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Pressure and Temperature Dependence of NMR Spin-lattice Relaxation in Plastic 2,2-Dimethylpropanoic Acid

Tooru Hasebe,*,† (the late) Gen Soda, and Hideaki Chihara
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka 560

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Proton spin-lattice relaxation time T_1 of 2,2-dimethylpropanoic acid in its plastic phase was measured at 10 MHz up to 120 MPa between 268 K and 330 K. A minimum in T_1 appears in the low-pressure region which is due to overall reorientation of molecules. The T_1 minimum value decreases as the pressure increases in a way different from simple-minded prediction. The activation volume, 25 ± 3 cm^3 mol^{-1}, is twice as large as in other plastic crystals when normalized by the molar volume. The pressure dependence of the activation enthalpy is also about twice as large. These can be rationalized by considering associated dimers as the reorienting unit. The phase diagram is given and the volume changes associated with the transition and with the fusion were derived (15.6 and 5.86 cm^3/mol of dimer).

2,2-Dimethylpropanoic acid $(CH_3)_3CCOOH$ has been investigated by various techniques[1-16] because it is a unique plastic crystal having a very small entropy of fusion 6.5 J K^{-1} mol^{-1} (309.7 K) in spite of the molecular polarity.

The NMR studies established the nature of the spin-lattice relaxation in solid as well as in liquid state. Thus, in the low-temperature brittle phase both methyl and t-butyl reorientations are responsible for the T_1 minimum, in the high-temperature plastic phase the overall molecular tumbling governs T_1, and in the liquid phase the self-diffusion is the dominant relaxation mechanism.

Since our previous analysis[7] of T_1 results in the plastic phase was not correct, we decided to carry out additional experiments, particularly about the effect of external pressure on T_1 in the plastic phase. The present paper reports such experimental results and proposes that the dynamical unit for molecular tumbling is probably an associated dimer.

Experimental

Material and T_1 Measurements. 2,2-Dimethylpropanoic acid (reagent grade) from Tokyo Kasei Kogyo Co., Ltd. was subjected to dehydration using Molecular Sieve 4A, vacuum distillation, and degassing by repeated freeze-pump-thaw cycles and then transferred into the pressure vessel *via* a specially designed adapter which will be described.

Proton spin-lattice relaxation time was measured using π-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 120 MPa and between 268 K and 330 K, respectively.

Pressure Vessel and Its Operation. Figure 1 is a schematic drawing of the high-pressure NMR vessel (hereafter referred to as the vessel). The vessel was machined from non-magnetic beryllium-copper alloy (Cu 97.57%, Be 1.86%, Co 0.27%, Fe 0.16%, and Ni 0.01%) and was annealed at 570 K for three hours after machining. The ratio of the outside to the inside diameter was nowhere less than 1.9. Hermetic closure of electrical leads was made by using phosphor bronze of cone shape (Fig. 1B) insulated from the body of the vessel with Epoxy putty XD 580 (Japan Ciba-Geigy Co.). At other places (j, k, and l for the lead-wire housing and e and f for the piston), three washers of Teflon, Be–Cu alloy, and lead metal were used in turn from inside to outside to secure pressure-tightness.

The working pressure gauge was a length of manganin wire (B. S. #38) wound round a Teflon bobbin (q) and annealed at 390 K for 17 h *in vacuo*. The gauge was calibrated against the standard Heise gauge up to 200 MPa at the High Pressure Laboratory, Faculty of Engineering Science, Osaka University after several cycles of pressurizing and releasing. The gauge reading was reversible above 100 MPa but showed a small hysteresis effect at lower pressures. The temperature dependence of the electrical resistance was also measured at 0.1 MPa; at other pressures

