^{35}Cl NQR Studies of Hydrogen Transfer in Crystalline *p*-Chlorobenzoic Acid

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^{35}Cl NQR frequencies and spin-lattice relaxation times T_{1Q} were measured in *p*-$ClC_6H_4CO_2H$(PCBA) and *p*-$ClC_6H_4CO_2D$(PCBA-d_1) at 77–333 K. T_{1Q} in PCBA gave a shallow minimum of 8.0 ms at ca. 110 K, which could be explained by a double proton transfer mechanism in the carboxylic acid dimer referring to ^{1}H NMR data giving a T_{1H} minimum at almost the same temperature. PCBA-d_1 showed temperature dependent NQR frequencies quite analogous to those in PCBA, whereas their T_{1Q} behaviour was quite different in its minimum value and its temperature as well as temperature gradient. These results were explained by suppressed deuteron tunnelling and the Ubbelohde effect.

Key words: Cl NQR; Hydrogen-Bond; Hydrogen-transfer; Tunneling.

Introduction

Intermolecular hydrogen bonds can be seen in many kinds of compounds which form molecular aggregates such as dimers, trimers, or 1,2 and 3-dimensional networks in solid, liquid and biological systems. Intermolecular hydrogen transfer through hydrogen bonds is an attractive phenomenon. As an example, the hydrogen exchange in solid dimerized benzoic acid has extensively been studied by ^{1}H NMR [1, 2]. The NMR measurement is, however, rather insensitive for this purpose owing to the small displacement of the H positions in the H-exchanging process, which usually requires the measurement of the relaxation times of the order of 10^2–10^3s [1, 2]. Here, we intend to detect this motion by the NQR measurement of chlorine introduced on the phenyl ring. This is because a subtle fluctuation of the electric field gradient throughout the π-electron system caused by a H-motion even in a remote position can be expected to be sensitively detected by the NQR technique. In the present study, the ^{35}Cl NQR frequencies and spin-lattice relaxation time were measured in *p*-chlorobenzoic acid and its partially deuterated analogue.

Experimental

Crystalline *p*-chlorobenzoic acid, *p*-$ClC_6H_4CO_2H$ (abbreviated to PCBA) was obtained by recrystallization of the commercial reagent from acetone. A partially deuterated analogue *p*-$ClC_6H_4CO_2D$(PCBA-d_1) was prepared by repeated crystallization of the protonated compound from CH_3OD.

The ^{35}Cl NQR frequencies and spin-lattice relaxation time (T_{1Q}) in both analogues were measured with a homemade pulsed spectrometer, described in [3], at 77–140 K. A 180°-τ-90° pulse sequence was used to determine T_{1Q}. The ^{1}H NMR spin-lattice relaxation time T_{1H} in PCBA was measured with a homemade spectrometer [4] at a Larmor frequency of 54.3 MHz at 30–300 K, using the saturation recovery pulse sequence.

Results

The temperature dependences of the ^{35}Cl NQR frequencies observed in PCBA and PCBA-d_1 are shown in Figure 1. The observed frequencies of 34.673±0.001 and 34.674±0.002 MHz in PCBA and PCBA-d_1, respectively, at 77 K agree well with 34.673 MHz reported for PCBA [5]. The resonance frequencies and their temperature dependences in both compounds were quite similar in the whole temperature range studied. The frequency difference at 130 K was 2.5 kHz. Upon heating, the resonance signals in both compounds gradually weakened and disappeared in the noise level at around 140 K.

The temperature dependences of ^{35}Cl NQR T_{1Q} observed in PCBA and PCBA-d_1 are shown in Figure 2.

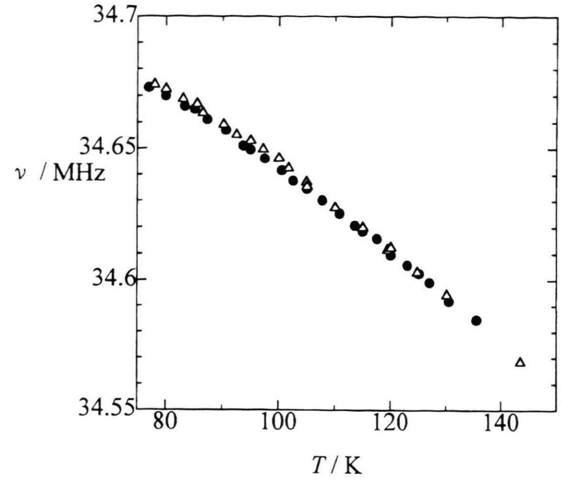


Fig. 1. Temperature dependences of ^{35}Cl NQR frequencies (ν) observed in *p*-$ClC_6H_4CO_2H$ (PCBA) (●), and *p*-$ClC_6H_4CO_2D$ (PCBA-d_1) (△).

