1H and 19F NMR Studies on Molecular Motions in Two Solid Phases of t-Butylammonium Tetrafluoroborate

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Differential thermal analysis (DTA), differential scanning calorimetry (DSC), and the temperature dependence of the spin-lattice relaxation time (T1) and the second moment (M2) of 1H and 19F NMR were studied in (CH3)3CNH2BF4 and (CH3)3CND2BF4. DTA and DSC revealed a solid-solid phase transition at 219 K for (CH3)3CNH2BF4 and at 221 K for (CH3)3CND2BF4. The motions of cations and anions in the two solid phases were studied by T1 and M2 experiments. The motional modes of the ions and their motional parameters were determined.

Key words: Molecular motion; Phase transition; Nuclear magnetic resonance.

Introduction

In previous papers we have studied (CH3)3CNH2NO3 [1] and (CH3)3CNH2ClO4 [2] by 1H NMR and thermal measurements. The nitrate was found to have seven solid phases (including three metastable phases) between 80 K and the melting point (418 K). The perchlorate has four solid phases (including a metastable phase) between 80 K and the melting point (414 K). We discussed the molecular motions of the cation in each phase and the relation between the motions and the polymorphic phase transitions.

Since a BF4- ion is expected to be able to move easily in crystals because of its highly symmetric shape and its size similarity to ClO4-, and since 19F NMR can be measured as easily as 1H NMR, t-butylammonium tetrafluoroborate seems to be an interesting candidate for studying the motions of both cation and anion, and the phase transition triggered by the molecular motion. In the present study, 1H and 19F NMR, differential thermal analysis (DTA), and differential scanning calorimetry (DSC) have been performed on (CH3)3CNH2BF4 and its partially deuterated analog, (CH3)3CND2BF4, to characterize the molecular motions of both cation and anion and to investigate possible phase transitions.

Experimental

(CH3)3CNH2BF4 was prepared by neutralizing t-butylamine with tetrafluoroboric acid. The obtained crystals were recrystallized twice from isopropyl alcohol. Found: C, 29.80; H, 7.45; N, 8.70%. Calcd for (CH3)3CNH2BF4: C, 29.85; H, 7.52; N, 8.61%. (CH3)3CND2BF4 was prepared for purified (CH3)3CNH2BF4 by three times repeated crystallization from D2O (99.8 D%). Because of the hygroscopicity of the purified crystals, they were handled in a dry bag and dried under a vacuum (ca. 10⁻¹ Pa) at room temperature for 5 h and then at 70 °C for 5 h before the NMR, DTA, and DSC measurements. The phase transition temperatures and the corresponding enthalpy changes were determined on a home-made DTA apparatus [3] and a Perkin-Elmer DSC7, respectively, at 100 to 410 K. The second moment of the 1H and 19F NMR linewidths (abbreviated to M2H and M2F, respectively) was determined by use of a JEOL JNM-MW-40S spectrometer. The spin-lattice relaxation times of 1H and 19F NMR (abbreviated to T1H and T1F, respectively) were measured using a pulsed NMR spectrometer [4] with the 180° - t - 90° pulse sequence.

Results and Discussion

DTA and DSC

A solid-solid phase transition and the melting point were located at 219 ± 1 and 404 ± 1 K, respectively.
for (CH₃)₃CNH₃BF₄ by DTA. Since the heat anomaly at the solid-solid phase transition showed a long tail on the low temperature side on both heating and cooling runs, we have assigned the peak temperature to the transition temperature. The revealed solid phases are designated in the order of decreasing temperature as Phases I and II. The enthalpy changes at transition and fusion determined by DSC were 0.49 ± 0.05 and 12.6 ± 0.5 kJ mol⁻¹, respectively; thus the associated entropy changes were calculated to be 2.2 ± 0.2 and 31 ± 1 J K⁻¹ mol⁻¹, in the same order. The solid-solid transition temperature determined for (CH₃)₃CND₂BF₄ by DTA was 221 ± 1 K.

