A Pulsed Proton Magnetic Resonance Study of Some Organic Compounds

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Spin-lattice relaxation times (T_1) of protons in polycrystalline dimethyl sulfone, stearic acid, stearyl alcohol, trimethylamine-N-oxide, tertiary-butylhydrazine hydrochloride and tertiary-butyl carbamate have been measured over a range of temperatures by pulsed proton magnetic resonance. Except for tertiary-butyl carbamate a single minimum in T_1 was observed for all the compounds. The T_1 results have been interpreted by considering the methyl group reorientations about the C_3 axis and the role of the spin diffusion of the other protons to the methyl protons in the compounds. The double minima in T_1 for tertiary-butyl carbamate have been attributed to reorientations of methyl groups in the tertiary-butyl group about the C_3' axis and reorientations of each methyl group about its C_3 axis. The spin-lattice relaxation parameters have been determined.

1. Introduction

Proton magnetic resonance spin-lattice relaxation time (T_1) measurements have been widely used to characterize molecular motions and motions of atomic groups of molecules in condensed matter. And it is now well known that T_1 measurements allow for the identification of reorientational, diffusional and rotational motion and give the whole microdynamics of spin systems.

In principle, the classical BPP theory of T_1 [1] explains the experimental results satisfactorily. However in some cases, especially for symmetric groups which have low energy barriers for reorientation or rotation, at low temperatures this theory fails [2] to explain the experimental T_1 results, and this case has been treated as tunnelling; current studies of this problem appear in the literature [3–7]. Furthermore, the derivation of the BPP theory is based on a model of noninteracting relaxing units, and as a consequence of this it is presumed that all the units are equivalent for spin-lattice relaxation. Therefore, this model becomes also unsatisfactory for solids wherein a fraction of the nuclei couples strongly to the lattice while the remainder experiences a weak coupling, and spin exchange between these units is rapid. In this case the use of the BPP theory predicts T_1 values much shorter than those experimentally observed [8–12]. It is the purpose of this study to give some more examples of this case.

2. Experimental

The spin-lattice relaxation times have been measured with an SXP type Bruker pulse spectrometer at 60 MHz employing $180° - \tau - 90°$ pulse sequences. The polycrystalline pure compounds used in this study were obtained from commercial sources and the samples were filled in glass tubes 9×10^{-3} m in diameter and 4×10^{-3} m in height. The samples were left under 1.33×10^{-2} Nm^{-2} vacuum for several hours and were then sealed off to erase any trace of water. The temperature control system was a Bruker B-ST 100/700 temperature controller, and approximately fifteen minutes were allowed after each setting of the temperature for the sample to reach the desired temperatures.

3. Results

The experimental results of spin-lattice relaxation times have been plotted on a semi-logarithmic scale as a function of $10^3/T$ in Figures 1–6. The T_1 results of dimethyl sulfone, stearic acid, stearyl alcohol, trimethylamine-N-oxide dihydrate and tertiary-butylhydrazine hydrochloride exhibit a single

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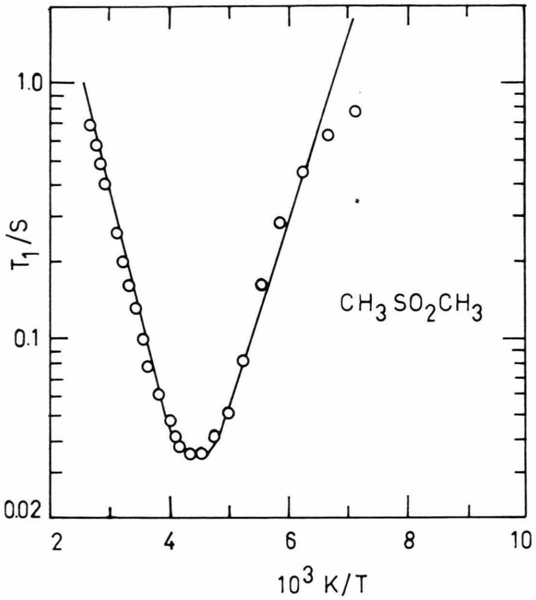

Fig. 1. Spin-lattice relaxation time of protons in dimethyl sulfone vs. 10^3 K/T.

