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Original Scientific Paper

Nuclear Spin-Lattice Relaxation in Taurine

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The temperature dependence of the spin-lattice relaxation time T_1 in taurine was studied between — 130° C and + 12° C. A value of $(T_1)_{min} = 24$ msec was obtained in quite good agreement with some other results. The difference between this and the theoretical value of $(T_1)_{min}$ was explained by the relaxation of CH_2 protons *via* the NH_3 protons. An activation energy $E_a = 4.6$ kcal/mole has been calculated. This value was ascribed to the NH_3^+ group motion.

INTRODUCTION

We have already studied[1] molecular motion in crystalline taurine by the C. W. NMR technique (^1H-resonance), following the temperature dependence of the second moment of the resonance lines. The low temperature transition in the second moment has been ascribed to changes in the NH_3^+ group mobility and assuming that the process was thermally activated, an activation energy E_a has been calculated.

A complementary approach to the molecular mobility problem is the study of the nuclear spin-lattice relaxation time T_1 as a function of temperature[2]. In this paper we present our results on T_1 measurements in taurine with a pulsed NMR method in the temperature range from — 130° C to + 12° C.

EXPERIMENTAL

The measurements were done on a polycrystalline sample of taurine (BDH product). The sample temperature was regulated by blowing nitrogen gas around the sample tube and a temperature controler (Brucker) was used to achieve and maintain the desired temperature.

The spin-lattice relaxation time T_1 was measured with a pulsed NMR spectrometer (spin-echo) using a radio-frequency of 37 MHz. The proton magnetic resonance signal following two $\pi/2$ pulses, separated by variable time t, was displayed on an oscilloscope, and from the time dependence of its amplitude:

$$s(t) = s_\infty \ [1 - e^{-t/T_1}] \quad (1)$$

the characteristic time T_1 was calculated for each temperature within the interval under investigation.

RESULTS AND DISCUSSION

The spin-lattice relaxation time of taurine within the investigated temperature range (Fig. 1) shows a characteristic V-shape curve with a single minimum around — 50° C. The minimum value $(T_1)_{min} = 24$ msec, and toward lower and higher temperatures T_1 increases steeply, so that at

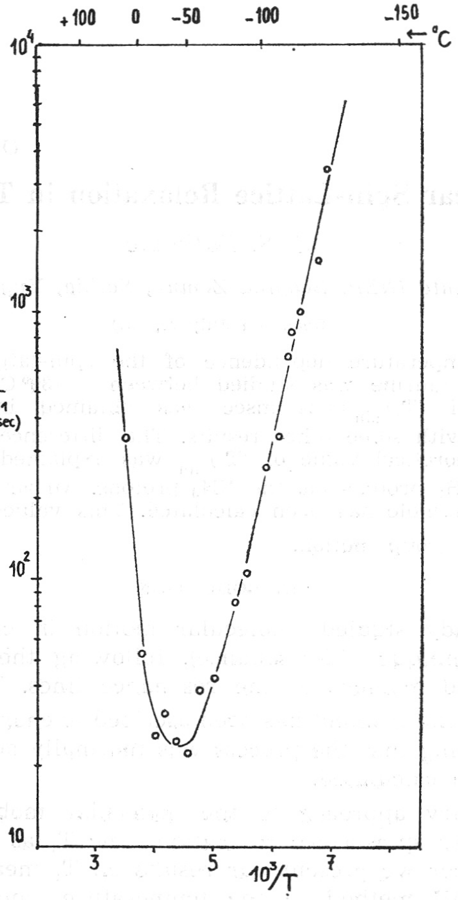

Fig. 1. Plot of T_1 *versus* $10^3/T$ for taurine.

— 128^0 C T_1 is 3.4 sec. This long relaxation time at low temperatures explains the difficulties in obtaining good PMR spectra of taurine below — 140^0 C, even with a minimum RF amplitude, due to the saturation effect[1].

The crystal structure data[3] show a dipolar ion configuration for crystalline taurine [NH_3^+ $(CH_2)_2SO_3^-$]. The amino group has an NH_3^+ form with an average N—H bond length of 0.85 Å and an average angle ∢ H—N—H = = 110^0. The molecules are held together in the crystal lattice by strong N—H ... O hydrogen bonds. Such a crystal structure suggests that free mobility of the NH_3^+ group is restricted by hydrogen bonding and that the amino group probably can reorient only within fixed positions in the crystal lattice. This motion provides a mechanism for the spin-lattice relaxation observed (Fig. 1).

