Motion of Methylammonium Ions in Solid $CH_3NH_3NO_3$ and CH_3NH_3SCN Studied by ^1H NMR

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The proton spin-lattice relaxation time T_1 at 20 MHz and the second moment of ^1H NMR absorptions at 40 MHz were determined at various temperatures between 77 and 300 K for $CH_3NH_3NO_3$ and CH_3NH_3SCN, and their partially deuterated analogs, $CH_3ND_3NO_3$ and CH_3ND_3SCN. A phase transition was located at 242 K for CH_3NH_3SCN. The fully protonated compounds yielded two T_1 minima, the low- and high-temperature one of which could be attributed to the reorientation of the CH_3 and NH_3^+ groups, respectively, of the cation about the C–N bond axis. The activation energy was evaluated for these motional modes.

The motion of methylammonium (MA) ions in crystals has been extensively studied for methylammonium halides[1-7] and hexahalometallates(IV)[8,9] by means of ^1H NMR experiments. From these works, it became evident that the motional modes responsible for the ^1H nuclear spin-lattice relaxation time T_1 observed below room temperature are usually the reorientations of the cation about the C–N bond axis. Two kinds of such reorientations are considered to be possible. The first one is the correlated reorientation of the CH_3 and NH_3^+ groups in the cation, *i.e.*, the reorientation of the cation as a whole about its C_3 axis with keeping its rigid structure. We already observed this kind of motion in the crystals of $(MA)_2MX_6$ (M: Pt, Sn, Te; X: halogens)[8,9] where the interionic potential barrier experienced by the cation for the reorientation is smaller than the intraionic one. Another kind of the motion is the uncorrelated reorientation of the CH_3 and NH_3^+ groups. This was observed, *e.g.*, for (MA)Cl in which crystal the interionic potential barrier is known to exceed the intraionic one.[1-5]

From the size and shape of the anions, methylammonium nitrate and thiocyanate are thought to form crystals, in which the motion of the cations is expected to be hindered from an intermediate interionic potential barrier between those of the chloride and the hexahalometallates(IV). Accordingly, it is interesting to investigate the motion of the cation in these crystals by use of the ^1H NMR methods.

Experimental

Continuous wave ^1H NMR spectra were recorded by means of a JEOL JNM-MW-40S spectrometer operated at 40 MHz. A home-made pulsed NMR spectrometer described elsewhere[10] was employed to determine the T_1 values of ^1H nuclei at 20 MHz. The experiments of differential thermal analysis (DTA) were carried out in order to detect possible phase transition in the crystal of (MA)SCN by use of an apparatus reported previously.[11] Sample temperatures were determined by use of a copper-constantan thermocouple in each of these experiments.

Methylammonium nitrate was prepared by mixing an aqueous solution of methylamine and dilute nitric acid. Methylammonium thiocyanate was synthesized after the method described in the literature.[12] The crystals obtained were purified by repeated recrystallizations from absolute ethanol, twice for the nitrate and three times for the thiocyanate. Partially deuterated compounds, $CH_3ND_3NO_3$ and CH_3ND_3SCN were prepared by dissolving $(MA)NO_3$ and (MA)SCN, respectively, in heavy water. The extent of deuteration was estimated for both compounds to be more than 95% from the analysis of the infrared spectra. Since all the compounds studied are very hygroscopic, they were handled in a dry bag and placed in glass ampouls. Then, the ampouls filled with helium were sealed off after evacuating for 8 hours to remove a trace of water or solvent involved.

Results and Discussion

The second moment M_2 of ^1H NMR absorptions was determined at various temperatures between 77 and 300 K for $(MA)NO_3$ and (MA)SCN. The temperature dependences of the observed M_2 values are shown in Fig. 1.

Below 120 K, the almost constant M_2 values of 23 and 26 G^2 were obtained for $(MA)NO_3$ and (MA)SCN, respectively. With increasing temperature, a new plateau value of *ca.* 8 G^2 was reached for both compounds above 150 K and it continued up to room temperature. The theoretical M_2 values have been calculated for several motional modes of the cation[1,2] and reported to be 30, 19, and 8 G^2 for the rigid cation, for the C_3 reorienting CH_3 groups with rigid NH_3^+ ones, and for both groups reorienting about the C–N bond

