^{13}C Spin-lattice Relaxation and Molecular Motion in Liquid and Plastic 2,2-Dimethylpropanoic Acid

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Individual ^{13}C spin-lattice relaxation times (T_1) of 2,2-dimethylpropanoic acid (DMPA) in plastic and liquid phases have been measured by a pulse Fourier transform NMR technique at 15.036 MHz. In the plastic phase (278.9 K to 308.5 K), the minimum in the T_1 was observed; 0.35 s at 289.0 K for methyl carbon and 2.67 s at 289.0 K for quaternary carbon. The temperature dependence of the T_1 was analyzed by extending Woessner's treatment to the case of three independent degrees of reorientational freedom; internal methyl reorientation, *t*-butyl reorientation about C–COOH bonding axis, and isotropic molecular reorientation. In the plastic phase the isotropic reorientation of molecular dimeric units formed through hydrogen bonds is responsible for the ^{13}C-relaxation. The activation parameters for this motion were obtained; $E_a = 56.4 \pm 6.3$ kJ mol^{-1} and $\tau_0 = (4.6 \pm 4.0) \times 10^{-19}$ s. In the liquid phase from the melting point to 351 K, the T_1 showed a monotonous increase with increasing temperature. In this liquid phase the isotropic molecular reorientation of the dimer units of DMPA is also responsible for the ^{13}C-relaxation. The E_a of 23.4 ± 2.4 kJ mol^{-1} and the τ_0 of $(9.6 \pm 5.8) \times 10^{-14}$ s for this motion were obtained.

2,2-Dimethylpropanoic acid (C(CH$_3$)$_3$COOH, hereafter abbreviated as DMPA) is a globular molecule and crystallizes in a face-centered cubic structure[1] which exists between 278.9 K and the melting point, 308.5 K. This phase is known as an orientationally disordered phase and its static and dynamic properties have been studied by various techniques.[2-11] A dielectric measurement by Kondo and Oda[2] reported relatively low dielectric constants both in the plastic and liquid phases in spite of the existence of the strongly polar carboxyl group in the molecule. They interpreted this phenomenon in terms of possible dimerization in these phases. They also observed that a small jump in the dielectric constant on passing the melting point is consistent with the change in the density accompanied with fusion, suggesting that the extent of the excitation of the molecular rotational motion in the plastic phase is comparable to that in the liquid. Measurements of the nuclear magnetic relaxation times provide information about the nature of the molecular translational diffusion in addition to the molecular rotational motion. Measurements of ^{1}H spin-lattice relaxation times T_1 in the laboratory-fixed coordinate system[6,8,10] as well as $T_{1\rho}$ in the rotating frame[6,10] on DMPA showed that the molecules undergo rapid isotropic reorientation in the plastic phase with the correlation time of about 10^{-9} s[10] at the melting point. The activation energy E_a in the plastic phase was reported to be 50.2 ± 8.4 kJ mol^{-1} (from $T_{1\rho}$)[10] and 63 ± 5 kJ mol^{-1} (from $T_{1\rho}$)[6] for the translational diffusion which are smaller than that found by a radio-active tracer experiment[4] by a factor of 0.55.

On the other hand, the correlation time at the infinite temperature, τ_0, determined by NMR[10] is larger than that by the tracer experiment[4] by a factor of 10^7. A similar discrepancy has been recognized in the case of cyclohexane.[12,13]

If it happens that the carboxyl proton can migrate

independently of the molecular body, the proton relaxation time should be affected by its motion. It should be noted here that the relaxation measurement of ^{13}C instead of ^{1}H might provide information about the motion of the molecule as a whole: For it is reasonable to consider that the T_1 of ^{13}C nuclei located in the inner part of the molecule is determined dominantly *via* the dipolar interaction with the intramolecular protons and weakly depends on the motion of the other molecules. In order to examine the characteristics of the motion of the molecular body as a whole in more detail, we measured the spin-lattice relaxation time of ^{13}C in both the plastic and the liquid phases of DMPA. In the course of the present study preliminary experimental results of the T_1 measurements of ^{13}C in DMPA were published by Graham and Darby,[11] but no detailed analysis was made as to the modes of molecular motions nor the activation parameters were presented. This paper will present the results of the measurements of T_1 of ^{13}C and report the activation parameters deduced from these experiments. The microscopic modes of the molecular motions in the plastic and liquid phase will be discussed in relation to the previous works on ^{1}H-NMR and Rayleigh scattering.[9]

