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Molecular Motions in Plastic Phase of 2-Methyl-2-nitropropane, $(CH_3)_3CNO_2$, by Pressure and Temperature Dependences of ^{1}H-NMR Spin-Lattice Relaxation

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Proton NMR spin-lattice relaxation time, T_1, in the plastic phase of 2-methyl-2-nitropropane $(CH_3)_3CNO_2$ was measured at 10 MHz up to 150 MPa between 262 and 320 K. The overall molecular reorientation with an activation enthalpy of $\Delta H^{\ddagger}_{\mathrm{r}}$=6.8±1.0 kJ mol^{-1} and an activation volume of $\Delta V^{\ddagger}_{\mathrm{r}}$= (0.07±0.02)$V_{\mathrm{m}}$ did not show significant pressure dependence up to 140 MPa, where V_{m} is the molar volume of $(CH_3)_3CNO_2$ at 273.2 K. The self-diffusion, which was treated by the Torrey's isotropic diffusion model, showed large pressure dependence; the activation enthalpy, $\Delta H^{\ddagger}_{\mathrm{d}}$, changed from 46±4 kJ mol^{-1} under saturated vapor pressure of the sample to 95±8 kJ mol^{-1} under 100 MPa and the activation volume, $\Delta V^{\ddagger}_{\mathrm{d}}$, changed from V_{m} at 278.0 K to 0.8V_{m} at 320.0 K. These results strongly suggest monovacancy mechanism for self-diffusion. The phase diagram of liquid-plastic and plastic-brittle phase transitions is also given.

The study of NMR spin-lattice relaxation time, T_1, brings us valuable information of structure and dynamics of molecules. The method is particularly useful in plastic crystals for studying both reorientational and translational molecular motions. Solids, of which the constituent molecules have a globular shape, generally form a plastic crystalline phase before melting. The plastic phase, in which the motion of overall molecular reorientation is already excited, has a cubic or hexagonal close-packed structure in a majority of cases and is mainly characterized by a low entropy of fusion ($\Delta S \lesssim 20$ J K^{-1}mol^{-1}). 2-Methyl-2-nitropropane is one of such globular molecules, but its plastic phase belongs to the orthorhombic system (a=0.612 nm, b=0.617 nm, and c=0.879 nm, $a \cong b \cong c/\sqrt{2}$) with two molecules in the unit cell.[1] This phase exists between 260.1 K and the melting point (299.2 K) with the entropy of fusion, 8.66 J K^{-1}mol^{-1}.

The molecular motions in this phase have been studied by a number of experimental methods. Dielectric relaxation study reported the potential barrier hindering rotation of the molecular electric dipole (3.77 D* at 299 K)[2] as 6.78±0.84 kJ mol^{-1} [3] and its correlation time (from 8.7×10^{-12} s at the melting point to ≈5×10^{-12} s near the transition point).[4] On the other hand, far infrared absorption study[5] reported that the residence time of a librator in the potential well was 10×10^{-12} s at 294 K.

Recently we reported the NMR study[6] of molecular motions in solid $(CH_3)_3CNO_2$. In our previous study[6] we obtained the values of the activation parameters, E_{a}=46.5±0.9 kJ mol^{-1} and τ_0=(4.6±1.8)×10^{-15} s for self-diffusion and the mean jump time (6×10^{-7} s) of the molecule at the melting point; however, we did not get enough information on the molecular reorientation and mechanism of self-diffusion in the plastic phase.

To get such information we measured temperature- and pressure-dependence of spin-lattice relaxation time in the plastic phase. In this paper we report on the molecular motions and their roles in the spin-lattice relaxation in the plastic phase, and on the phase diagram of 2-methyl-2-nitropropane.

Experimental

2-Methyl-2-nitropropane (Aldrich Chemicals Co., Inc.) was purified by a preparative gas chromatograph. The purity of this specimen was estimated to be higher than 99.87 mol per cent by a gas chromatographic analysis. Furthermore the specimen was subjucted to dehydration using Molecular Sieve 4A, vacuum distillation, and degassing by the conventional freeze-pump-thaw technique and then transferred into the NMR pressure vessel via a specially designed adapter which was already reported.[7]

Proton spin-lattice relaxation time was measured using $(\pi/2)_{\mathrm{satn}}$-τ-$\pi/2$ pulse sequences with an operating frequency of 10.0 MHz. The working pressure and temperature ranges over which T_1 was measured were between the saturated vapor pressure of the sample and 150 MPa and between 262.0 K and 320.0 K, respectively. The pressure was measured with a manganin gauge.[7] The uncertainty of the pressure value in the present study was estimated to be within 1.4 MPa. The temperature was controlled to within 0.1 K and measured with a Chromel-P/Constantan thermocouple attached to the NMR pressure vessel.

