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## Proton Magnetic Resonance Study of the Amino Group of Thioacetamide (TA) I. Quadrupole Relaxation Effects in NH<sub>2</sub> of Thioacetamide

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Nitrogen-14 quadrupolar relaxation has been observed in the amino proton nmr spectra of TA in acetone and methanol solutions over the temperature range  $-83^{\circ}\text{C}$  to  $+35^{\circ}\text{C}$ . The proton nmr lineshapes were analyzed to yield a  $^{14}\text{N}$  spin lattice relaxation time  $(T_1)_N$  as a function of temperature. Activation energies and correlation times at  $25^{\circ}\text{C}$  for the molecular reorientation in the two solution phases have been calculated and the results are discussed.

### Introduction

Nuclei with large electric quadruple moment are relaxed so effectively by the mechanism of quadrupolar relaxation that they usually show no observable effects in the spectrum of a spin-1/2 nucleus. But if there is no or incomplete washing-out of spin-spin coupling between a spin-1/2 nucleus and spin-1 nucleus, the coupling constant can be directly observed<sup>1-3</sup>. It is because the fluctuating electric field gradient is either zero by symmetry or small as for isocyanides<sup>3</sup>. In that case, the lineshape analysis of the former nuclei gives us an alternative method to obtain an information about the quadrupolar interactions<sup>4,5</sup>. The theoretical basis of this method lies in the fact that under the fast exchange conditions the scalar coupling can become the second kind of scalar relaxation mechanism for spin-1/2 nuclei<sup>6</sup>.

The  $^1\text{H}$ -nmr spectra of amino group of TA in some solvents are split into three lines even at room temperature. This means that the nitrogen nucleus of TA in those solvents has an increased symmetric environment in the electric field

gradients. Therefore it is possible to obtain the  $^{14}\text{N}$  relaxation times of TA quantitatively by analyzing the lineshapes of the proton spectra.

In the present paper we study the nuclear magnetic relaxation behavior of the amino group of TA in acetone and methanol solutions. From the lineshape analysis we obtained the reorientational correlation times of the amino group as a function of temperature, and tried to interpret them in terms of possible structural changes in the above two systems.

### Experimental

The TA (GR-grade) from Merck AG., Darmstadt was used without further purification. Deuterated acetone (d-6) and methanol (d-3) were obtained from Sharp & Dohme, Munich, and Deuterium content was more than 99 atom %. An nmr glass tube of 5-mm diameter was filled with 0.5 ml of liquid samples and sealed after degassing by several freeze-pump-thaw cycles. The concentration of both TA solutions was

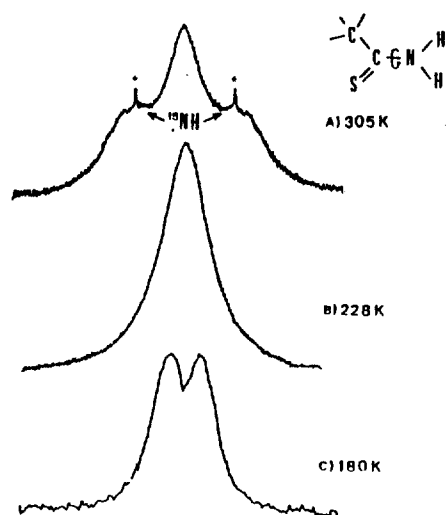


Figure 1.  $^1\text{H}$ -nmr spectra of amino group of TA in acetone solution.

$6.36 \times 10^{-1}\text{M}$ .

The nmr spectra were obtained using Bruker WP 80-FT and WP 80-CW spectrometers equipped with Bruker B-VT 1000 variable temperature unit.

### Results

The  $^1\text{H}$  nmr spectra of amino group of TA in acetone were recorded as a function of temperature and the typical amino proton nmr spectra are shown in Figure 1. Figure 2 shows the spectra for TA in methanol solution. As shown in the figures, direct measurement of  $J_{14\text{N-H}}$  was not possible from the broad triplet lines. However, the  $J_{14\text{N-H}}$  constant was indirectly determined from experimental observed  $J_{15\text{N-H}}$  coupling constant. As shown in Figure 1, the proton spectrum coupled with  $^{15}\text{N}$  (natural abundance 0.36%) appeared as a doublet in the broad triplet lines. From the  $^{15}\text{N-H}$  satellite doublet,  $J_{15\text{N-H}}$  was evaluated to be  $90 \pm 0.2$  Hz over the temperature range from 300K to 335K. It is a very reasonable value compared to the literature one<sup>7</sup>. Such a small uncertainty obtained from the satellite analysis probably precludes observation of any variation in  $J$  with temperature.