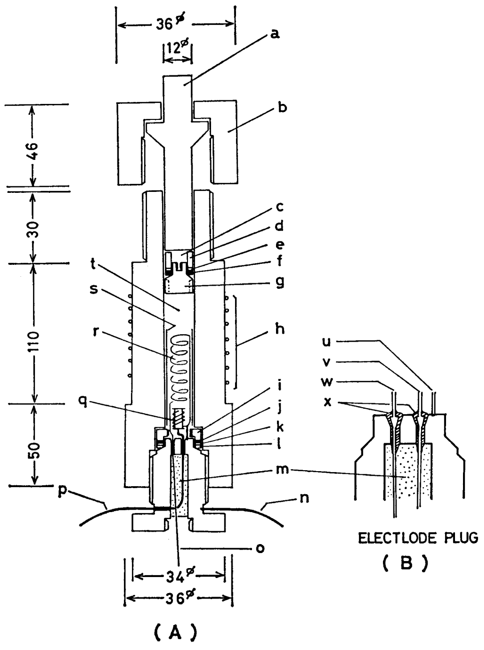

Fig. 1. Pressure vessel.
a: Be–Cu piston plunger, b: Be–Cu clamp, c: unsupported area, d: Be–Cu supporter, e: Be–Cu washer, f: Teflon washer, g: Be–Cu piston, h: heater, i: Be–Cu extractor ring, j: Teflon washer, k: Be–Cu washer, l: Pb washer, m: epoxy resin, n: lead-wire, o: Cu rf lead-wire, p: Cu lead-wire for manganin gauge, q: manganin gauge, r: rf coil, s: Teflon seal, t: sample space, u: electric ground terminal, v: rf lead-wire, w: lead-wire for manganin gauge, x: epoxy putty, All dimensions are given in millimeters.

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† Present address: Department of Chemistry, Faculty of Education, Fukushima University, Matsukawa-machi, Fukushima 960-12.

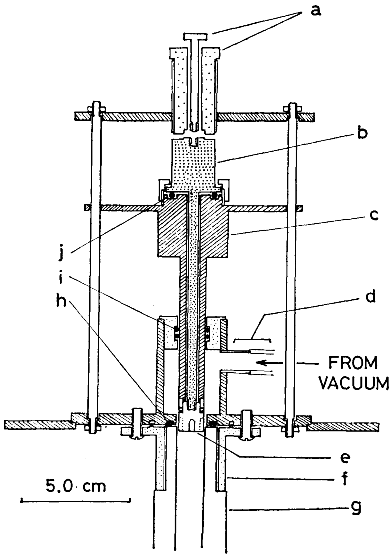

Fig. 2. Pressure vessel and adapter.
a: Brass stopper, b and c: co-axial stainless steel supporter for piston, d: Kovar seal, e: piston, f: brass connector; g: pressure vessel, h—j: fluororubber O-ring.

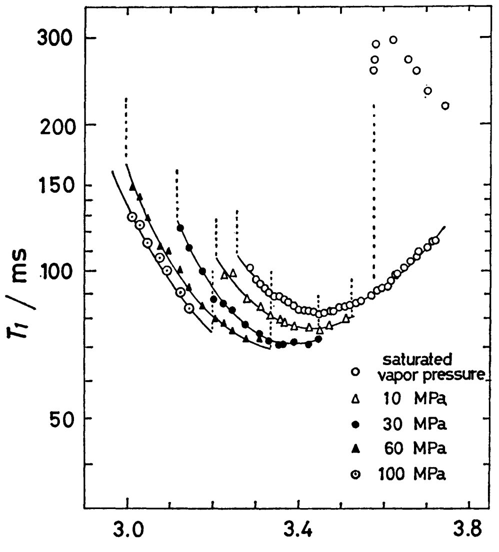

Fig. 3. Temperature dependence of T_1 at various pressures.

we used the pressure coefficient values reported by Wang.[17] The overall uncertainty of the pressure values in the present study was estimated as ± 1.4 MPa.

The temperature of the specimen was controlled by non-inductive winding of KARMA heater (h) (B. S. #36, Driver Harris Co.) and cold nitrogen stream evaporated from the bottom of the Dewar flask in which the vessel was placed. The electrical current through the heater was controlled automatically with a Chromel-P/Constantan thermocouple attached to the outer surface of the vessel as the temperature sensor.

Figure 2 shows the connecting device for distilling the specimen from outside into the vessel. The plunger and the screwed cap (a and b of Fig. 1A) were removed from the top of the vessel and then the body was attached to the connecting device from below (g of Fig. 2). The plug was pulled up with movable supporters b and c to connect the inside of the vessel to the outside vacuum/purification line. The system was made vacuum-tight with a number of fluoride rubber O rings as shown in Fig. 2. When distillation of the specimen is over, the piston (e) was dropped into the vessel using the rods a, b, and c, the vessel was taken off the connecting device, and piston/plunger was pressed and clamped. Because the plastic phase of 2,2-dimethylpropanoic acid is extremely soft for a crystal, we may safely assume that the pressure applied is hydrostatic.

Results and Discussion

Spin-lattice Relaxation Time. The results of experimental determination of T_1 under various pressures are given in Fig. 3. The upper and lower bounds of the existence of the plastic phase of 2,2-dimethylpropanoic acid are indicated by vertical broken lines. The curves in Fig. 3 do not correspond to the results of a continuous run under a given pressure, except the one at the saturated vapor pressure of the specimen, because the pressure inside the vessel changed when the specimen temperature changed. Therefore, the primary results were rearranged to show, in Fig. 3, the temperature dependence of T_1 under a constant pressure. It is seen that the plastic phase is readily undercooled down to about 269 K ($1/T = 3.72 \times 10^{-3}$ K^{-1}), some 10 K below the transition point, giving smooth extrapolation of the T_1 curve under the ordinary pressure.