Results and Discussion

Molecular Motions. The results of experimental determination of T_1 under various pressures are given in Fig. 1. The upper and lower bounds of the existence of the plastic phase of 2-methyl-2-nitropropane are indicated by vertical dotted lines. The T_1 curves in Fig. 1 do not directly correspond to the results of a continuous run under a given pressure, except the one at the saturated vapor pressure of the sample, because the pressure inside the vessel changed when the temperature of the sample changed. Therefore, the primary results were rearranged to show the temperature dependence of T_1 under a constant pressure

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*1D=3.33×10^{-30} C m.

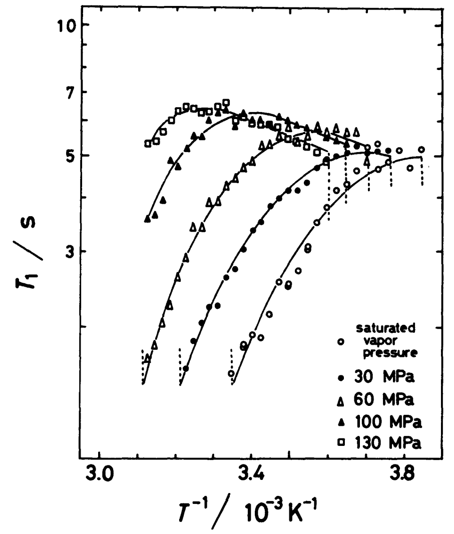

Fig. 1. Temperature dependence of T_1 under various pressures in plastic 2-methyl-2-nitropropane. The upper and lower bounds of the existence of the plastic phase of $(CH_3)_3CNO_2$ are indicated by vertical dotted lines.

in Fig. 1.

It is seen from Fig. 1 that the T_1 at a constant pressure of larger than 60 MPa has a maximum; it indicates that a change occurs in the molecular motion that is responsible for the relaxation on either side of the maximum. It is interpreted to be a change from overall molecular reorientation to translational self-diffusion as reported in our previous NMR study.[6] When such two different relaxation mechanisms contribute to the observed T_1 and if we can treat the motions independently, the relaxation rate, $T_1(\mathrm{obsd})^{-1}$, can be expressed by the sum of the two relaxation rates as follows:

$$T_1(\mathrm{obsd})^{-1} = T_{1r}^{-1} + T_{1d}^{-1}, \tag{1}$$

where the subscripts, r and d, denote overall molecular reorientation and molecular translational self-diffusion, respectively. At this stage it is necessary to separate T_{1r} and T_{1d} from $T_1(\mathrm{obsd})$. Here the value of T_{1r} may be estimated by extrapolating from the T_1 data at 130 MPa from the low temperature side of the maximum, since the pressure dependence of the temperature coefficient of T_1 on the lower temperature side of the T_1 maximum was not large at pressure values below 140 MPa. The T_{1r} is related to the correlation time τ_r associated with overall molecular reorientation as follows:

$$T_{1r}^{-1} \propto \tau_r \ (\omega\tau_r \ll 1). \tag{2}$$

On the other hand, the T_{1d} (in this case, $\omega\tau_d \gg 1$) is given by Torrey's isotropic diffusion model[8,9] as follows:

$$T_{1d}^{-1} = 2.67\,\gamma^2\langle\Delta M_2\rangle/(\omega^2\tau_d), \tag{3}$$

where γ is the gyromagnetic ratio of proton, $\langle\Delta M_2\rangle$ is the part of the second moment (in Gauss unit**) that is modulated by translational self-diffusion, and τ_d is the mean diffusional jump time of molecules. Boden et al.[10] reported that Torrey's isotropic diffusion model was a good model especially for organic plastic crystals with a low value of the entropy of fusion; the entropy of fusion of $(CH_3)_3CNO_2$ is only 8.66 J K^{-1} mol^{-1}.[11]

For thermally activated motions, the correlation time τ should obey the relation of Arrhenius type,

$$\tau = \tau_0 \exp(\Delta G^*/RT), \tag{4}$$

where ΔG^*, the Gibbs energy of activation, is defined by

$$\Delta G^* = \Delta H^* - T\Delta S^*. \tag{5}$$

According to thermodynamics, the activation volume is defined by

$$\Delta V^* = (\partial\Delta G^*/\partial P)_T, \tag{6}$$

so that, if one assumes that the pressure dependence of τ_0 is negligible,[11] the values of τ derived by fitting the experimental data to Eqs. 2 and 3 may be used to obtain ΔV^* and ΔH^* through the relation,

$$\Delta V^* = RT(\partial \ln \tau/\partial P)_T, \tag{7}$$

and

$$\Delta H^* = R\{\partial \ln \tau/\partial(1/T)\}_P. \tag{8}$$

The volume of the plastic phase decreased linearly with increasing pressure up to ≈73 MPa at 291 K, and it was described by a constant isothermal compressibility $(7.1\pm0.8)\times10^{-4}$ MPa^{-1}, which was determined from the distance of the piston plunger traveled into the pressure vessel upon compression.