The magnetudes of the  $J_{14\text{N-H}}$  are theoretically related through the magnetogyric ratio for the two nuclei,

$$J_{14\text{N-H}} = \frac{\gamma_{14\text{N}}}{\gamma_{15\text{N}}} J_{15\text{N-H}} \quad (1)$$

The obtained  $J_{14\text{N-H}}$  coupling constant is  $64.5 \pm 0.2$  Hz in this system. We used this value for the analysis of proton lineshapes.

The amino proton nmr spectra were analyzed for  $^{14}\text{N}$  spin lattice relaxation time using lineshape function proposed by Sack and Pople<sup>4,5</sup>. The lineshape is given by eq. (2),

$$I(x) = \frac{45 + \alpha^2(5x^2 + 1)}{225x^2 + \alpha^2(34x^4 - 2x^2 + 4) + \alpha^4(x^6 - 2x^4 + x^2)} \quad (2)$$

The intensity of absorption in the proton spectrum,  $I(x)$ , is given as a function of dimensionless parameters:

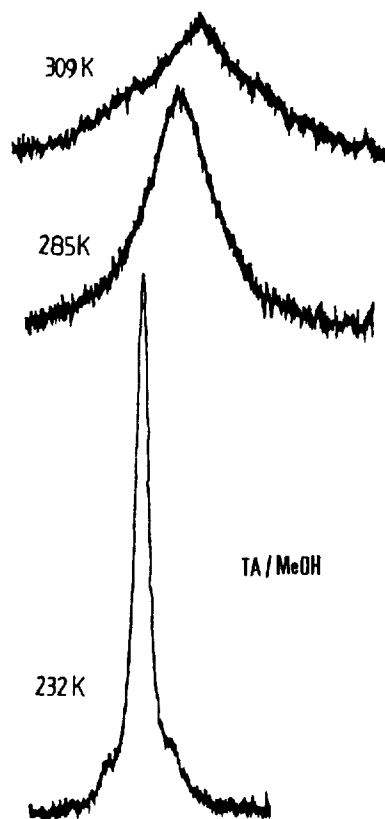


Figure 2.  $^1\text{H}$ -nmr spectra of amino group of TA in methanol solution.

$$x = \Delta\nu/J_{14\text{N-H}} \text{ and } \alpha = 10\pi(T_1)_N J_{14\text{N-H}}$$

where  $\Delta\nu$  is the frequency in Hz relative to the Larmor frequency of the proton and  $(T_1)_N$  is the spin-lattice relaxation time of the nitrogen nucleus.

The lineshape function  $I(x)$  were calculated using the Sack-Pople equation with the coupling constant given by eq. (1) and the various  $(T_1)_N$  values, and the spectra calculated by a computer program were well fitted with the observed spectra within an experimental error (less than 5%), and used to obtain the  $(T_1)_N$ . The  $\log [1/(T_1)_N]$  for TA in acetone and methanol solutions are plotted as a function of temperature in Fig. 3.

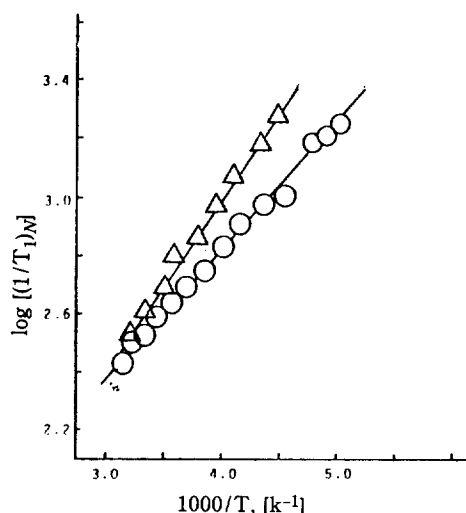
### Discussions

As shown above, the analysis of proton nmr lineshapes in the amino group has enabled us to evaluate the  $^{14}\text{N}$  spin-lattice relaxation time,  $(T_1)_N$  in solutions as a function of temperature. These  $(T_1)_N$  may be used to calculate the effective correlation times,  $\tau_c$  characterizing the reorientation of amino group in solutions, and the activation parameters for the above reorientation.