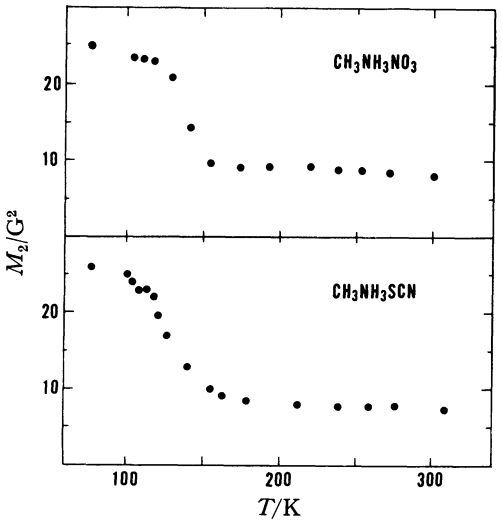

Fig. 1. Temperature dependences of the second moment M_2 of ^1H NMR absorptions for $CH_3NH_3NO_3$ and CH_3NH_3SCN.

axis, respectively. Although the exact interionic M_2 values of these compounds could not be calculated because of the lack of the crystal-structure data, they could be roughly estimated by referring to the data of (MA)Cl.[1] The resultant M_2 values including the interionic ones amount to 38, 23, and 9 G^2 for the three motional states described above in the same order. Comparing the observed and calculated values, the plateau value of M_2 obtained below 120 K for the two compounds can be interpreted in terms of the reorientation of the CH_3 groups alone, and the second plateau obtained above 150 K in terms of the reorientation of both CH_3 and NH_3^+ groups. These results indicate that the CH_3 group of the cation is quite free to reorient in the temperature range, 77—300 K. This is supported from the fact that the partially deuterated analog

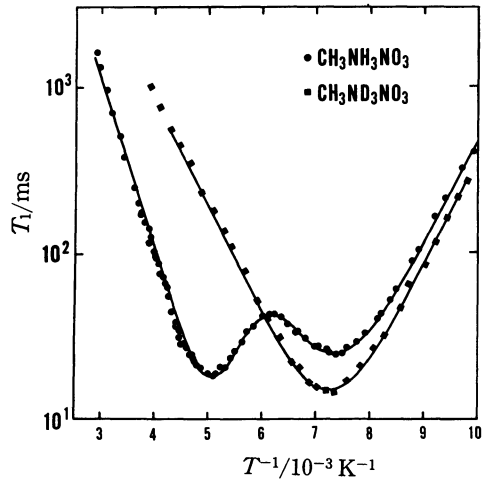

Fig. 2. Temperature dependences of T_1 values determined at 20 MHz for $CH_3NH_3NO_3$ and $CH_3ND_3NO_3$. The full lines are theoretical curves calculated in the manner described in the text.

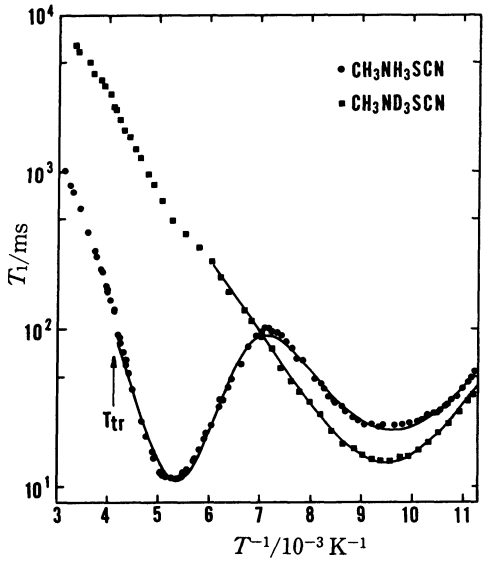

Fig. 3. Temperature dependences of T_1 values observed at 20 MHz for CH_3NH_3SCN and CH_3ND_3SCN. The full lines are theoretical curves calculated in the manner described in the text.

CH_3ND_3SCN yielded the M_2 value of 7.4 G^2 at 77 K. This value is very close to 6.3 G^2 which is calculated for the partially deuterated cation having the reorienting CH_3 group.[5]

The values of T_1 observed at various temperatures for the nitrates and the thiocyanates are shown in Figs. 2 and 3, respectively. The fully protonated nitrate exhibited two considerably well-separated T_1 minima, 24 and 18 ms at *ca.* 135 and 198 K, respectively. Its partially deuterated analog $CH_3ND_3NO_3$, on the other hand, yielded a single minimum of 14 ms at 137 K. Two well-separated T_1 minima, 24 and 11 ms were observed at *ca.* 105 and 192 K, respectively, for CH_3NH_3SCN, while a single minimum of 14.5 ms at *ca.* 105 K was obtained for CH_3ND_3SCN.

The observed T_1 curves can be analyzed by assuming the magnetic dipolar relaxation mechanism formulated by the following BPP equation[13]

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

where C, τ, and ω denote a constant depending on a motional mode in question, the correlation time of the motion, and an angular resonance frequency, respectively. The correlation time can be related to the activation energy E_a for the motion by assuming the Arrhenius relationship,

$$\tau = \tau_\infty \exp(E_a/RT). \quad (2)$$

Here, τ_∞ and R denote the correlation time at the infinite temperature and the gas constant, respectively.