There is a distinct minimum of T_1 in the plastic phase which has been substantiated as caused by reorientational motion of molecules.[6,7,13] The relaxation rate T_1^{-1} can be expressed in terms of the correlation time τ and the part of second moment M_2 modulated by such molecular motion;[18]

$$T_1^{-1} = C[\{\omega\tau/(1+\omega^2\tau^2)\} + \{4\omega\tau/(1+4\omega^2\tau^2)\}], \qquad (1)$$

where

$$C = (2/3)\gamma^2\{M_2(\text{intra}) + M_2(\text{inter})\}, \qquad (2)$$

and γ is the gyromagnetic ratio of the proton. The T_1 minimum tends to move to higher temperatures as the pressure is increased although more slowly than the movement of the phase boundaries. Also the minimum value of T_1 decreases as the pressure is increased. This indicates that M_2, particularly M_2(inter), increases its magnitude upon compression. In the case of fast isotropic reorientation of molecules, M_2(inter), for the fcc lattice is given by

$$M_2(\text{inter}) = 4.14 \times 10^{-2} N_0\, a^{-6}, \qquad (3)$$

where N_0 is the number of protons per molecule and a is the lattice constant in the units of nanometer. Since M_2(inter) depends on the inverse sixth power of intermolecular proton-proton distances, we would expect that T_1^{-1}(max) changes linearly with the inverse square of the crystal volume. Thus, T_1^{-1}(max) is plotted against $(V_0/V)^2$ in Fig. 4, where V_0 is the crystal volume at the saturated vapor pressure. The volume at other pressures were determined from the distance of travel of the piston plunger into the pressure vessel by compression. The compression was ap-

Table 1. The enthalpy of activation ΔH^*, τ_0, T_1(min), and its temperature at different pressures

P/MPa	ΔH^*/kJ mol^{-1}	$\tau_0/10^{-14}$ s	T_1(min)/ms	T/K at T_1(min)
Saturated vapor pressure	32.8±2.0	1.1 ±1.0	82.0±1.0	289.4
10	33.0±2.7	1.2 ±1.0	77.1±1.9	290.7
20	33.4±1.2	1.1 ±1.0	73.0±2.2	292.0
30	35.7±1.3	0.48±0.30	71.6±1.4	294.6
40	37.8±3.0	0.22±0.15	69.8±1.8	296.3
50	38.7±1.7	0.17±0.08	69.1±2.4	297.6

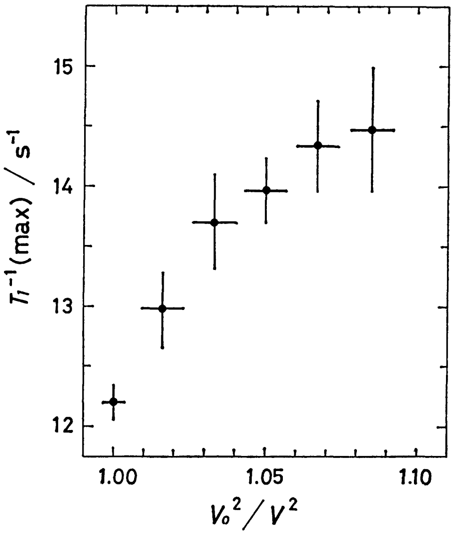

Fig. 4. T_1^{-1}(max) against the square of reduced crystal volume, V_0/V.

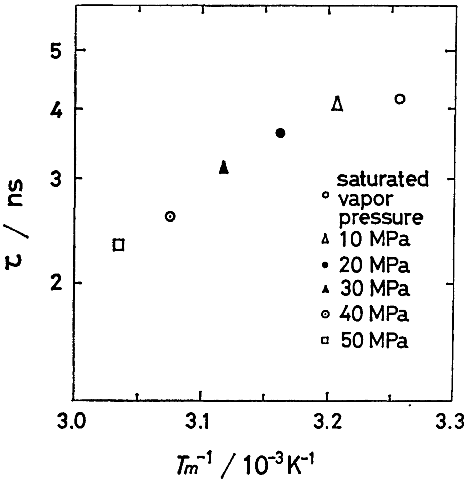

Fig. 5. The correlation time of the overall molecular reorientation at the melting points under different pressures.

parently linear in the pressure increase within the experimental error and it was approximately described by a constant isothermal compressibility (8±2)× 10^{-4} MPa^{-1}. It is seen that T_1^{-1}(max) is not linear in $(V_0/V)^2$ contrary to expectation. The reason is not apparent at present although it is possible that the pressure range studied was not wide enough to cause such a significant volume change that a very meaningful analysis could be made.