When one attempts to calculate the value of τ_d under various pressures using Eq. 3, one should consider a change of $\langle\Delta M_2\rangle$ by the pressure. Because the second moment $\langle\Delta M_2\rangle$ is inversely proportional to the square of the volume of the unit cell, one expects the value of $\langle\Delta M_2\rangle$ to increase with increasing pressure. This would be the case only if the effect of pressure is such as to decrease the intermolecular distance rather than to decrease the number of vacancies that exist in plastic crystals, e.g. in solid argon and krypton[12] or even in solid chlorine.[13] Actually, as is seen from Fig. 1, the T_{1d} increases with pressure at a constant temperature, which fact, together with the large value of compressibility, suggests that the second moment is not significantly affected by the application of pressure. An approximate estimate indicates that the T_{1d} at 73 MPa would be 10% smaller than the T_{1d} under the

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**$1\,\mathrm{G}=10^{-4}$ T.

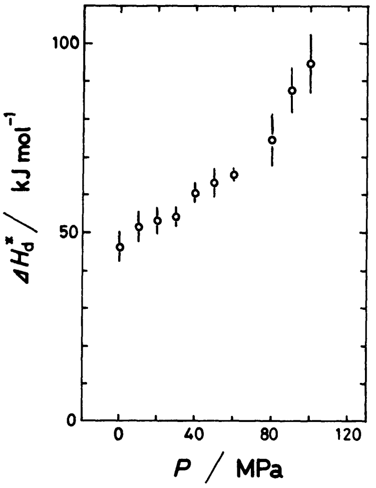

Fig. 2. Pressure dependence of activation enthalpy, $\Delta H_d^\ddagger$, for the molecular self-diffusion in plastic $(CH_3)_3CNO_2$.

saturated vapor pressure if the pressure compressed the intermolecular distance. We now use the value of $\langle \Delta M_2 \rangle = 1.0\,G^2$ ($0.01\,mT^2$) calculated from $T_{1\rho}$ minimum value[6] under saturated vapor pressure of the sample, in calculating τ_d using T_1 data and Eq. 3.

The activation enthalpy of self-diffusion ($\Delta H_d^\ddagger$) obtained in this study shows remarkable pressure dependence from 46±4 kJ mol^{-1} under saturated vapor pressure to 95±8 kJ mol^{-1} under 100 MPa as shown in Fig. 2; These can be compared with the cases of 2,2,3,3-tetramethylbutane (from 70 kJ mol^{-1} to 90 kJ mol^{-1}) and hexamethyldisilane (from 40 kJ mol^{-1} to 50 kJ mol^{-1}) in the same pressure range. The value of $\Delta V_d^\ddagger$ decreased gradually from 101±35 cm^3 mol^{-1} at 278 K {this value of $\Delta V_d^\ddagger$ is equal to V_m (=101 cm^3 mol^{-1}) which is the molar volume at 273.2 K} to 77±6 cm^3 mol^{-1} ($\approx 0.8 V_m$) at 320.0 K with increasing temperature. This tendency is very similar to the case of plastic phases of 2,2,3,3-tetramethylbutane and hexamethyldisilane,[14] and thus these values of the activation volume strongly suggest the monovacancy mechanism for self-diffusion.[14] Figure 3 shows the calculated correlation time, τ_d, of the molecular self-diffusion at the melting point and at the plastic-brittle phase transition point under various pressures. In contranst to the behavior of the values of τ_d at the melting point, which is almost constant ($\approx 9 \times 10^{-7}$ s), the values at the plastic-brittle phase transition increase as the transition point moves to higher temperatures (from 1.5×10^{-5} s under the saturated vapor pressure to 2×10^{-4} s under 80 MPa). These results suggest that the self-diffusion is the direct trigger of the fusion phenomenon but it is not a direct trigger of the plastic-brittle phase transition.