From the experimental results of T_1 and the foregoing discussion on the ^{1}H NMR second moment, it is evident that the T_1 minimum observed at the lower temperature in each of the fully protonated salts is attributable to the CH_3 reorientation about its C_3 axis, while that at the higher temperature to the NH_3^+ reorientation. The single T_1 minimum observed for the partially deuterated analogs can be naturally attributed to the CH_3 reorientation. For the T_1 curve of CH_3ND_3SCN, a shoulder appeared at *ca.* 200 K. This seems to be another minimum resulting from the incomplete deuteration of the NH_3^+ group in our experiments.

On the high-temperature side of each T_1 minimum, both of $CH_3NH_3NO_3$ and CH_3NH_3SCN showed somewhat nonexponential behavior on the free-induction decay signals plotted against the interval time between the 180° and 90° pulses. This seems to be explainable by the theory of symmetry-restricted spin diffusion by Emid *et al.*[14] When the nonexponential relaxation behavior was observed, the experimental T_1 values were evaluated from the initial linear portion of the recovery of the ^{1}H nuclear magnetization observed after the 90° pulse.

The temperature dependence of T_1 values determined for the thiocyanate showed a small T_1 jump at 242 K. The partially deuterated analog, CH_3ND_3SCN also exhibited a discontinuity in the temperature coefficient of the T_1 curve at 250 K. These experimental facts suggest the existence of a phase transition in these compounds. In fact, the measurements of DTA gave rise to a thermal anomaly for each compound at the same temperature as the T_1 anomaly was observed. Since no thermal hysteresis was observed, these anomalies

TABLE 1. THE ACTIVATION ENERGY E_a AND THE CORRELATION TIME τ_∞ FOR THE CH_3 AND NH_3^+ REORIENTATIONS OF METHYLAMMONIUM NITRATE AND THIOCYANATE

Compound	Reorientational mode	E_a/kJ mol^{-1}	τ_∞/s
$CH_3NH_3NO_3$	CH_3	11.7	1.5×10^{-13}
	NH_3^+	20.0	2.6×10^{-14}
$CH_3ND_3NO_3$	CH_3	12.2	1.2×10^{-13}
CH_3NH_3SCN			
High temp phase	NH_3^+	17.0	—
Low temp phase	CH_3	8.2	3.6×10^{-13}
Low temp phase	NH_3^+	19.9	1.3×10^{-14}
CH_3ND_3SCN			
High temp phase	CH_3	8.3	—
Low temp phase	CH_3	8.9	1.9×10^{-12}

are attributable to a second or higher-order phase transition. Because the transition temperature was observed to be shifted by as much as 8 K on the deuteration of the NH_3^+ group, it is anticipated that the NH_3^+ group plays an important role on the mechanism of the phase transition revealed.

When the reorientation of the CH_3 and NH_3^+ groups about the C–N bond axis is assumed to take place independently of each other, the resultant T_1 value arising from these two relaxation processes can be expressed by

$$T_1^{-1} = \frac{1}{2}[T_1^{-1}(CH_3) + T_1^{-1}(NH_3^+)], \quad (3)$$

where $T_1(CH_3)$ and $T_1(NH_3^+)$ are the relaxation times for the CH_3 and NH_3^+ reorientations, respectively, and are given by Eq. 1. The unknown parameters E_a, τ_∞, and C for the reorientations of these two groups were calculated by a least-squre fitting of Eq. 3 to the observed T_1 curves. The calculation was performed at the computation center of Nagoya University by used of the computer program SALS.[15] The values of E_a and τ_∞ thus calculated for the CH_3 and NH_3^+ reorientations are given in Table 1.

The E_a values obtained for both groups in the nitrate are greater than 8 kJ mol^{-1} which is the E_a value evaluated previously for the internal rotation of the methylammonium cation.[8,9] This means that not only the intraionic potential barrier but also the interionic one is responsible for the present E_a values. For the CH_3 reorientation, the fully and partially protonated thiocyanates yielded the E_a values of 8.2 and 8.9 kJ mol^{-1}, respectively. The fact that these E_a values are very close to that for the internal rotation of the cation, indicates that the barrier hindering the CH_3 reorientation originates almost from the intraionic interaction and the interionic contribution is quite small in this case. For the NH_3^+ reorientation, on the other hand, the thiocyanate gave rise to fairly large E_a values of 19.9 and 17.0 kJ mol^{-1} in the low- and the high-temperature phases, respectively, indicating the existence of interionic interaction, probably, considerably strong hydrogen bonding.

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