Experimental

DMPA (G.R.) was purchased from Tokyo Kasei Kogyo Co., LTD. The material was subjected to vacuum distillation and degassing *via* freeze-pump-thaw cycles and then sealed under vacuum in a Pyrex 8 mm tube in outside diameter. The ^{13}C spin-lattice relaxation time was measured at the frequency of 15.036 MHz by the $[\pi - t - \pi/2$ (FID)$-t_0-]_n$ pulse sequences ($n=20$ and t_0-10T_1 in our experiment) using pulse Fourier transform NMR equipment JEOL-PFT-60, where FID stands for the free induction decay of magnetization. These measurements were performed between 278.9 K and 351 K. The proton decoupling technique was used at a power of 4 W of a noise modulated continuous rf wave at 59.80165 MHz; the noise band width was 2.5 kHz. A nuclear Overhauser effect (NOE) for the methyl carbon was determined by dividing the integrated intensity in the proton-decoupled ^{13}C-NMR spectra by the total integrated intensities in the proton-coupled ^{13}C-NMR spectra. The overall spec-

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tral frequency range was 800 Hz and the number of accumulation was 500. The temperature was measured with a copper-constantan thermocouple and was controlled to within ± 1 K by means of a gas-flow crystat. The static magnetic field was controlled by the technique of NMR locking using an external deuteron standard.

Results and Discussion

Plastic Phase. Three resonance lines were observed in the ¹³C-NMR of DMPA by the proton decoupling method. The most intense line at the highest frequency was assigned to the methyl carbon by means of the proton-coupling method. The lowest frequency line was due to the carboxyl carbon and the other one was due to the quaternary carbon. The temperature dependence of the line shapes of these signals are shown in Fig. 1. The chemical shift of the quaternary carbon
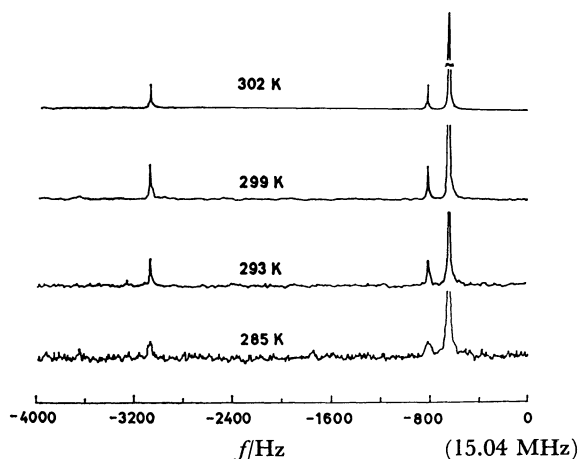

Fig. 1. Temperature dependence of line shape in plastic DMPA.

with respect to the methyl carbon is 11.44 ± 0.07 ppm and that of the carboxyl carbon is 158.62 ± 0.07 ppm. The magnitudes of these chemical shifts were almost temperature-independent. A coupling constant (J_{C-H}) between ¹³C and ¹H nuclei in the methyl group is 127 ± 2 Hz at 302.2 K. Graham and Darby[11] pointed out that the J_{C-H} in the plastic phase differs by ≈ 20 Hz from that in the liquid phase, but such a difference was not observed in the present experiment within the experimental error. The line-width of each signal decreases gradually with increasing temperature in a way similar to the case of ¹H-NMR experiments,[3,5] suggesting the onset of the progressive excitation of self-diffusion. The temperature dependence of the T_1 for the methyl and the quaternary carbon is shown in Fig. 2, which shows the existence of a shallow minimum in T_1 of the methyl carbon at 289.0 K (0.35 s) and of the quaternary carbon at 289.0 K (2.67 s).

