

Structural Phase Transitions in Solid tert-Butylammonium Nitrate as Studied by Differential Thermal Analysis and ^1H -NMR

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Seven solid phases including three metastable phases of $(\text{CH}_3)_3\text{CNH}_3\text{NO}_3$ were revealed by differential thermal analysis in the temperature range between 80 K and the melting point (418 K), and cationic dynamics in each phase was studied by use of ^1H -NMR techniques. The highest-temperature solid phase obtainable above 412 K was found to be an ionic plastic phase, where the cations perform rapid translational self-diffusion and overall rotation about their center of gravity.

1. Introduction

It has been revealed by thermal analysis that simple alkylammonium nitrates [1–4] and perchlorates [1, 5–10] exhibit several solid phases under ambient pressure, each of which has usually been characterized through its cationic dynamics studied by means of NMR techniques. The highest-temperature solid phases of mono- and trimethylammonium nitrates, and mono-, di-, and trimethylammonium perchlorates have been attracted much attention because liquid-like properties were observed in these solid phases. Namely, the cations in these phases were shown to perform rapid translational self-diffusion as well as isotropic rotation as a whole. These properties of the cations bear strong resemblance to those of molecules in the plastic crystal [11], and, therefore, the above phases have been called as “ionic plastic phase”. The reason why the plastic phase is realized even in ionic crystals in which Coulomb forces much stronger than van der Waals forces are operative is attributable to the high-symmetric shapes of both ions, and also to the molecular-like structure of the cations as well as the delocalized electronic charge distribution assumed in the anions.

A tert-butylammonium ion is expected to be easily rotatable because of its globular shape similar to monomethyl- and trimethylammonium ions. In the present study, we have looked for new solid phases of tert-butylammonium nitrate and found some phases including metastable phases. They were characterized through cationic dynamics in crystals using differential thermal analysis (DTA) and ^1H -NMR. This paper describes the novel results obtained.

2. Experimental

Tert-Butylammonium nitrate was prepared by neutralization of tert-butylamine with nitric acid. The obtained crystals were purified by threefold recrystallization from a mixed solvent of ethanol and diethylether. Since the crystals were hygroscopic, they were carefully handled in a glove box, and dried under vacuum obtained by a vacuum pump at room temperature for 24 h and then at 333 K for 24 h. The sample thus obtained was sealed off in a glass ampoul for measurements. Measurements of DTA, broadline ^1H -NMR absorption, and ^1H spin-lattice relaxation time (T_1) at the Larmor frequencies of 20 and 32 MHz were carried out using respective apparatus already reported [12–14].

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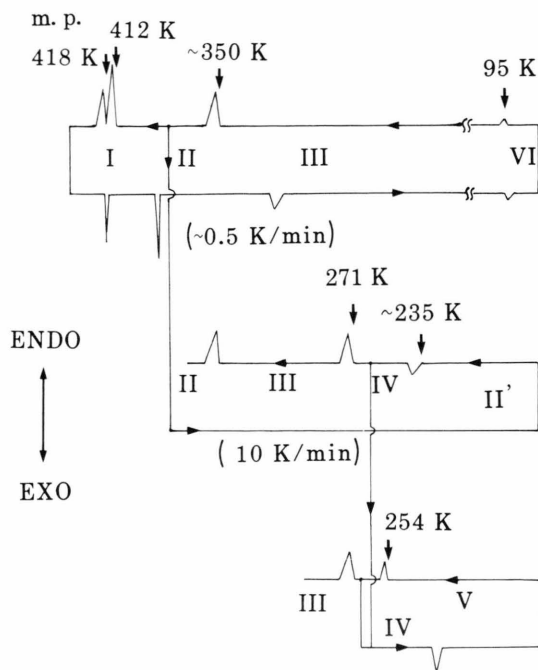


Fig. 1. Differential thermal analysis (DTA) curves of $(\text{CH}_3)_3\text{CNH}_3\text{NO}_3$. The cooling and heating rate normally used is ca. 1 K/min.

3. Results and Discussion

DTA curves recorded in the temperature range of (80–420) K are shown in Figure 1. When the sample was heated from room temperature, three endothermic anomalies appeared at ca. 350, 412, and 418 K. The first two anomalies are attributed to solid-solid phase transitions and the last one to the melting. The temperature of the first anomaly depends on the history of the thermal treatment of the sample: a sample warmed for the first time above 350 K showed an anomaly at (355 ± 2) K, while this temperature shifted to (347 ± 2) K on the second and subsequent runs of heating. The transition temperature, T_{tr} , reverted to 355 K by annealing the sample at room temperature for two months. This suggests that the decrease of T_{tr} , is not caused by thermal decomposition of the sample. When the sample was cooled from room temperature down to liquid N_2 temperature, an anomaly was detected around 95 K, which was so small that only the peak temperature of the anomaly could be determined. With increasing the temperature from liquid N_2 temperature, a small endothermic anomaly appeared at almost the same temperature as above.