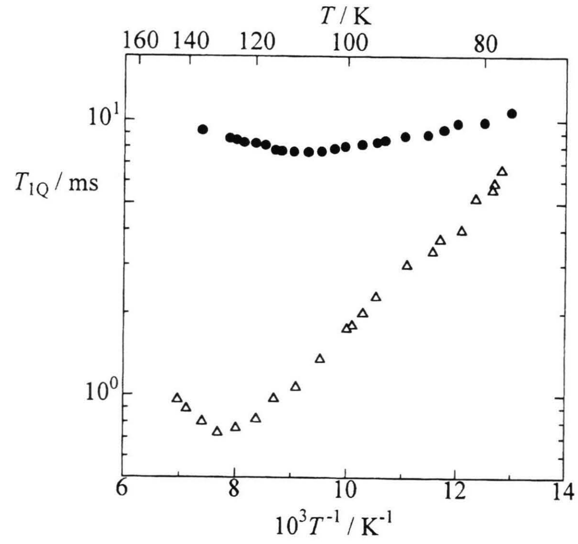


Fig. 2. Temperature dependences of the ^{35}Cl NQR spin-lattice relaxation times T_{1Q} observed in *p*-$ClC_6H_4CO_2H$ (PCBA) (●), and *p*-$ClC_6H_4CO_2D$ (PCBA-d_1) (△).

A shallow minimum of (8.0±1.0) ms was observed at ca. 110 K in PCBA, while a deep minimum of (0.80±0.10) ms was obtained at ca. 130 K in PCBA-d_1.

The temperature dependence of ^{1}H NMR T_{1H}, observed in PCBA at 54.3 MHz, is shown in Figure 3. Our results agree well with data in the high-temperature range reported by Nagaoka et al. [1, 2]. An asymmetric T_{1H} curve with a minimum at ca. 105 K was clearly observed in the present work.

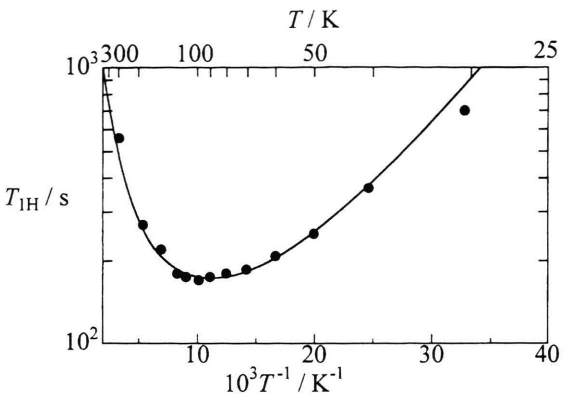


Fig. 3. A temperature dependence of the ^{1}H NMR spin-lattice relaxation time T_{1H} observed in *p*-$ClC_6H_4CO_2H$ (PCBA) at a Larmor frequency of 54.3 MHz. The solid curve is best-fitted (see text).

Discussion

^{1}H NMR Spin-Lattice Relaxation Time

The asymmetric temperature dependence of T_{1H} in PCBA, shown in Fig. 3, is quite analogous to T_{1H} data reported for crystalline benzoic acid (BA) [1, 2] in which the double proton transfer between the hydrogen bonded two molecules was shown to contribute to the relaxation. Referring to the analysis of T_{1H} in benzoic acid [6], the steep temperature dependence observed on the high-temperature side of the minimum can be explained by the BPP type relaxation [7] due to the classical random hydrogen jumps in an asymmetric double-well potential formed in the dimer structure. On the other hand, the relaxation on the low-temperature side is attributed to quantum mechanical proton tunnelling coupled to crystalline phonons. We analysed the obtained T_{1H} data using the theoretical treatment performed on benzoic acid given in [6]:

$$T_1^{-1} = C \frac{a}{(1+a)^2} \left[\frac{\tau_c}{1+(\omega \tau_c)^2} + \frac{4\tau_c}{1+4(\omega \tau_c)^2} \right], \tag{1}$$

$$a = \exp(A / RT), \tag{2}$$

$$\frac{1}{\tau_c} = k_{AB} + k_{BA}, \tag{3}$$

$$k_{AB} = k_{AB}^{\mathrm{L}} + k_{AB}^{\mathrm{H}}, \quad k_{BA} = k_{BA}^{\mathrm{L}} + k_{BA}^{\mathrm{H}}, \tag{4}$$

$$k_{AB}^{\mathrm{L}} = k_0 \, n(A), \quad k_{BA}^{\mathrm{L}} = k_0 \, [n(A)+1], \tag{5}$$

$$n(A) = \frac{1}{\exp(A/RT) - 1}, \tag{6}$$

$$k^{\mathrm{H}}_{AB} = \frac{1}{\tau_0}\exp(-V/RT), \qquad k^{\mathrm{H}}_{BA} = \frac{1}{\tau_0}\exp[-(V-A)/RT], \tag{7}$$

where A, k_0 and V denote the potential energy difference, the tunnelling rate and the barrier height. The definitions of the other parameters are given in [6]. We fitted (1)–(7) to the data in Fig. 3, where C in (1), expressing the magnetic dipolar interaction modulated by this proton transfer, was estimated from the C value reported for benzoic acid, where we assumed that the ratio of C in the two compounds is roughly equal to that of the observed $T_{1\mathrm{H}}$ minima. This is because no data on H positions in crystals are available for PCBA. The derived best fitted $T_{1\mathrm{H}}$ curve and determined parameters are shown in Fig. 3 and Table 1, respectively.