Jackson and Strange[6] observed a sudden jump of T_1 just below the melting point in their ¹H-NMR and attributed this phenomenon to some kinds of liquid-like behavior in the plastic phase. However, we did not find such a jump of T_1 up to the melting point in our ¹³C-relaxation study. Kimtys[14] reported from his high
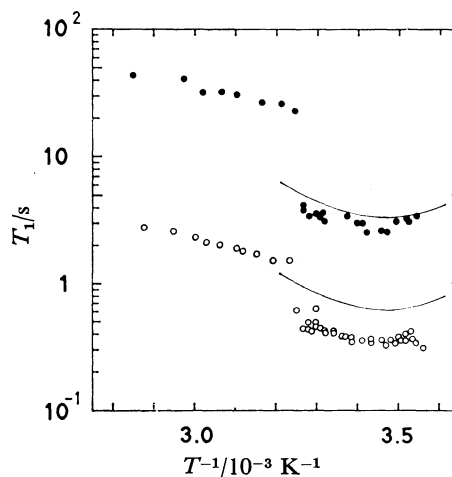

Fig. 2. Temperature dependence of spin-lattice relaxation times; ● for quaternary carbon and ○ for methyl carbon.

Two solid lines are calculated T_1 values.

resolution ¹H-NMR experiment that the carboxyl proton signal was accompanied with a satellite line on the low frequency side which he regarded as due to the hydrogen bonding effect; The intensity of that satellite line increased with decreasing temperature, whereas the intensity of the main carboxyl proton line decreased. In the case of the carboxyl ¹³C signal in our experiment, however, such a phenomenon was not observed as is evident from Fig. 1. This fact suggests that the contribution of the motion of the carboxyl proton to the relaxation time of ¹³C would be much smaller than that of the carboxyl proton to the ¹H-relaxation. Therefore, we can safely disregard the effect of the dynamics of the carboxyl proton in the analysis of the relaxation results of ¹³C.

The basic expression for the ¹³C nuclear spin-lattice relaxation rate due to dipole-dipole interaction under the proton-decoupled conditions is given by[15]

$$1/T_1 = \gamma_C^2 \gamma_H^2 \hbar^2 I(I+1)\sum\{J^{(0)}(\omega_C-\omega_H)/12$$
$$+ 3J^{(1)}(\omega_C)/2 + 3J^{(2)}(\omega_C+\omega_H)/4\} \qquad (1)$$

where γ_C and γ_H are the nuclear gyromagnetic ratios for ¹³C and ¹H nuclei, respectively, $\hbar$ is Dirac's constant, I is the nuclear spin quantum number of the ¹H nucleus ($I=1/2$), and ω_C and ω_H are the Larmor frequencies of precession in the static magnetic field; In the present case these values are $\omega_C/2\pi=15.036$ MHz and $\omega_H/2\pi=59.802$ MHz, respectively. The sum in Eq. 1 is taken over all ¹³C-¹H pairs. We assume that the following three types of molecular motions may occur in the plastic phase: (1) the internal reorientation of the methyl groups (C_3-reorientation), (2) the reorientation of the *t*-butyl group about the bonding axis between the quaternary carbon and the carboxyl carbon in the molecule (C_3'-reorientation), and (3) the isotropic molecular reorientation. These motions may be characterized by three different correlation times: τ_m (C_3-reorientation), τ_M (C_3'-reorientation), and τ_r (isotropic molecular reorientation). The self-diffusion is not taken into the consideration because it was found by our experiment[16] of the pressure dependence of the T_1

(^{1}H-NMR) that the self-diffusion was not responsible for the T_1 in the plastic phase of DMPA.

Woessner calculated T_1 for two identical spins (I=1/2) in the presence of anisotropic reorientation.[17] By extending his treatment to the case of three independent degrees of reorientational freedom mentioned above, we obtained the theoretical T_1 for the methyl carbon as follows:

$$1/T_1 = (3\gamma_C^2\gamma_H^2\hbar^2/10r^6)\{Wg(\omega_C, \omega_H, \tau_r) + Xg(\omega_C, \omega_H, \tau_1)$$
$$+ Yg(\omega_C, \omega_H, \tau_2) + Zg(\omega_C, \omega_H, \tau_3)\}, \quad (2)$$

where r is the ^{13}C–^{1}H internuclear distance in a methyl group and the function $g(\omega_C,\omega_H,\tau)$ has the form

$$g(\omega_C,\omega_H,\tau) = \tau/\{1+(\omega_C-\omega_H)^2\tau^2\} + 3\tau/\{1+\omega_C^2\tau^2\}$$
$$+ 6\tau/\{1+(\omega_C+\omega_H)^2\tau^2\}. \quad (3)$$