Second Moment (M₂) of ¹H and ¹⁹F NMR Linewidths

The temperature dependences of M₂H and M₂F observed for (CH₃)₃CNH₃BF₄ are shown in Figure 1. The M₂H and M₂F values at 77 K are 40 ± 0.5 and 19 ± 0.3 G² (1 G = 1 x 10⁻⁴ T), respectively. These values imply that both cation and anion are rigid at 77 K because the observed M₂H and M₂F values are much larger than 25.7 G² [2] and 14.5 G² [5], respectively, as calculated for the rigid states of the isolated cation and anion. The differences between the observed and calculated values are attributable to intermolecular contributions. With increasing temperature, M₂F decreased rapidly and a constant value of 2.3 ± 0.2 G² was obtained above 120 K. This value can be attributed to the isotropic reorientation of the BF₄⁻ ion, referring to the M₂F results obtained in NH₄BF₄ [5, 6], in which an M₂F of 2.5 - 2.8 G² was reported for the anionic motion. M₂H decreased, on the other hand, in three steps and reached a constant value of 3.2 ± 0.2 G² above 340 K. This value agrees fairly well with the 3.8 G² calculated for the cation which performs the C₃' reorientation of the t-butyl group about the C-N bond axis together with the C₃ reorientations of the CH₃ and NH₃⁺ groups about the C-C and C-N bond axes, respectively [2]. The result that the observed M₂H value is smaller than the calculated M₂H value is explainable in terms of the contribution to M₂H from the large-amplitude librations of the cation about its C-C and/or C-N bond axes as discussed in previous papers [2, 7 - 9].

Spin-lattice Relaxation Time (T₁H) of ¹H NMR

The temperature dependence of T₁H observed for (CH₃)₃CNH₃BF₄ at Larmor frequencies of 8.5 and 32 MHz is shown in Figure 2. T₁H at 8.5 MHz showed three minima at 155, 245 and 345 K, and a shoulder around 200 K. No marked change in T₁H was observed at the transition point of 219 K. The temperature dependences of T₁H at 8.5 and 32 MHz in (CH₃)₃CND₂BF₄ are shown in Figure 3. T₁H at 8.5 MHz shows two minima at 155 and 345 K, and a shoulder around 200 K. Among the three kinds of cationic motions observed, i.e., the CH₃, NH₃⁺, and t-butyl groups reorientations, the NH₃⁺ group motion was found to correspond to the T₁H minimum at
245 K in (CH₃)₃CNH₄BF₄, comparing the T₁H data in (CH₃)₃CNH₄BF₄ with those in (CH₃)₃CND₃BF₄. The T₁H minimum and the shoulder in Phase II can, therefore, be attributed to the CH₃ group reorientation and the T₁ minimum at 345 K in Phase I to the t-butyl group motion because the CH₃ group motion is expected to occur more easily, i.e., at lower temperatures than the t-butyl group motion.

The broad and asymmetric T₁H minimum in Phase II, assignable to the CH₃ group motion, can be explained in terms of the existence of crystallographic non-equivalent CH₃ groups. Assuming two kinds of CH₃ groups in this phase, T₁H can be expressed by considering the ¹H-¹H and ¹H-¹⁹F magnetic dipolar interactions [10 - 12],

\[ \frac{1}{T_{1H}} = C_{HH(1)}g(\omega_H, \tau_{H(1)}) + C_{HH(2)}g(\omega_H, \tau_{H(2)}) + C_{HF(1)}g(\omega_{HF}, \tau_{H(1)}) + C_{HF(2)}g(\omega_{HF}, \tau_{H(2)}); \]

\[ g(\omega_H, \tau_{H(i)}) = \frac{\tau_{H(i)}}{1 + \omega_H^2 \tau_{H(i)}^2} + \frac{4\tau_{H(i)}}{1 + 4\omega_H^2 \tau_{H(i)}^2}, \]

\[ g(\omega_{HF}, \tau_{H(i)}) = \frac{\tau_{H(i)}}{1 + (\omega_H - \omega_F)^2 \tau_{H(i)}^2} + \frac{3\tau_{H(i)}}{6\tau_{H(i)}} + \frac{\tau_{H(i)}}{1 + (\omega_H + \omega_F)^2 \tau_{H(i)}^2}, \]

\((i = 1, 2).\)

Here \(\tau_{H(1)}\) and \(\tau_{H(2)}\) denote the reorientational correlation times of the two kinds of CH₃ groups giving the T₁H minimum at the low and high temperatures, respectively; \(\omega_H\) and \(\omega_F\) are the ¹H and ¹⁹F Larmor frequencies. \(C_{HH(i)}\) and \(C_{HF(i)}\) stand for the motional constants related to the reduction of M₂H through the ¹H-¹H and ¹H-¹⁹F interactions, respectively, due to the i-th CH₃ group motion. Equations (1) - (3) were fitted to the T₁H observed in Phase II of (CH₃)₃CNH₄BF₄ and (CH₃)₃CND₃BF₄. In the calculations, we assumed an Arrhenius-type relationship between \(\tau_{H(i)}\) and the activation energy \(E_a\) (i = 1, 2) of the motional process expressed as

\[ \tau_{H(i)} = \tau_{0(i)} \exp(E_a / RT), \]

where \(\tau_{0(i)}\) is the correlation time at the limit of infinite temperature. The optimum values of \(C_{HH(i)}, C_{HF(i)}, \tau_{0(i)}\), and \(E_a\) are shown in Table 1 and the fitted curves are shown in Figs. 2 and 3. We obtained