The phase obtained between 350 and 412 K could easily be supercooled down to ca. 80 K by cooling from 350 to 200 K at a rate faster than 10 K min^{-1} . With increasing the temperature of the sample cooled rapidly to ca. 80 K, an unusual exothermic anomaly appeared at ca. 235 K. On further warming, an endothermic anomaly was observed at (271 ± 1) K. When the sample was cooled again immediately after finishing the foregoing exothermic anomaly on warming, a new phase transition was observed at ca. 220 K on the cooling run whereas its T_{tr} was located at (254 ± 1) K on heating. As shown in Fig. 1, the solid phases revealed by DTA are designated in the order of decreasing temperature as phases I, II, III, IV, V, VI, and II'. The phase IV could also be obtained by keeping the phase III at ca. 240 K for three days. From the exo- and endothermic anomalies of the DTA curves, the phases; I ($418 \geq T/\text{K} \geq 412$), II ($412 \geq T/\text{K} \geq \sim 350$), III ($\sim 350 \geq T/\text{K} \geq 271$), IV ($271 \geq T/\text{K} \geq 254$), and V ($254 \geq T/\text{K}$), are considered to be stable phases, and the phases II' ($\sim 235 \geq T/\text{K}$), III ($271 \geq T/\text{K} \geq 95$) for the sample obtained by normal cooling, and VI ($95 \geq T/\text{K}$) to be metastable. The phase VI is considered as a metastable phase because no heat anomaly was detected at 95 K for the sample in the phase V.

To confirm the existence of these phases and to characterize the cationic motion in each phase, we have carried out cw and pulsed ^1H -NMR measurements. The M_2 values observed are $(13.4 \pm 1.0) \text{ G}^2$ at 151 K (Phase V), $(12.0 \pm 1.0) \text{ G}^2$ at 154 K (Phase II'), $(12.0 \pm 1.0) \text{ G}^2$ at 160 K (Phase III), $(3.1 \pm 0.5) \text{ G}^2$ at 278 K (Phase III), and $(3.0 \pm 0.5) \text{ G}^2$ at 255 K (Phase IV). Comparing these M_2 values with the calculated ones for tert-butylammonium halides listed in literature [15, 16], we can conclude that reorientation of the three CH_3 groups in a cation about their respective C_3 axis takes place more frequently than 10^4 Hz even around 150 K. The reorientations of the tert-butyl group and also of the NH_3^+ group about the C-N bond axis are expected to occur around 250 K by referring to the above M_2 data. A constant M_2 value of $(2.7 \pm 0.5) \text{ G}^2$ was observed in the phase II, indicating the onset of another motion, possibly a whole-cationic reorientation.

The temperature dependence of ^1H T_1 in the phases I, II, III, and VI at the Larmor frequencies of 20 and 32 MHz is shown in Figure 2. When the sample was cooled from room temperature, ^1H T_1 at 20 MHz gave two T_1 minima around 180 and 295 K, and a shoulder at ca. 100 K. No discontinuity in the T_1 curve

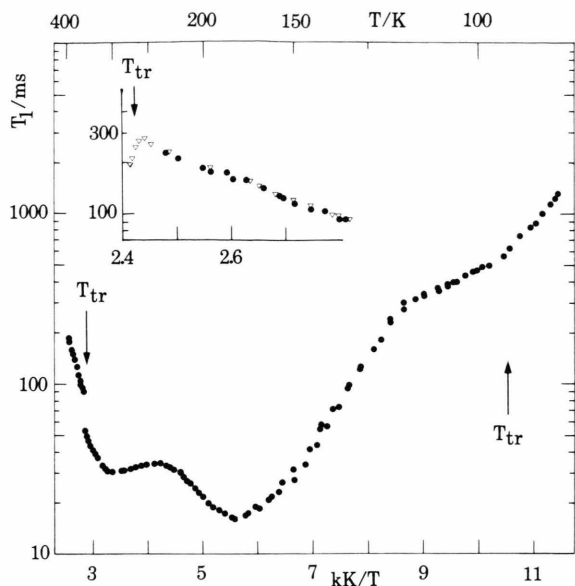


Fig. 2. Temperature dependence of ^1H T_1 in the phases I (418–412 K), II (412–~350 K), III (~271–95 K), and VI (95 K \geq) of $(\text{CH}_3)_3\text{CNH}_3\text{NO}_3$ observed at the Larmor frequencies of 20 (●) and 32 (▽) MHz.