On the other hand, the activation enthalpy for overall molecular reorientation, $\Delta H_r^\ddagger$, was obtained to be 6.8±1.0 kJ mol^{-1} which did not show remarkable pressure dependence up to 140 MPa. The activation

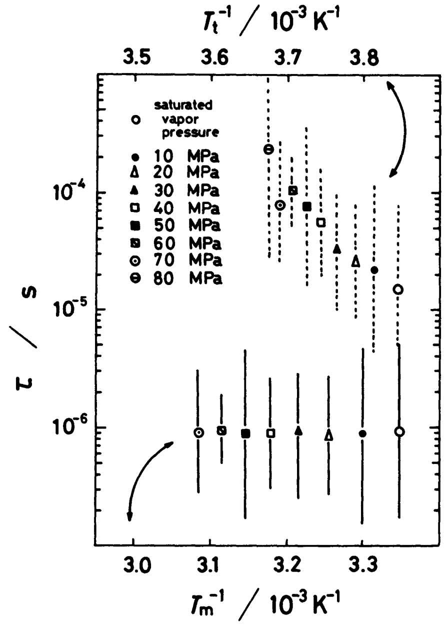

Fig. 3. The correlation time of molecular self-diffusion at the melting points (T_m) and the plastic-brittle phase transition points (T_t) under different pressures in $(CH_3)_3CNO_2$.

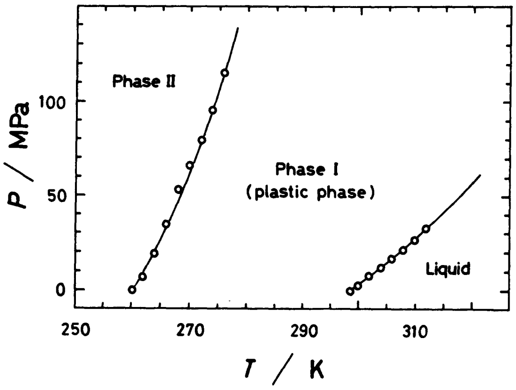

Fig. 4. Phase diagram of 2-methyl-2-nitropropane.

volume of the overall molecular reorientation, $\Delta V_r^\ddagger$, increased slightly with increasing temperature from 7±2 cm^3 mol^{-1} at 274.0 K to 8±1 cm^3 mol^{-1} at 320.0 K. However, the ratio of $\Delta V_r^\ddagger$ to the molar volume V_m is expected to be a constant value of 0.07±0.02, because the value of V_m, which depends on the lattice spacing, would also be expected to increase with increasing temperature. The value of the ratio, 0.065, is in good agreement with results on overall molecular reorientation in other plastic crystals; in cases[7,11] of norbornane, cyclohexane, 2,2,3,3-tetramethylbutane, and 2-methylpropanoic acid, the ratios are 0.04, 0.07, 0.07—0.09, and 0.12, respectively.

Phase Diagram. The phase diagram is shown in Fig. 4, which was obtained by determining the temperature of phase changes from the jumps of the T_1 values. Figure 4 shows that the two curves become further separated as the pressure increases, and this separation is more remarkable than in the case of $(CH_3)_3CCOOH$.[7] The average slopes of the boundary curves are

$$\frac{dP}{dT} = 7.65\ \mathrm{MPa\ K^{-1}}\ \text{(on the plastic-brittle phase transition curve: } \Delta S = 17.9\ \mathrm{J\ K^{-1}\ mol^{-1}})$$
$$= 2.5\ \mathrm{MPa\ K^{-1}}\ \text{(on the melting curve: } \Delta S = 8.66\ \mathrm{J\ K^{-1}\ mol^{-1}}).$$

The average slope for the melting in $(CH_3)_3CNO_2$ is very similar to the slope (2.22 MPa K^{-1}) in $(CH_3)_3CCOOH$ but the slope for the plastic-brittle phase transition is about twice as large as that (3.26 MPa K^{-1}) of $(CH_3)_3CCOOH$. The volume changes at these transition points were calculated by the use of the Clapeyron-Clausius equation from the entropy changes; they were 2.34 $cm^3\,mol^{-1}$ for the plastic-brittle phase transition and 3.46 $cm^3\,mol^{-1}$ for the melting. It is interesting to note that an application of external pressure displaces the region of the existence of the plastic crystal phase to a higher and a wider temperature, and that the volume changes of $(CH_3)_3CNO_2$ and $(CH_3)_3CCOOH$ at their melting points are not so different from each other but their volume changes at the respective plastic-brittle phase transition points are very different. Different crystal conditions of the two brittle crystal phases are reflected in the latter difference of the volume change. By comparison of $(CH_3)_3CNO_2$ with $(CH_3)_3CCl$ and $(CH_3)_3CBr$, it is also interesting to note that the temperature region (ΔT) of existence of their plastic phase relates to the entropy of fusion, i.e. ΔT=24.7 K and ΔS_m=7.53 J K^{-1} mol^{-1} for $(CH_3)_3CBr$, ΔT=29.0 K and ΔS_m=7.99 J K^{-1} mol^{-1} for $(CH_3)_3CCl$, and ΔT=39.1 K and ΔS_m=8.66 J K^{-1} mol^{-1} for $(CH_3)_3CNO_2$, respectively.

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