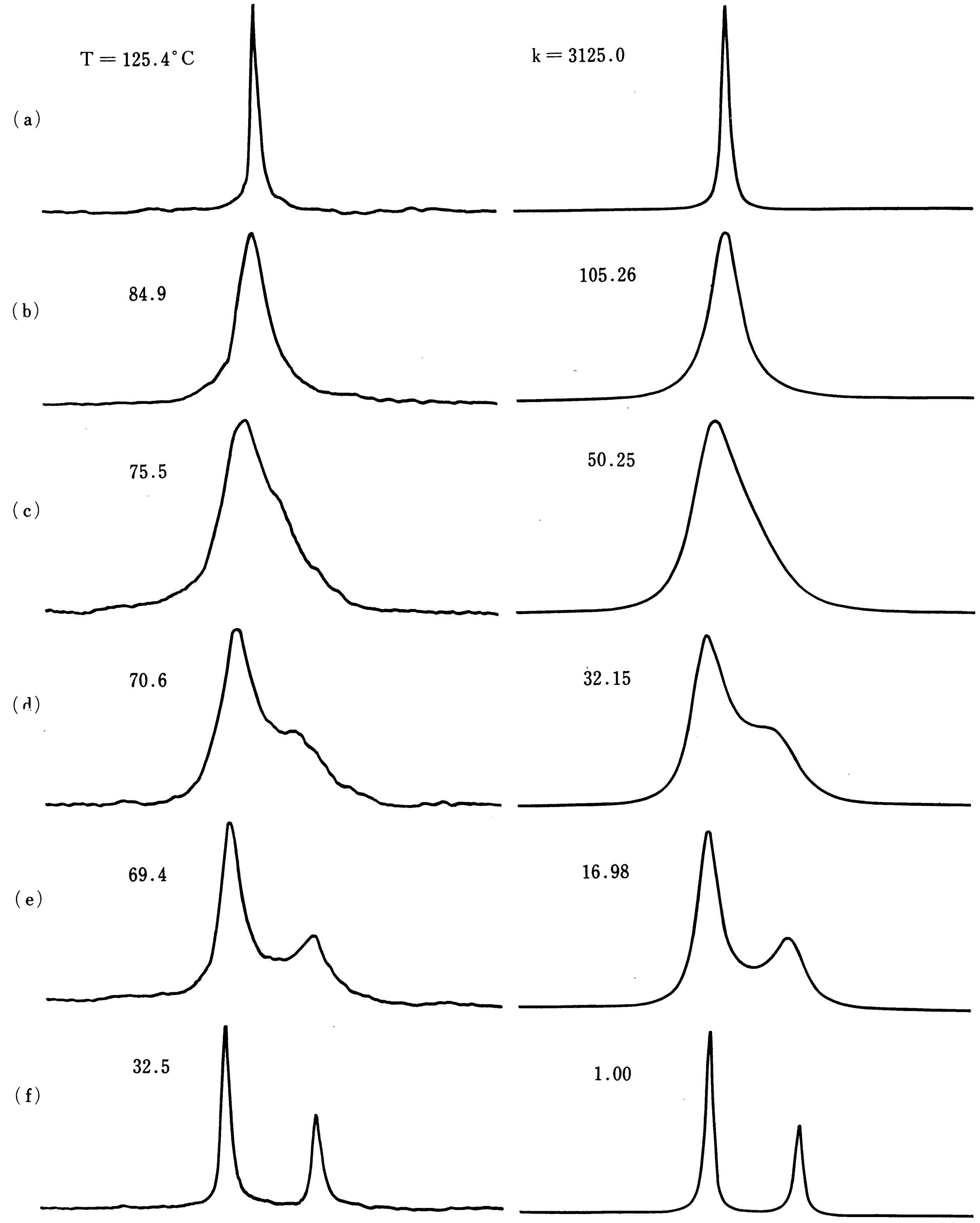

Fig.3. The observed (left) and the calculated (right) ^{13}C NMR spectra of ortho carbons of formanilide in $CDCl_3$ at several temperatures.

Table 1. The activation parameters of the rotation of 1 at 25.0°C.

solvent	Ea (Kcal/mole)	$\Delta G^{\ddagger}$ (Kcal/mole)	$\Delta H^{\ddagger}$ (Kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)
$CDCl_3$	20.0 ± 0.5	18.2 ± 0.1	19.4 ± 0.5	4.0 ± 1.7
Dioxane-d_8	20.7 ± 0.7	18.2 ± 0.1	20.1 ± 0.7	6.3 ± 2.3

time scale and the line broadening due to the exchange between two isomers does not occur (from -30°C to ca.40°C in $CDCl_3$ sample), the populations of the isomers can be determined accurately by fitting the calculated spectrum with the observed in the try and error method. At the elevated temperatures when the line broadening takes place to a considerable extent, both lifetimes and the populations of isomers are changed independently at small intervals in the spectral calculations to obtain the best fitted calculated spectrum with the observed: in the calculations, the tendency of the population changes at lower temperatures is taken into account carefully in determining the populations at higher temperatures.

The complete line shape analyses were performed independently in two regions of carbonyl and ortho carbon signals (A and E in Fig.2.). The lifetimes determined in two regions at each temperature agree well with each other within experimental errors. The Arrhenius plot between log k and 1/T shows a good straight line. The activation parameters obtained are given in Table 1.

All activation parameters in $CDCl_3$ and dioxane-d_8 are almost the same within experimental errors. The absence of the solvent effect on the rotational energy may probably be attributed to a larger effect of the self-association of 1 than that of the intermolecular interaction between the amide and dioxane. The value of activation free energy of 1 obtained in this work is somewhat larger than that obtained from coalescence temperature method (17.7 Kcal/mole).$^{3)}$ It is interesting that Ea of 1 is much larger than that of N-o-tolyl formamide (ca. 16 Kcal/mole).$^{4)}$

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