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Deuteron Spin Relaxation in the Plastic and Liquid Phases of Pivalic Acid

DAGFINN W. AKSNES [a] and LIUDVIKAS L. KIMTYS [b]

[a] Department of Chemistry, University of Bergen, Allegaten 41, N-5014 Bergen-Univ., Norway and [b] Department of General Physics and Spectroscopy, Vilnius V. Kapsukas State University, 232734 Vilnius, Lithuanian SSR, USSR

Deuteron line-widths and T_1 values have been measured in the plastic and liquid phases of deuterated pivalic acid, $(CH_3)_3CCOOD$. The good fits between the experimental and calculated relaxation times imply that a single correlation time, τ_r, is adequate to characterize the reorientation motion. The correlation times at the melting point are 5.0×10^{-9} s and 8.1×10^{-11} s in the plastic and liquid phases, respectively. The temperature variation of τ_r shows an Arrhenius behaviour with activation energies of reorientation of 25 ± 2 kJ/mol and 17 ± 2 kJ/mol for the plastic and liquid phases, respectively. From the observed minimum of T_1 in the plastic phase a quadrupole coupling constant of 160 ± 2 kHz has been calculated.

Many molecular solids which consist of spherical or almost spherically symmetric (globular) molecules are known to exist in an orientationally disordered crystalline phase of high symmetry.[1] In this phase, which is stable immediately below the melting point, the molecules undergo rapid reorientation simultaneously with slower translational diffusion. Evidence for rapid reorientational motion in the plastic phase has previously been obtained from thermodynamic, crystallographic, dielectric relaxation and nuclear magnetic resonance studies.[1]

The plastic phase of pivalic acid, $(CH_3)CCOOH$, extends from the transition point at 280 K to the melting point at 309 K.[2] X-Ray studies [3] have established that this high-temperature phase has a face-centred cubic crystal structure with four molecules in the unit cell. Dielectric,[4] ^{1}H NMR [5,6] and light scattering experiments [7] have suggested that the molecules in the plastic phase are randomly dimerized with one of their twelve nearest neighbours, fluctuating among them by means of molecular reorientation. However, considerable discrepancies exist in the reported activation energies for the overall molecular tumbling (20–36 kJ/mol).[5,6,8]

Deuteron relaxation provides an excellent method for the study of molecular reorientations in plastic crystal because it is dominated by a single intramolecular mechanism. It therefore seemed to be a reasonable approach to study the reorientational motion of pivalic acid by deuteron spin relaxation.

EXPERIMENTAL

The deuterated pivalic acid, $(CH_3)_3CCOOD$, was prepared from the corresponding chloride, $(CH_3)_3CCOCl$ and D_2O. The extent of deuteration of the investigated samples was 50 and 99% as established by high-resolution ^{1}H NMR.

The ^{2}H NMR spectra were measured at 13.82 MHz on a Bruker CXP 100 spectrometer equipped with external deuterium lock. The sample temperature was stabilized to within ± 0.5 K by means of a Bruker B-ST 100/700 c temperature control unit.

The deuteron spin-lattice relaxation time, T_1, was measured using the conventional $180° - \tau - 90°$ pulse sequence. Prior to the T_1 measurements, the 90° pulse width of 13.4 μs was evaluated by determining the value required for a 180° pulse corresponding to a null in the free-induction decay (FID). The T_1's were calculated by means of semi-logarithmic regression using from 10 to 20 measured points. The estimated accuracy

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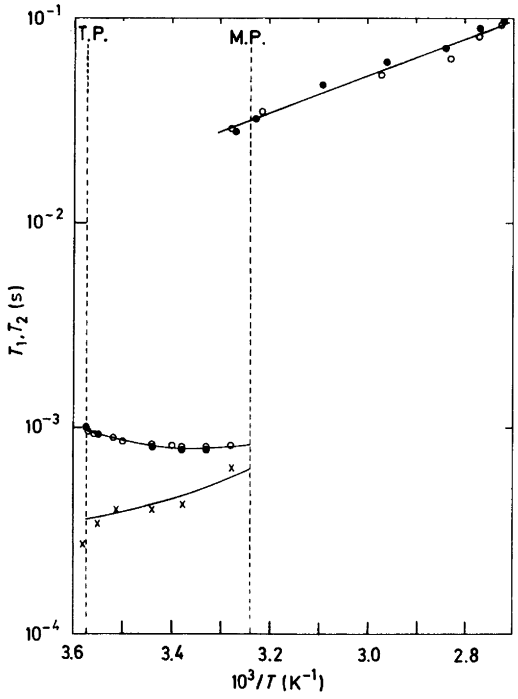

Fig. 1. Deuteron relaxation times, T_1 and T_2 at 13.82 MHz in deuterated pivalic acid, $(CH_3)_3CCOOD$, plotted *versus* $10^3/T$. ○, T_1 in a sample containing 99 % D; ●, T_1 in a sample containing 50 % D; ×, T_2 from line-width measurements on the 50 % D sample. The solid lines are theoretical fits as explained in the text.

of the T_1 values is 3–4 %. The half line-width ($\nu_{1/2}$) was measured from the Fourier transformed spectrum after applying a very small exponential weighting factor to the FID. The uncertainty in the half line-width values is *ca.* ±5 %.