**Table 1. Activation energies \(E_a\), correlation times \(\tau_{0}\) at the limit of infinite temperature, and motional constants evaluated for anionic and cationic motions in Phases I and II of (CH₃)₃CNH₄BF₄ and (CH₃)₃CND₃BF₄ by measurement of ¹H and ¹⁹F NMR spin-lattice relaxation time.**

<table>
<thead>
<tr>
<th>(E_a) / kJ mol⁻¹</th>
<th>(\tau_{0}) / 10⁻¹³ s</th>
<th>C / 10⁸ s⁻²</th>
<th>Reorienting group</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₃CNH₄BF₄, Phase I:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40*</td>
<td>0.11*</td>
<td></td>
<td>t-butyl</td>
</tr>
<tr>
<td>16*</td>
<td>4*</td>
<td></td>
<td>CH₃</td>
</tr>
<tr>
<td>24 ± 1</td>
<td>1.4 ± 0.1</td>
<td>11.5 ± 0.5 C_{HH(1)}</td>
<td>NH₃⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30 ± 0.05 C_{HH(1)}</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₃CNH₄BF₄, Phase II:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 ± 1</td>
<td>4.9 ± 0.5</td>
<td>50 ± 2 C_{HH(1)}</td>
<td>CH₅(1)</td>
</tr>
<tr>
<td>16 ± 1</td>
<td>7.5 ± 0.5</td>
<td>23 ± 1 C_{HH(2)}</td>
<td>CH₅(2)</td>
</tr>
<tr>
<td>4 ± 1</td>
<td>40 ± 1 C_{HH(1)}</td>
<td>0.25 ± 0.02 C_{HF(1)}</td>
<td>CH₃</td>
</tr>
<tr>
<td>10 ± 1</td>
<td></td>
<td>40 ± 1 C_{HH(2)}</td>
<td>BF₄⁻</td>
</tr>
<tr>
<td>(CH₃)₃CND₃BF₄, Phase I:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 ± 1</td>
<td>5.2 ± 0.5</td>
<td>53 ± 1 C_{HH(1)}</td>
<td>CH₅(1)</td>
</tr>
<tr>
<td>16 ± 1</td>
<td>8.0 ± 0.5</td>
<td>25 ± 1 C_{HH(2)}</td>
<td>CH₅(2)</td>
</tr>
<tr>
<td>10.3 ± 0.4</td>
<td>3 ± 1</td>
<td>34 ± 3 C_{HF(1)}</td>
<td>BF₄⁻</td>
</tr>
<tr>
<td>17.2 ± 0.8</td>
<td>0.07 ± 0.04</td>
<td>34 ± 3 C_{HF(2)}</td>
<td>BF₄⁻</td>
</tr>
</tbody>
</table>

* Values obtained in Phase I of (CH₃)₃CND₃BF₄.
\[ C_{HH(1)} = 50 \times 10^8 \text{ and } C_{HH(2)} = 23 \times 10^8 \text{ s}^{-2} \text{ for (CH}_3)_3\text{CNHBF}_4 \text{ and } C_{HH(1)} = 53 \times 10^8 \text{ and } C_{HH(2)} = 25 \times 10^8 \text{ s}^{-2} \text{ for (CH}_3)_3\text{CND}_3\text{BF}_4 \text{, implying that the nonequivalent CH}_3 \text{ groups can be classified into two groups with an abundance ratio of 2:1. The activation energies of 13 and 16 kJ mol}^{-1} \text{ obtained for the CH}_3 \text{ reorientations are comparable to the potential barrier of 17.21 kJ mol}^{-1} \text{ for the internal rotation of the CH}_3 \text{ group in an isolated t-butylammonium ion calculated by ab initio MO [13], when one takes into account the zero-point energy. The reorientation of the CH}_3 \text{ group in this phase is, therefore, expected to be mostly hindered by the intracationic potential barrier, and the intermolecular hindrance to the reorientation is considered to be small.}