The quadrupolar correlation time,  $\tau_c$  is related to the spin-lattice relaxation rate,  $(1/T_1)_N$  and the quadrupolar coupling constant,  $\chi = e^2q_zQ/h$  through the eq. (3)

$$(T_1)_N^{-1} = \frac{3}{10}\pi^2 \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\pi^2}{3}\right) \chi^2 \tau_c \quad (3)$$

where  $\eta$  is the asymmetry parameter of the electric field gra-



**Figure 3.** Plots of  $\log [(1/T_1)_N]$  vs.  $1000/T$ .  $\circ$ : acetone solution;  $\triangle$ : methanol solution.

**Table 1.** Calculated  $\tau_c$  at 25°C and the required parameters for their calculations

Parameters	TA/ACETONE	TA/MeOH
$\chi$ , (MHz)	2.56	2.56
$(1/T_1)_N$ , ( $\text{sec}^{-1}$ )	339	378
$\tau_c$ , ( $\mu\text{sec}$ )	3.5	3.9

dient and is given by.

$$\eta = (q_{xx} - q_{yy})/q_{zz} \quad (4)$$

The axes are chosen such that  $q_{zz} > q_{xx} > q_{yy}$  and  $\eta$  lies between 0 and 1. Often  $\eta$  is sufficiently small, so that the term  $(1 + \eta^2/3)$  equals unity.

For  $^{14}\text{N}$  with  $I = 1$ , eq. (3) can be simplified to eq. (5)

$$(T_1)_N^{-1} = (3/2) \pi^2 \chi^2 \tau_c \quad (5)$$

In order to obtain the effective correlation time from  $(1/T_1)_N$ , one must know the exact value of the nuclear quadrupolar coupling constant,  $\chi$  in solutions. However, it is unknown in our systems.

A best value of  $\chi$  for formamide at 25°C has been reported by Hertz<sup>8</sup>. If we assume that the value for TA is not so different from that for formamide, the  $^{14}\text{N}$  coupling constant of formamide may be used for TA with minor correction. The  $\chi$  value for formamide is 2.56 MHz at 25°C. With the above  $\chi$  and the  $^{14}\text{N}$  spin-lattice relaxation rate measured, at 25°C were calculated for our systems and are given in Table 1. With assumption that the  $\chi$  for TA in our systems will be 10 to 20% higher than that for formamide, we obtained  $\tau_c = 2.5 \mu\text{sec}$  for the acetone solution and  $2.8 \mu\text{sec}$  for the methanol solution at 25°C.

Alger and Gutowsky<sup>9</sup> have suggested that solvents induce variations about 10% of  $^{14}\text{N}$  quadrupolar coupling constant and 60% of  $(T_1)_N$  in 2-fluoropyridine. If we accept the above information to be true, then the difference of  $\tau_c$  for our two

**Table 2.**  $E_a$  for Molecular Reorientation of TA in Acetone and Methanol Solutions

System	$E_a$ [ $\text{kJ mole}^{-1}$ ]
TA/ACETONE	8.4
TA/MeOH	10.4

systems could be mainly attributed to the effect of molecular association. However, molecular size and shape of solvents were assumed not to be important factors.

As shown in Figure 3, plots of  $\log [(1/T_1)_N]$  vs.  $1/T$  yield good straight line for TA in both solutions and the slopes give the Arrhenius type activation energies,  $E_a$ . Although the physical meaning of the activation energies is not clear<sup>10</sup>, the variations of  $(1/T_1)_N$  with temperature may be characterized by the molecular reorientational energies. The  $E_a$  for our systems are given in Table 2.

According to the  $E_a$  values, the molecular reorientational energy for the TA-MeOH system was about 23% higher than that for the TA-Acetone system. We can consider that the difference of  $E_a$  may be due to the different interactions in these two systems, in which methanol can possibly make hydrogen bonds with both thionyl and amino groups in TA, but acetone can only interact with  $\text{NH}_2$  group in TA. Therefore, the extent of the molecular association in methanol solution is greater than that in acetone solution.

Similar solvent effects were found for the hindered internal rotation in formamide by Kamei<sup>11</sup>. It has been pointed out that the  $E_a$  value for the hindered rotation about C-N bond was increased by H-bond formation on the carbonyl oxygen of formamide.

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