Here τ_i's are defined by

$$\tau_1 = 1/(1/\tau_r+1/\tau_M),$$
$$\tau_2 = 1/(1/\tau_r+1/\tau_m), \quad (4)$$
$$\tau_3 = 1/(1/\tau_r+1/\tau_M+1/\tau_m).$$

Coefficients W, X, Y, and Z were calculated to be

$$W = (3 \cos^2\Delta-1)^2(3 \cos^2\theta-1)^2/16,$$
$$X = 3(3 \cos^2\Delta-1)^2(\sin^2 2\theta + \sin^4\theta)/16,$$
$$Y = 9(\sin^2 2\Delta \sin^2 2\theta+\sin^4\Delta \sin^4\theta)/32,$$
$$Z = 3\{4 \sin^2 2\Delta(2-3 \sin^2 2\theta/4)$$
$$+ \sin^4\Delta(3 \sin^2 2\theta/4+3 \cos^2\theta+5)\}/32, \quad (5)$$

where Δ is the angle between the ^{13}C–^{1}H internuclear vector and the C_3-axis, and θ is the angle between the C_3-axis and the molecular C_3'-axis. Here intermethyl interactions and cross-correlation effect have been ignored. In our model $\Delta=\theta=\cos^{-1}(1/3)$ and these coefficients become W=1/81, X=8/81, Y=160/729, Z= 488/729; Here the bond angles of H–C–H in methyl group and C–C–H has been assumed to be tetrahedral. As the C_3- and the C_3'-reorientations are rapid enough in the plastic phase (*e.g.*, $\tau_m \approx 10^{-11}$ s and $\tau_M \approx 10^{-12}$ s just below the transition point[10]), all terms except the first in the braces of Eq. 2 are negligibly small compared with the first term. Hence Eq. 2 can be written as

$$1/T_1 = (3W\gamma_C^2\gamma_H^2\hbar^2/10r^6)g(\omega_C, \omega_H, \tau_r). \quad (6)$$

The activation parameters for the isotropic molecular reorientation were obtained by fitting the T_1 data of Fig. 2 to Eq. 6 assuming the Arrhenius type of activation process

$$\tau = \tau_0 \exp (E_a/RT). \quad (7)$$

The results for the methyl carbon are E_a(methyl)= 56.4 ± 6.3 kJ mol^{-1} and τ_0(methyl)=$(4.6\pm4.0) \times 10^{-19}$ s, and tabulated in Table 1 together with the results

reported previously. The theoretical T_1 calculated by use of Eq. 6 is given in Fig. 2 where r=0.109 nm was assumed; $T_{1\,min}$(calcd)=0.64 s at 287.2 K. If the same mechanism governs the T_1 of the quaternary carbon, we obtain the T_1 for this carbon as follows,

$$1/T_1 = (9W'\gamma_C^2\gamma_H^2\hbar^2/10l^6)g(\omega_C, \omega_H, \tau_r) \quad (8)$$

where $\Delta=28.2°$ and $\theta=\cos^{-1}(1/3)$ and the coefficient W' is 0.04911. l is the internulear distance between the quaternary carbon and a methyl proton. We obtained from the curve-fitting the activation parameters for the quaternary carbon as E_a(quat.)=56 ± 11 kJ mol^{-1} and τ_0(quat.)=$(4.3\pm4.0)\times10^{-19}$ s. These activation parameters coincide with those for the methyl carbon. The calculated T_1 curve with l=0.216 nm is shown in Fig. 2; $T_{1\,min}$(calcd)=3.23 s at 287.2 K. The activation parameters obtained here do not agree with the results of the ^{1}H-NMR experiments; E_a is twice as large as E_a from ^{1}H-NMR (25.1—36.0 kJ mol^{-1})[6,10,16] and τ_0 is very short compared with that of ^{1}H-NMR (10^{-13}—10^{-15} s).[6,10,16] Our results agree well with the results` (E_a=60.0 ± 4 kJ mol^{-1} and τ_0= 3.7×10^{-19} s) of depolarized Rayleigh scattering experiment by Bird, *et al.*[9] but do not agree with the results (E_a=30.9 ± 3.9 kJ mol^{-1} and τ_0=3.1×10^{-14} s) obtained by Beysens, *et al.*[18] Although our activation parameters may involve some error which comes from the neglect of the contributions to the T_1 other than the molecular overall rotation, the discrepancy between our value and those obtained by the ^{1}H resonance exceeds the combined experimental uncertainty. This fact suggests that the migration of the acidic protons with some smaller activation energy[7] contributes to the relaxation times of the protons.