The \( T_1\text{H} \) minima at 8.5 and 32 MHz in Phase I of (CH\(_3\)_3CND\(_3\)BF\(_4\)) are attributed to the t-butyl group reorientation, as mentioned above. The \( T_1\text{H} \) increase with temperature in the low-temperature range of Phase I is attributable to the CH\(_3\) group motion. Since the correlation time (\( \tau_\text{H} \)) for the CH\(_3\) group motion is considered to be much shorter than that (\( \tau_\text{H}'' \)) for the t-butyl group, as predicted from the \( T_1\text{H} \) results in Phase II, \( T_1\text{H} \) in Phase I can be approximately expressed [10-12, 14] by considering \( ^1\text{H}-^1\text{H} \) and \( ^1\text{H}-^{19}\text{F} \) dipolar interactions, as

\[
\frac{1}{T_1\text{H}} = C'_\text{HH}g(\omega_\text{H}, \tau_\text{H}') + C'_\text{HF}g(\omega_\text{HF}, \tau_\text{H}') + C_{\text{HH}}g(\omega_\text{H}, \tau_\text{H}).
\]

(5)

Here \( C'_\text{HH} \) and \( C'_\text{HF} \) are the motional constants related to the t-butyl group motion, and \( C_{\text{HH}} \) is related to the CH\(_3\) group motion. We assumed a single correlation time for the CH\(_3\) group motion and ignored the contribution from the \( ^1\text{H}-^{19}\text{F} \) interaction caused by the CH\(_3\) group motion for simplicity. Equation (5) is fitted to the \( T_1\text{H} \) data using the Arrhenius-type relation-ship as given by (4) for these two motions.

The \( T_1\text{H} \) data in Phase I of (CH\(_3\)_3CNHBF\(_4\)) can be explained by the t-butyl, NH\(_3^+\) and CH\(_3\) group motions, referring to the \( T_1\text{H} \) data of (CH\(_3\)_3CND\(_3\)BF\(_4\)) and the \( M_{2\text{H}} \) results. \( T_1\text{H} \) can, therefore, be expressed as

\[
\frac{1}{T_1\text{H}} = C''_\text{HH}g(\omega_\text{H}, \tau_\text{H}'') + C''_\text{HF}g(\omega_\text{HF}, \tau_\text{H}'') + C_{\text{HH}}g(\omega_\text{H}, \tau_\text{H}),
\]

(6)

where \( \tau_\text{H}'' \) is the correlation time of NH\(_3^+\) reorientation, and \( C''_\text{HH} \) and \( C''_\text{HF} \) are the motional constants. The motional parameters \( (C''_\text{HH}, C''_\text{HF}, E_a, \text{ and } \tau_0'') \) for the NH\(_3^+\) motion were evaluated using a fitting calculation with the \( E_a \) and \( \tau_0 \) values of the t-butyl and CH\(_3\) group motions obtained from the \( T_1\text{H} \) data in Phase I of (CH\(_3\)_3CND\(_3\)BF\(_4\)). The \( E_a \) value of 24 kJ mol\(^{-1}\) obtained for the NH\(_3^+\) motion is considerably smaller than 38.5 - 44.2 kJ mol\(^{-1}\) for the same motion in t-butylammonium chloride and bromide [15], in which a strong hydrogen bond N-H...X (X = Cl, Br) is expected. The value of 24 kJ mol\(^{-1}\) is, however, much larger than 12.41 kJ mol\(^{-1}\), the calculated potential barrier for the internal rotation of NH\(_3^+\) [13]. This implies that the primary origin of the hindering force for the NH\(_3^+\) reorientation is intermolecular interactions including N-H...F hydrogen bonds.

**Spin-lattice Relaxation Time (\( T_{1\text{F}} \)) of \(^{19}\text{F} \) NMR**

The \( T_{1\text{F}} \) data of (CH\(_3\)_3CND\(_3\)BF\(_4\)) observed at 30.1 MHz are shown in Figure 3. The deep \( T_{1\text{F}} \) minimum of 18 ms around 160 K is assignable to the isotropic rotation of the BF\(_4^-\) ion based on the above discussion on \( M_{2\text{F}} \). Since the observed \( T_{1\text{F}} \) yielded an asymmetric log \( T_{1\text{F}} \) vs. \( T^{-1} \) curve, we can expect that at least two kinds of crystallographically nonequivalent anions exist in Phase II. Here we assume that the \(^{19}\text{F} \) - \(^{19}\text{F} \) and \(^{19}\text{F} \) - \(^{11}\text{B} \) magnetic dipole-dipole interactions are the dominant relaxation processes affecting \( T_{1\text{F}} \) and that two kinds of anion exist with an abundance ratio of 1:1, in which case \( T_{1\text{F}} \) can be expressed approximately as [10-12]

\[
\frac{1}{T_{1\text{F}}} = C_{\text{FF}(1)}g(\omega_\text{F}, \tau_\text{F}(1)) + C_{\text{FB}(1)}g(\omega_\text{FB}, \tau_\text{F}(1)) + C_{\text{FF}(2)}g(\omega_\text{F}, \tau_\text{F}(2)) + C_{\text{FB}(2)}g(\omega_\text{FB}, \tau_\text{F}(2));
\]