The T_1 curves in Fig. 3 were fitted to Eq. 1 assuming the Arrhenius type of activation process

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

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

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

Since the volume of activation ΔV^* is given by

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

values of τ derived from the curve fitting may be used to obtain ΔV^* and ΔH^* through the relations,

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

and

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

The value of ΔV^* thus derived was 25±3 cm^3 mol^{-1} between 290 K and 305 K. The magnitude of uncertainty attached to this derived quantity did not permit determination of its dependence on temperature.

The ratio of the volume of activation to the molar volume, $\Delta V^*/V_m$, is 0.24±0.03, considerably larger than for other plastic crystals. Thus, in the case of 2-methyl-2-nitropropane, it is 0.07.[19] In fact, values between 0.04 and 0.08 are more common for this quantity if ΔV^* corresponds to activation of molecular reorientation. Now, if one considers that the plastic phase of 2,2-dimethylpropanoic acid consists of dimeric units in which the two acid molecules are associated with a pair of hydrogen bonds, the ratio $\Delta V^*/V_m$ to be compared would be 0.12 rather than 0.24. However, this value is larger yet than the values for overall molecular reorientation in other plastic organic materials; *e.g.* in cases[20,21] of norbornane, cyclohexane, and 2,2,3,3-tetramethylbutane, they are 0.04, 0.07, and 0.07—0.09, respectively.

The activation enthalpy, ΔH^*, and the value of τ_0 for the overall molecular reorientation under some typical pressure conditions are listed in Table 1. The value of ΔH^* is also much larger than other typical plastic crystals; even a molecule as large as adamantane has a value of only 15 kJ mol^{-1}.[22] The ΔH^* exhibits a pressure dependence with the best slope 0.13 kJ MPa^{-1} mol^{-1} between the saturated vapor pressure of the sample and 50MPa. The slope is also very much larger than the case of adamantane (0.0069 kJ MPa^{-1} mol^{-1}).

Figure 5 shows the correlation time, τ, of the overall molecular reorientation at the melting points under different pressures. In contrast to the behavior of the correlation time for self-diffusion, which assumes

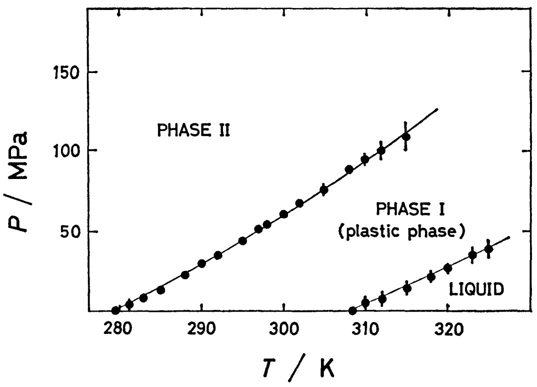

Fig. 6. Phase diagram of 2,2-dimethylpropanoic acid.

an almost constant value at melting points, the correlation time for reorientation decreases as the melting occurs at higher temperatures. This suggests the reorientational motion is not the direct trigger of the fusion phenomenon.

To summarize this subsection, the characteristic quantities, *i.e.* the volume and the enthalpy, of activation for overall molecular reorientation are about twice as large as those for other typical plastic crystals. However, these magnitude can be rationalized if one takes a dimer as the dynamical unit of motion. The molecule would then be not very spherical in shape, which fact explains why T_1 minima can be observed in the temperature region in which the plastic phase exists. This fact also corresponds to much longer correlation time in the plastic solid at its melting points.

Phase Diagram. Figure 6 is the phase diagram obtained by determining the temperature of phase changes from the jumps of the T_1 values. The average slopes of the boundary curves are

$$dP/dT = 3.26\,\mathrm{MPa\,K^{-1}}\ \text{(transition)}$$
$$= 2.22\,\mathrm{MPa\,K^{-1}}\ \text{(fusion)}$$

and show that the two curves become separated further as the pressure increases. The volume changes at these transition points were calculated by use of Clapeyron-Clausius equation from the entropy changes, 25.5 and 6.5 J K^{-1} mol^{-1} at the transition and the melting point, respectively. These were 7.82 and 2.93 cm^3 mol^{-1}, respectively, or 15.6 and 5.86 cm^3/mol of dimer.

It is interesting to note that application of external pressure displaces the region of the existence of the plastic crystal to a higher temperature whereas the T_1 minimum moves more slowly with the result of a shorter correlation time at a higher pressure. This means that although the compression should slow down molecular reorientation, additional thermal energy more than compensates the effect.

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