Assuming that the relaxation of an isolated NH_3^+ group can be described[4] by the equation:

$$\frac{1}{T_1} = K \left[\frac{\tau_c}{1 + 4/9\, \omega_0^2\, \tau_c^2} + \frac{\tau_c}{1 + 16/9\, \omega_0^2\, \tau_c^2} \right] \tag{2}$$

where $K = 3\,\gamma^4\,\hbar^2/4\,\pi\,r^6$, ω_0 is the radio-frequency, r is the interproton distance in NH_3^+ group, and τ_c the correlation time of the motion in question, we have calculated the $(T_1)_{min}$ value using the condition $\omega_0\,\tau_c = 1.2$. From the crystal structure data[3] one obtains for an average H—H distance in the NH_3^+ group of taurine $r = 1.39$ Å. After introducing this in equation (2), we obtained a theoretical value $(T_1)_{min} = 11.7$ msec, which is lower than the experimental value (Fig. 1). The difference between these two values can be ascribed to relaxation of CH_2 protons *via* the amino group protons. Zaripov *et al.*[4] have shown that a linear dependence obtains between $(T_1)_{min}$ and the p — ratio of the total number of protons and the number of protons in the NH_3^+ group for a few compounds. In the case of taurine, $p = 2.33$, and for this we find $(T_1)_{min} = 23$ msec, in fair agreement with our experimental value.

Equation (2) can be used to calculate a correlation time τ_c for assumed NH_3^+ group mobility. For the low temperature data (Fig. 1) correlation times were obtained using $\tau_c = (2.81\,K/\omega_0^2)\,T_1$ and for the high temperature data using $\tau_c = 1/(2\,KT_1)$. The plot log τ_c *versus* $10^3/T$ (Fig. 2) gives a straight line, which means that the NH_3^+ movement is a thermally activated process, so that the following relation can be applied:

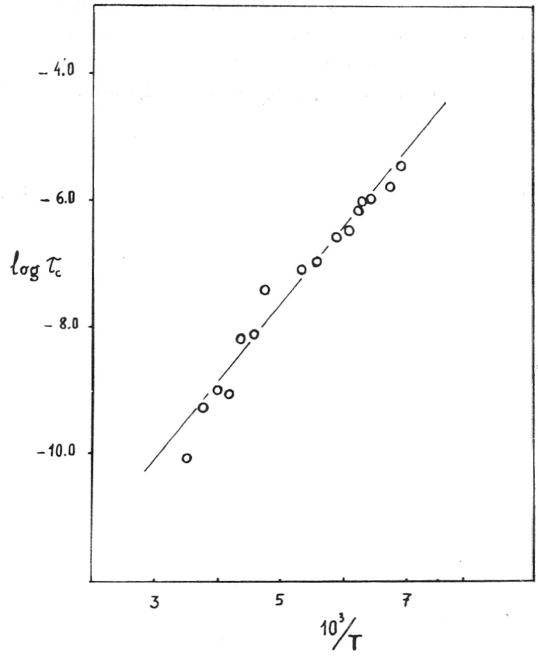

Fig. 2. Plot of log τ_c against $10^3/T$.

$$\tau_c = \tau_0 \exp(E_a/RT) \qquad (3)$$

in which τ_0 is a constant and E_a an activation energy. Extrapolating the straight line from Fig. 2, a value of $\tau_0 = 1.3 \times 10^{-14}$ sec was found. From the log T_1 *versus* $10^3/T$ plot using the low temperature experimental points (Fig. 1) a value of $E_a = 4.6$ kcal/mole was calculated. This agrees with the activation energy $E_a = 4.8$ kcal/mole calculated from the second moment data for taurine[5].

An attempt was also made to measure T_1 in deuterated taurine $ND_2(CH_2)_2SO_3D$, but the proton signal was too low to give any reliable result.

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IZVOD

Relaksacija nuklearni spin-rešetka u taurinu

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Ispitana je temperaturska zavisnost relaksacionog vremena spin-rešetka T_1 kod taurina između -130^0 i $+12^0$. Dobijena je vrednost $(T_1)_{min} = 24$ msec u dobroj saglasnosti sa nekim drugim rezultatima. Razlika između ove i teorijske vrednosti $(T_1)_{min}$ objašnjena je relaksacijom protona CH_2 grupa preko protona NH_3 grupe. Izračunata je aktivaciona energija $E_a = 4.6$ kcal/mole. Ova vrednost pripisana je pokretljivosti NH_3^+ grupe.

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