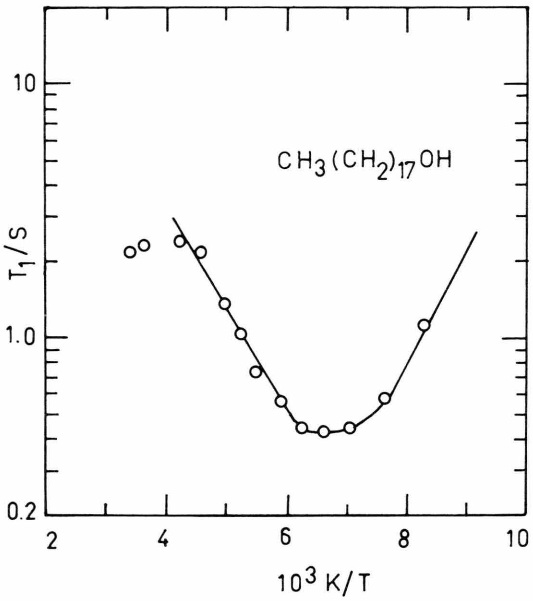

Fig. 3. Spin-lattice relaxation time of protons in stearyl alcohol vs. 10^3 K/T.

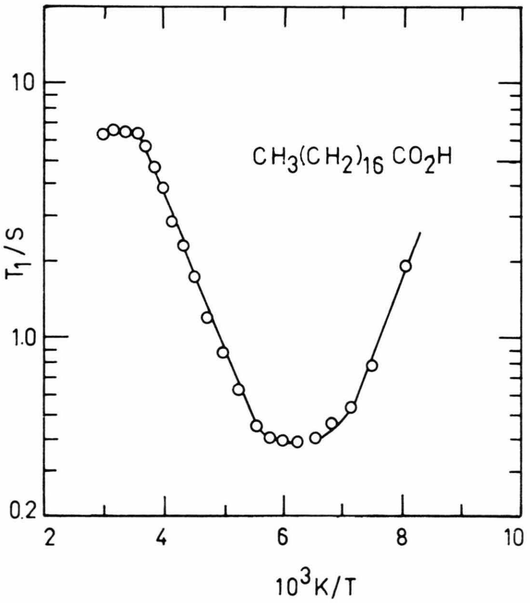

Fig. 2. Spin-lattice relaxation time of protons in stearic acid vs. 10^3 K/T.

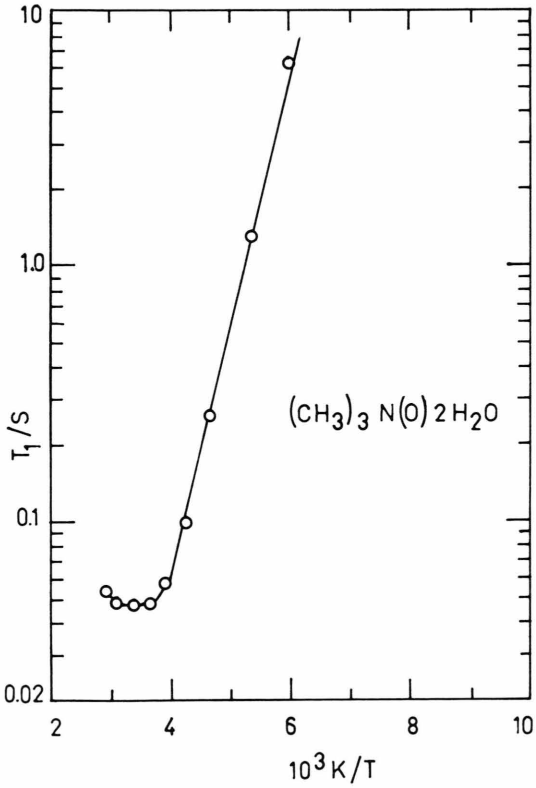

Fig. 4. Spin-lattice relaxation time of protons in trimethyl-amine-N-oxide vs. 10^3 K/T.

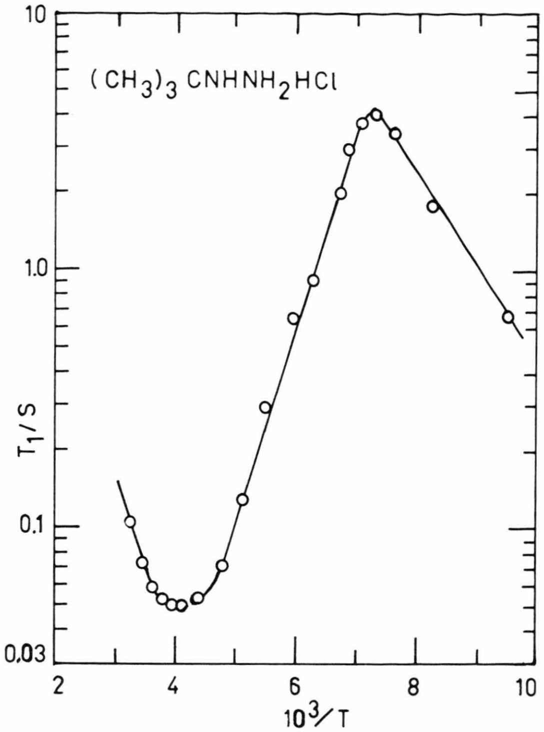

Fig. 5. Spin-lattice relaxation time of protons in tertiary-butylhydrazine hydrochloride vs. 10^3 K/T.