was observed at the transition point, T_{tr} (III→VI). On the other hand, a T_1 jump and the inversion of the sign of its temperature gradient, respectively, were observed at T_{tr} (III→II) and T_{tr} (II→I) [in a temperature range around and above this T_{tr} , observation was made at 32 MHz]. The M_2 value $< 0.5 \text{ G}^2$ obtained in the phase I indicates the presence of self diffusion and overall rotation of the cation faster than 10^4 Hz in this phase. From these results, the phase I can be considered as an ionic plastic phase similar to the highest-temperature solid phases of mono- and trimethylammonium nitrates. The T_1 decrease with increasing temperature observed at 32 MHz in the phase I is attributable to cationic self-diffusion because of its large activation energy $> 150 \text{ kJ mol}^{-1}$, roughly estimated from the $\log T_1$ vs. T^{-1} slope.

The gradient of the $\log T_1$ vs. T^{-1} curve becomes milder at and below 8.5 kK/T , as if a phase transition takes place at this temperature. However, this anomalous curve can be interpreted as two overlapping BPP curves. This is because the turning temperature was observed to be shifted by measurements tentatively carried out using different Larmor frequencies.

The temperature dependence of ^1H T_1 determined at 32 MHz in the phases II', III, IV, and V are shown in Figure 3. In the phase II', a T_1 minimum of 26 ms

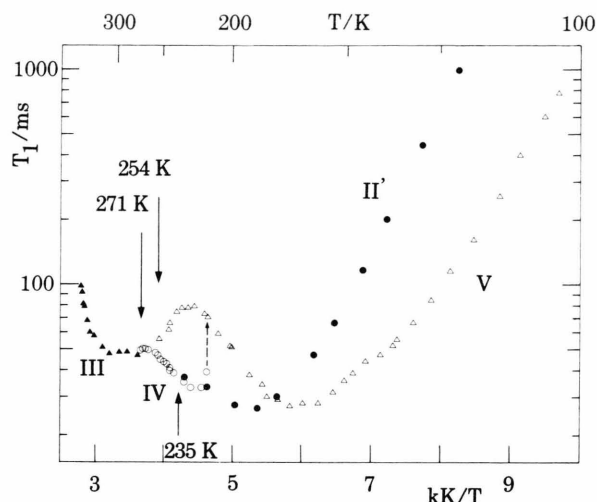


Fig. 3. Temperature dependence of ^1H T_1 observed for the sample obtained by rapid cooling. Observation was made at 32 MHz in the phase III (~350–271 K) (▲), IV (271–254 K) (○), V (254 K \geq) (△), and II' (~235 K \geq) (●). T_{tr} values of 271, 254, and 235 K in the figure were determined from DTA. The arrow with dotted line indicates that the phase IV is transformed into the phase V at this temperature with decreasing temperature. T_{tr} (IV→V) was not definite and depended on the cooling rate.

appeared around 190 K. At T_{tr} (II'→IV) observed by DTA, no marked discontinuity of T_1 was observed. When the sample kept at 255 K (Phase IV) for several hours, was cooled, a discontinuous T_1 increase was detected at T_{tr} (IV→V). In the phase V, a T_1 minimum of 27 ms and a maximum of 80 ms appeared at 167 and 225 K, respectively.

Considering the M_2 data given above, we can assign the T_1 minima observed in the phases II' and V as well as that appearing in the phase III at ca. 180 K to the C_3 -reorientation of the CH_3 groups. The activation energy for the motion was estimated from the slope of the $\log T_1$ vs. T^{-1} curve on the low temperature side of each minimum observed in the phases II', III, and V. The obtained activation energies are 13, 11, and 10 kJ mol^{-1} in the order of the foregoing phases. It is interesting that the activation energy for the CH_3 groups in the stable phase V is smaller than that in the metastable phases II' and III. The high temperature T_1 minimum in the phase III is attributable to the reorientation of the tert-butyl and NH_3^+ groups. The activation energy evaluated from the high temperature side of the T_1 minimum is 16 kJ mol^{-1} , which is about a half of that obtained for tert-butylammonium halides [15, 16].

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