As shown in Fig. 2 the calculated T_1(methyl) is twice as large as the observed T_1(methyl), and the calculated T_1(quat.) is larger than the observed T_1 (quat.) by about 20 per cent. Such a discrepancy is probably due to the neglect of contributions of the C_3- and C_3'-reorientations to the T_1. It is interesting to see that the correlation time (10^{-8} to 10^{-9} s) for the isotropic molecular reorientation is much longer in DMPA than those in other undimerized plastic crystals. For example, the correlation time of 5.5×10^{-12} s (at 295 K) in plastic $C_6F_9H_3$ was obtained from the neutron scattering study[19] and that of 10^{-12}—10^{-13} s in plastic $C(CH_3)_4$ was obtained by the infrared,[20] the Raman scattering,[20] and the cold neutron scattering studies.[21] The very slow reorientational motion of DMPA may be attributed to the hydrogen bonding between neighbouring molecules which probably hinders the reorientation. This mechanism is supported by the

Table 1. The activation parameters in the plastic phase of DMPA

E_a/kJ mol^{-1}	τ_0/s	Experimental method	Ref.
36.0 ± 3	2.8×10^{-15}	broad line ^{1}H-NMR (T_1)	6
25.1 ± 2.5	$(1.69\pm0.2)\times10^{-13}$	broad line ^{1}H-NMR (T_1)	10
35.0 ± 0.8	$(4.9\pm1.6)\times10^{-15}$	broad line ^{1}H-NMR (T_1)	16
60.0 ± 4	3.7×10^{-19}	Rayleigh scattering	9
30.9 ± 3.9	3.1×10^{-14}	Rayleigh scattering	18
56.4 ± 6.3	$(4.6\pm4.0)\times10^{-19}$	high resolution ^{13}C-NMR (T_1)	this work

dielectric study[2] and also by the X-ray diffraction study[1] which reports that the crystal is made up of dimers orienting randomly. Recently we measured T_1 of DMPA as a function of pressure and obtained the activation volume of $\Delta V^* = (0.24\text{—}0.26) V_m$,[16] which is about twice as large as those in normal undimelized plastic crystals.[22] This fact also supports the formation of the dimers in the plastic phase of DMPA. Therefore, we conclude that the isotropic molecular reorientation of the dimer units is responsible for the ¹³C spin-lattice relaxation in the plastic phase.

Liquid Phase The observed T_1 for the methyl and quaternary carbon in the liquid phase increase monotonously as shown in Fig. 2. The T_1 values of the quaternary carbon are larger than those of the methyl carbon by a factor of 16 but the slopes of the T_1 for these two kinds of carbons agree with each other within experimental error. No change has been observed on melting in the magnitude of the relative chemical shifts of the quaternary carbon as well as the carboxyl carbon with respect to the methyl carbon. The J_{C-H} values in a methyl group are 128.0 ± 0.3 Hz at 319 K and 128.0 ± 0.3 Hz at 333 K, respectively, and depend little on temperature.

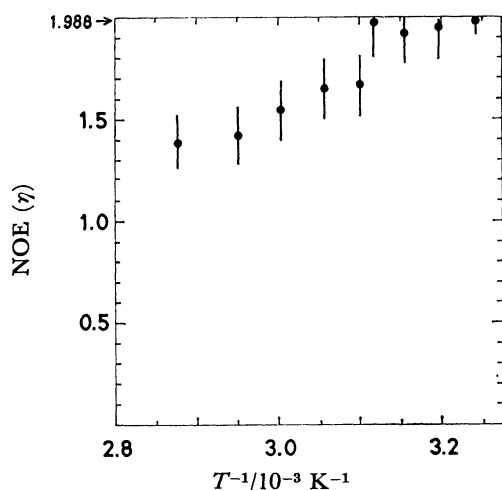Fig. 3. Temperature dependence of NOE for methyl carbon.