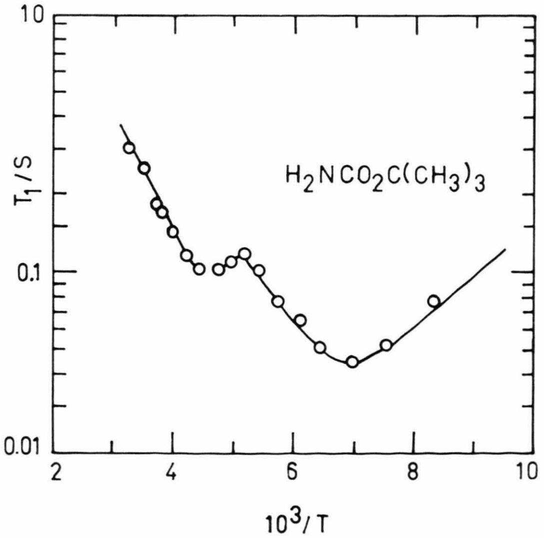

Fig. 6. Spin-lattice relaxation time of protons in tertiary-butyl carbamate vs. 10^3 K/T.

minimum and the value of $T_{1\min}$ changes as the number of protons other than those of methyl groups changes. The results for tertiary butylcarbamate show two minima in T_1. All the measurements are very well reproducible over the whole temperature range in which the experiments were performed.

4. Analysis and Discussion

The spin-lattice relaxation results of the compounds can be analyzed by assuming reorientational motions of a CH_3 group about its C_3 axis. When the spin-lattice relaxation of the methyl group is only due to reorientation about the C_3 axis the rate is given by [13]

$$\frac{1}{T_1} = \frac{9}{20}\,\frac{\gamma^4 \hbar^2}{r^6}\left(\frac{\tau_c}{1+\omega_0^2\,\tau_c^2} + \frac{4\,\tau_c}{1+4\,\omega_0^2\,\tau_c^2}\right). \qquad (1)$$

It is apparent from (1) that for a specific correlation time τ_c, and consequently for a specific reorientation frequency, T_1 will be minimum when $\omega_0\,\tau_c = 0.6158$. As a result, for $(T_1)_{\min}$ the spin lattice relaxation rate becomes

$$\frac{1}{(T_1)_{\min}} = \frac{9}{20}\left(\frac{\gamma^4 \hbar^2}{r^6}\right)\left(\frac{1.43}{\omega_0}\right). \qquad (2)$$

When the spin-lattice relaxation of the t-butyl group is due to C_3' reorientation superimposed on very fast C_3 motion of the methyl groups then, neglecting the intermethyl contribution, the rate can be written as [13–14]

$$\frac{1}{T_1} = \frac{3}{20}\,\frac{\gamma^4 \hbar^2}{r^6}\left(\frac{\tau_{c1}}{1+\omega_0^2\,\tau_{c1}^2}\;\frac{4\,\tau_{c1}}{1+4\,\omega_0^2\,\tau_{c1}^2}\right), \qquad (3)$$

where τ_{c1} is the correlation time of the reorientational motion about the C_3' axis. Then, T_1 will be minimum when $\omega_0\,\tau_{c1} = 0.6158$ and

$$\frac{1}{(T_1)_{\min}} = \frac{3}{20}\left(\frac{\gamma^4 \hbar^2}{r^6}\right)\left(\frac{1.43}{\omega_0}\right). \qquad (4)$$

Computation of $(T_1)_{\min}$ in these two cases using $r_{H-H} = 17.9$ nm gives 34 and 102 ms, respectively, in the above order.

a) Dimethyl sulfone

The spin-lattice relaxation time of dimethyl sulfone becomes minimum at 220 K with $(T_1)_{\min} =$

35 ms. This result is in good agreement with the above mentioned calculated value of 34 ms if we assume that the spin-lattice relaxation is due to dipolar interaction of methyl protons modulated by reorientations about the C_3 axis. From the straight line portions of the experimental results an activation energy $E_a = 17.0\ \mathrm{kJ\ mol^{-1}}$ is obtained. Using this activation energy, the $\omega_0 \tau_c = 0.6158$ condition at the minimum and the Arrhenius equation

$$\tau_c = \tau_c^0 \exp(E_a/RT) \tag{5}$$

in (1), the solid line in Fig. 1 was obtained. The curve is in good agreement with the experimental results, but below 160 K another relaxation mechanism seems to become effective. This mechanism may be the tunnelling of the methyl groups through the hindering barriers.