The k_0 in PCBA (2.0×10^{10} s^{-1}) is larger than that in BA (4.5×10^{8} s^{-1}), indicating that tunnelling in PCBA is larger than in BA. This is explainable by a stronger H-bonding in PCBA which results in a short O–O distance of 2.615 Å [8] compared to 2.64 Å in BA [9]. This difference comes from the more acidic protons in PCBA due to the electron attracting effect of chlorine. The remarkable difference in $T_{1\mathrm{H}}$ minimum values in PCBA and BA, which gave ca. 6 s at 59.53 MHz [1, 2], implies that the H displacement in the double proton transfer process in PCBA is smaller than in BA. This can also be explained by the difference in the O–O separations or the strength of H-bonding in the two carboxylic acids.

^{35}Cl NQR Frequencies and T_{1Q}

The temperature dependence of the ^{35}Cl NQR frequencies above 77 K in both PCBA and PCBA-d_1, shown in Fig. 1, is normal and explainable by the Bayer theory [10]. At around 140 K the signals disappear. The two analogues showed almost the same frequencies in the whole temperature range, suggesting that the average electric field gradients at the Cl nuclei are almost unaffected by the deuteration in the carboxyl group.

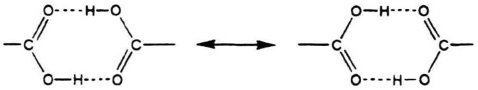
The facts that $T_{1\mathrm{Q}}$ in PCBA has a minimum at almost the same temperature of ca. 105 K as $T_{1\mathrm{H}}$, and also the slope of $T_{1\mathrm{Q}}$ of ca. (0.78±0.3) kJ mol^{-1} on the low-temperature side of the minimum is close to 0.98± 0.2 kJ mol^{-1} in $T_{1\mathrm{H}}$, indicate that the relaxation mechanisms in $T_{1\mathrm{Q}}$ and $T_{1\mathrm{H}}$ are the same, i.e., a double proton transfer in the dimer. A marked difference for PCBA and PCBA-d_1 was observed in the $T_{1\mathrm{Q}}$ temperature dependences shown in Fig. 2, where a shallow minimum of ca. 8.0±1.0 ms was observed in PCBA around 110 K, while a deep minimum of 0.80±0.10 ms in PCBA-d_1 at ca. 130 K. This indicates that the observed $T_{1\mathrm{Q}}$ temperature dependence is closely connected with the hydrogen transfer process in carboxylic acid dimers. The markedly smaller $T_{1\mathrm{Q}}$ values obtained in NQR than in NMR imply that the H-transfer in these systems can be observed much more sensitively in NQR than in NMR studies.

Table 1. Motional parameters of the proton transfer in carboxylic acid dimers determined in *p*-chlorobenzoic acid from ^{1}H NMR relaxation data together with the reported values in benzoic acid.

	V/kJ · mol^{-1}	τ_0/s	A/kJ · mol^{-1}	k_0/s^{-1}	C/s^{-2}
p-chloro-benzoic acid (PCBA)	8±2	1.3×10^{-12}	0.98±0.2	2.0×10^{10}	2.40×10^{7}
benzoic acid (BA) [5]	5.5	3.3×10^{-12}	0.72	4.5×10^{8}	2.84×10^{8}

An interesting result in the $T_{1\mathrm{Q}}$ data is that the deuterated and undeuterated analogues exhibited a quite different $T_{1\mathrm{Q}}$ behaviour, even though they showed quite analogous resonance frequencies in a wide temperature range. An important characteristic of H-transfer in PCBA-d_1 is the much smaller tunnel interactions than that in PCBA because of the marked mass effect on tunnelling which results in quite small tunnelling probability in deuterated systems [11]. If we can ignore the contribution from the tunnelling to $T_{1\mathrm{Q}}$ in the deuterated analogue, the steep $T_{1\mathrm{Q}}$ slope observed on the low-temperature side of the minimum is mostly explainable by the classical H-jumps. The fact that the minimum temperature of $T_{1\mathrm{Q}}$ in PCBA-d_1 is higher than in PCBA can be understood by the shorter O–D, that is longer O–O distance in the deuterated dimer, the so-called Ubbelohde effect [12], resulting in a slower jumping rate of D than that of H.

A remarkable difference between the two analogues is that $T_{1\mathrm{Q}}$ in PCBA-d_1 is about ten times shorter than in PCBA. This can be explained by considering the tunnelling which enables quantum mechanical proton delocalization by overlapping two protonic wave functions implying that the tunnelling process is not a motion but a state giving no marked fluctuation of the electric field gradient. Since, in PCBA, the efg fluctuation at Cl nuclei at high temperatures made by the exchange



is partly averaged by the tunnelling, the effective fluctuation in PCBA occurring around the T_{1Q} minimum is expected to be smaller than in the deuterated analogue with the markedly diminished tunnelling.

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