The nuclear Overhauser effect (η) for the methyl carbon decreases from $\eta = 1.988$ to 1.38 with increasing temperature as shown in Fig. 3. It shows that dipolar contribution to the relaxation becomes small with increasing temperature. When the ¹³C–¹H dipole-dipole interaction is the dominant mechanism in the ¹³C-relaxation, the theoretical maximum NOE (η) shoud be $\eta = 1.988$.[23] In the present case, the dipole-dipole relaxation competes with other relaxation mechanisms, e.g. spin-rotational relaxation, chemical shift anisotropy relaxation, scalar relaxation, etc. The contribution of the dipole-dipole interaction to the spin-lattice relaxation time, T_1^{DD}, may be calculated by using the experimental NOE;[23,24]

$$T_1^{DD} = 1.988 T_1^{obsd}/\eta, \tag{9}$$

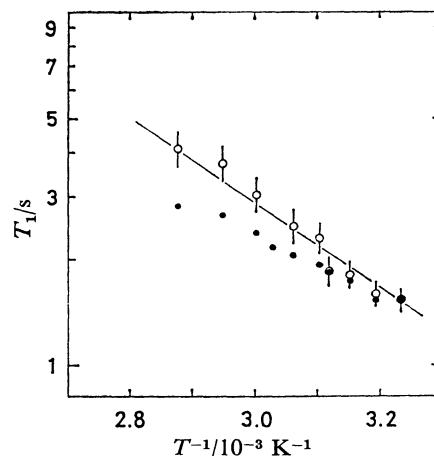where T_1^{obsd} stands for the observed value. The temperature dependences of T_1^{obsd} and T_1^{DD} are shown

Fig. 4. Temperature dependence of T_1 for methyl carbon in the liquid phase; ● for T_1^{obsd} and ○ for T_1^{DD}.

in Fig. 4 by closed circles and open circles, respectively. Under the condition of the proton decoupling it may be assumed that the intermolecular dipole-dipole relaxation is insignificant, as has been mentioned by Kuhlmann et al.[23] We may also neglect the contribution of the C_3- and C_3'-reorientations to the T_1^{DD} in the liquid state. Therefore only one dominant relaxation mechanism is the isotropic reorientation of the molecules and, under the condition of the extreme narrowing limit, Eq. 6 leads to the expression of the T_1^{DD} as

$$1/T_1^{DD} = 3W\gamma_C^2\gamma_H^2\hbar^2\tau/r^6, \tag{10}$$

where τ is the correlation time for the isotropic molecular reorientation. The correlation time, which decreases slightly from 8.8×10^{-10} s at the melting point to 2.9×10^{-10} s at 351 K calculated from Eq. 10 with $r = 0.109$ nm is longer by a factor of ten than the correlation time $(6.5 \times 10^{-11}$ s at the melting point decreasing to 3.1×10^{-11} s at 351 K) of the liquid DMPA obtained by depolarized Rayleigh scattering experiment by Beysens et al.[18] From the slope of the correlation time against the inverse of temperature, we obtained the activation parameters of $E_a = 23.4 \pm 2.4$ kJ mol⁻¹ and $\tau_0 = (9.6 \pm 5.8) \times 10^{-14}$ s. These parameters are to be compared with those obtained by Beysens et al.[18]—$E_a = 15.4 \pm 1.0$ kJ mol⁻¹ and $\tau_0 = 1.6 \times 10^{-13}$ s. It is interesting to see that the correlation time obtained here is longer than those in the non-associated globular compounds by a factor of 10^2 to 10^3, e.g., liquid $C(CH_3)_4$ $(10^{-12}$— 10^{-13} s),[20] and liquid norbornadiene $(\approx 10^{-13}$ s).[25] This fact also suggests that the DMPA molecules behave as the self-associated dimeric units even in the liquid state.

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