RESULTS AND DISCUSSION

Deuteron line-widths and T_1 values were measured throughout the plastic phase and up to 368 K in the liquid phase. The measured line-widths were used to calculate T_2 in the plastic phase using the relation applicable to a Lorentzian line narrowed by a unique motional process, eqn. (1),

$$\nu_{1/2} = 1/\pi T_2 \tag{1}$$

where $\nu_{1/2}$ is the width of the line at half the maximum height. Semi-log plots of T_1 and T_2 *versus* the inverse temperature are shown in Fig. 1. It is seen that the T_1 values of the two measured samples are in good agreement. However, the T_1 values in the plastic phase show very little dependence on the temperature. It will be shown later that this apparent lack of temperature dependence is due to the existence of a minimum in T_1 at 13.82 MHz. It is interesting to note that a corresponding minimum in the methyl proton T_1 values of pivalic acid has been observed at 10 MHz.[5] This is reasonable because the dominant proton T_1 relaxation mechanism was attributed to overall molecular tumbling.

A few degrees below the melting point a small "spike" appeared on the high-field side of the broad deuterium signal of the solid. This narrow component had a width and T_1 characteristic of a liquid. A similar phenomenon has also been observed in the methyl proton signal of pivalic acid.[5] These observations indicate that there are liquid-like regions within the crystal just below the melting point.

For isotropic reorientation the contributions of the quadrupole mechanism to the deuteron spin-lattice (T_1) and spin-spin (T_2) relaxation times are given by eqns. (2) and (3),[9] where e^2qQ/h is the quadrupole coupling constant, η is the asymmetry parameter of the field gradient, ω_o is the resonance

$$\frac{1}{T_1} = \frac{3}{40}\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \cdot \left[\frac{\tau_r}{1+\omega_o^2\tau_r^2} + \frac{4\tau_r}{1+4\omega_o^2\tau_r^2}\right] \tag{2}$$

$$\frac{1}{T_2} = \frac{3}{80}\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \cdot \left[3\tau_r + \frac{5\tau_r}{1+\omega_o^2\tau_r^2} + \frac{2\tau_r}{1+4\omega_o^2\tau_r^2}\right] \tag{3}$$

frequency and τ_r is the correlation time of the molecular reorientation. Under the condition of extreme narrowing ($\omega_o\tau_r << 1$) eqns. (2) and (3) reduce to eqn. (4).

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{8}\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \tau_r \tag{4}$$

Eqn. (2) predicts a minimum in T_1 when $\omega_o\tau_r = 0.616$.[5] From the depth of the minimum which is

observed at 298.5 K we obtain $(1+\eta^2/3)^{\frac{1}{2}}e^2q\Omega/h = 160.4$ kHz.

The asymmetry parameter of O–D bonds is generally small ($\eta \lesssim 0.2$) in organic solids, *e.g.* 0.12 and 0.19 in the related systems formic acid [10] and potassium bicarbonate,[11] respectively. The asymmetry term may therefore be dropped from eqns. (2)–(4) to a very good approximation. It follows that $e^2q\Omega/h = 160 \pm 2$ kHz for pivalic acid. This value is very close to the values reported for formic acid (159–161 kHz)[10] and potassium bicarbonate (152–155 kHz).[11] These compounds also form dimers and the deuteron quadrupole coupling constant was found to increase with the deuteration ratio due largely to the lattice expansion. However, in pivalic acid the effect is apparently too small to have an observable effect on the measured T_1 values which are identical within experimental error for the two investigated samples (50 and 99 % deuteration).

By using the value 160 ± 2 kHz for the quadrupole coupling constant in eqn. (2), we obtain the temperature dependence of τ_r from the measured T_1 values. The T_1 and T_2 curves corresponding to these τ_r values were calculated from eqns. (2)–(4) and are shown in Fig. 1. The good fits between the experimental and calculated relaxation times imply that a single correlation time τ_r, is adequate to characterize the reorientation motion. It follows, as expected, that the quadrupole relaxation through molecular reorientation is the main line broadening mechanism. The correlation times at the melting point are 5.0×10^{-9} s and 8.1×10^{-11} s in the plastic and liquid phases, respectively.

The temperature variation of τ_r shows an Arrhenius behaviour with activation energies of reorientation, E_a, of 25 ± 2 kJ/mol and 17 ± 2 kJ/mol for the plastic and liquid phases, respectively. The large change in E_a at the melting point, accompanied by a corresponding discontinuity in T_1, suggests that a discontinuous change in the type of motion governing the quadrupole relaxation is taking place. We believe, in accordance with previous results,[5] that a quasi-isotropic monomer reorientation involving the making and breaking of hydrogen bonds, is the dominant T_1 relaxation mechanism in the plastic phase. In the liquid phase, however, rapid overall tumbling of complete dimers probably governs T_1.

Our value of the reorientational activation energy in the plastic phase is practically identical with that found by Albert *et al.*[6] (25.1 ± 2.5 kJ/mol) for the same deuterated compound. This value, however, is between the two previously reported values for ordinary pivalic acid (20 kJ/mol and 36 ± 3 kJ/mol).[5,8] It is thus clear that the sizable discrepancies are not the result of an isotopic effect caused by a large difference between the hydrogen and deuterium bond strengths. This conclusion is consistent with the present observation that the deuterium content has no observable effect on T_1 and E_a.

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