b) Stearic acid and stearyl alcohol

The spin-lattice relaxation for these two compounds becomes minimum at 161 K and 149 K, respectively, and the minimum values are 390 and 430 ms. These values do not agree with the computed value of 34 ms for the CH_3 groups. However, if we consider the effect of the spin diffusion then 34 ms should be multiplied by the ratio of the total protons to the number of CH_3 protons [8, 9]. In this case we obtain $34 \times \frac{36}{3} = 408$ ms for stearic acid and $34 \times \frac{38}{3} = 430$ ms for stearyl alcohol, and they are in good agreement with the experimental results. The activation energies are 11.1 and $9.0\ \mathrm{KJ\ mol^{-1}}$, and the curves obtained as above agree with the experimental points in Figs. 2 and 3. The levelling off of T_1 at high temperatures is due to the spin rotational interaction contribution to the relaxation of CH_3 groups. These results indicate that methylene protons in these substances are not effective in carrying the spin energy directly to the lattice, but they are effective in establishing the spin temperature by spin diffusion, that is methylene protons relax through $-CH_3$ protons.

c) Trimethylamine-N-Oxide

The T_1 for this compound becomes minimum at 280 K and $(T_1)_{\min} = 46$ ms. Taking into account the effect of the spin diffusion the calculated value becomes 49 ms, and that is in good agreement with the experimental result. The activation energy for the methyl groups has been found to be $18.6\ \mathrm{kJ\ mol^{-1}}$ and the calculated results, using (1) and (5), agree with the experimental dots as shown in Figure 4. This indicate that water protons in this compound relax through spin diffusion.

d) t-butylhydrazine hydrochloride and t-butyl carbamate

For t-butylhydrazine hydrochloride T_1 becomes minimum at 241 K and $(T_1)_{\min} = 49$ ms. This is due to reorientation of each CH_3 group about its own C_3 axis. The calculated value, taking account of the spin diffusion effect, becomes $34 \times \frac{13}{9} = 49$ ms, and that is in exact agreement with the experimentally observed minimum value. The activation energy obtained from the experimental results on both sides of the T_1 minimum is $E_a = 14.6\ \mathrm{kJ\ mol^{-1}}$ and the calculated results give the solid line, which is in agreement with the experimental results in Figure 5. T_1 begins to decrease at 137 K, and this is due to the reorientational motion of the NH_3 group in the compound, but we could not reach a minimum with our temperature controller to corroborate the assignment of the motion.

The T_1 results for t-butyl carbamate show two minima, one at 212 K and the other at 142 K. The higher temperature minimum is due to the reorientation of the t-butyl group about its C_3' axis (here, the C−O bond). A t-butyl group which contains three 3-spin groups, each of which may reorient about its own C_3 axis, may reorient also about the C_3' axis. Therefore if we use (4) and the effect of spin diffusion we obtain $(T_1)_{\min} = 124$ ms, and this result is in good agreement with the experimental result in Figure 6. The activation energy for this

Table 1. Activation parameters for spin-lattice relaxation of protons in six substances.

Substance	E_a/ kJ mol^{-1}	τ_c^0/s	$(T_1)^*_{\min}$/ ms
$CH_3SO_2CH_3$	17.0	1.5×10^{-13}	34
$CH_3(CH_2)_{16}CO_2H$	11.1	4.2×10^{-13}	408
$CH_3(CH_2)_{17}OH$	9.0	1.1×10^{-12}	430
$(CH_3)_3N(O) \cdot 2H_2O$	18.6	5.5×10^{-13}	49
$(CH_3)_3CNHNH_2HCl$	14.6	1.1×10^{-12}	49
$(CH_3)_3CO_2CNH_2$	8.0	1.9×10^{-12}	41.6
	10.0 (C_3')	5.7×10^{-12} (τ_{c1}^0)	124

motion has been found to be 10 kJ mol^{-1}. The lower temperature minimum, $(T_1)_{\min} = 45$ ms, is due to the methyl group reorientation about the C_3 axis. The calculated value, using (2) and considering the spin diffusion, becomes $(T_1)_{\min} = 41.6$ ms, which is in good agreement with the experimental result. This indicates that the $-\mathrm{NH}_2$ protons relax through $-\mathrm{CH}_3$ protons by spin diffusion. The activation parameters for spin-lattice relaxation of all the compounds are given in Table 1.

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