(7)

\[
g(\omega_\text{F}, \tau_\text{F}(i)) = \frac{\tau_\text{F}(i)}{1 + (\omega_\text{F} - \omega_\text{FB})^2 \tau_\text{F}(i)} + \frac{4\tau_\text{F}(i)}{1 + 4\omega_\text{F}^2 \tau_\text{F}(i)};
\]

(8)

\[
g(\omega_\text{FB}, \tau_\text{F}(i)) = \tau_\text{F}(i) + \frac{3\tau_\text{F}(i)}{1 + (\omega_\text{F} - \omega_\text{FB})^2 \tau_\text{F}(i)} + \frac{6\tau_\text{F}(i)}{1 + (\omega_\text{F} + \omega_\text{FB})^2 \tau_\text{F}(i)}
\]

(9)

(i = 1, 2).
Here $\tau_F(i)$ and $\omega_B$ are the correlation time of isotropic reorientation of the $i$-th anion and the Larmor frequency of $^{11}$B. The motional constants, $C_{FF(i)}$ and $C_{FB(i)}$, are the contributions to $M_{2F}$ caused by $^{19}$F-$^{19}$F and $^{19}$F-$^{11}$B interactions, respectively, due to the $i$-th anionic motion. Since the intra-anionic interaction is dominant for the $^{19}$F-$^{11}$B interaction, $C_{FB(i)}$ is expressed as \[ C_{FB(i)} = \frac{1}{4} \gamma_F^2 \gamma_B^2 \omega_B^2 r_{FB}^{-6} \] (10)

where $\gamma_F$, $\gamma_B$, and $r_{FB}$ are the gyromagnetic ratios of $^{19}$F and $^{11}$B, and the B-F bond distance, respectively. Assuming an Arrhenius-type relationship given by (4), (7) - (9) were fitted to the observed $T_{1F}$ values, where the theoretical value, $C_{FB(1)} = C_{FB(2)} = 15 \times 10^8$ s$^{-2}$ ($r_{FB} = 1.43$ Å) [5], was used. The motional parameters determined are given in Table 1, and the best-fit curves are shown in Figure 3.

The $T_{1F}$ minimum observed in Phase I is thought to originate from the inter-ionic $^{19}$F-$^{11}$H dipolar interactions modulated by the t-butyl group motion because in Phase I the $^{19}$F-$^{19}$F and $^{19}$F-$^{11}$B dipolar interactions are considered to be completely averaged out by the anionic isotropic reorientation whose onset is detected in Phase II. $T_{1F}$ in Phase I can be stated in terms of $\tau_H'$ and $\tau_F$, the correlation times of the t-butyl group and the anion isotropic reorientation, respectively, as

$$\frac{1}{T_{1F}} = C_{FH}'g(\omega_{FH}, \tau_H') + (5C_{FF} + 10C_{FB})\tau_F. \quad (11)$$

Here a single correlation time $\tau_F$ which is short enough to satisfy the condition of $\omega_F\tau_F, (\omega_F + \omega_B)\tau_F \ll 1$, is assumed for the anionic motion. Using the correlation time of t-butyl group obtained from the $T_{1H}$ data of $(\text{CH}_3)_3\text{CND}_3\text{BF}_4$, (11) was fitted to the $T_{1F}$ data in Phase I. The results are shown in Fig. 3 and Table 1.

Conclusion

The three kinds of cationic motions (reorientations of the CH$_3$ groups about their C-C bond axes, the NH$_3^+$ group about its C-N bond axis, and the t-butyl group about the C-N bond axis) and the anionic isotropic reorientation were observed in the two solid phases (Phases I and II) of t-butylammonium tetrafluoroborate. Since the entropy change at the solid-solid phase transition is small compared with that (\(\sim R\ln 2\)) expected for the transition accompanying a gain in orientational disorder of ions [16], and since no marked change in $M_{2H}$, $M_{2F}$, $T_{1H}$, or $T_{1F}$ was observed, the crystal structure change here is considered to be so slight that the motional states of the cation and anion are little affected; probably only the correlation times of the motions in Phase II decrease to some extent at the transition.