Molecular Motions of *t*-Butylammonium Ions and Structural Phase Transitions in Solid *t*-Butylammonium Perchlorate Studied by ^{1}H NMR and Thermal Measurements

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Differential thermal analysis (DTA), differential scanning calorimetry (DSC), and the temperature dependences of the ^{1}H spin-lattice relaxation time (T_1) and the second moment (M_2) of ^{1}H NMR absorptions were studied in $(CH_3)_3CNH_3ClO_4$ and its partially deuterated analogs, $(CH_3)_3CND_3ClO_4$ and $(CD_3)_3CNH_3ClO_4$. DTA and DSC studied revealed four solid phases, including a metastable phase, in the temperature range between 80 K and the melting point (414 K). The stable phases (named as I, II, and III) were obtained above 394 K, between 394 and 327 K, and below 327 K, respectively. The metastable phase II′, prepared by rapid cooling the phase II to ca. 100 K, exists below ca. 245 K. The cationic motions in each solid phase were studied by T_1 and M_2 experiments. Three kinds of 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) were observed in these phases and their motional parameters were determined

The solid methyl-substituted ammonium perchlorates, $(CH_3)_nNH_{4-n}ClO_4$ (n=1—4), are known to undergo polymorphic phase transitions which are interrelated with changes in the motional states of the cations and anions in crystals.[1—8] In the highest-temperature solid phases of these salts, both ions are in a highly disordered state, obtaining the greatest part of their motional freedom. Especially, in the phases of mono-, di-, and trimethylammonium perchlorates the cations were shown to perform rapid translational self-diffusion as well as isotropic rotation as a whole by NMR techniques.[2—4,6,7]

Since a *t*-butylammonium ion is expected to be easily movable in crystals because of its higher symmetry and more spherical shape than mono- and trimethylammonium ions, *t*-butylammonium perchlorate seems to be an interesting candidate for studying the relation between ionic motions and the polymorphic phase transitions expected to occur. The motions of *t*-butylammonium ions in a solid have been investigated by ^{1}H NMR techniques for *t*-butylamine tropolone adduct,[9] *t*-butylammonium halides,[10—12] and nitrate;[13] in these salts the cations have been found to be tightly fixed in the crystal lattice and to form fairly strong N–H···X type hydrogen bonds between the cation and the anion. Since a perchlorate ion is expected to form a hydrogen bond with a counter cation much weaker than halide ions, it is interesting to elucidate the molecular motions of the *t*-butylammonium ion expected to be more loosely bound in a crystal.

In the present study measurements of the temperature dependences of the ^{1}H spin-lattice relaxation time (T_1) and the second moment (M_2) of the ^{1}H NMR absorptions, differential thermal analysis (DTA), and differential scanning calorimetry (DSC) have been carried out for *t*-butylammonium perchlorate and its partially deuterated analogs to reveal the phase transitions, possible cationic motions, and their time scales in respective solid phases.

Experimental

^{1}H T_1 was determined at 32 and 8.5 MHz by means of a pulsed NMR spectrometer described elsewhere.[14] A 180°—τ—90° pulse sequence was employed. Continuous-wave ^{1}H NMR spectra were recorded at 40 MHz by using a JEOL JNM-MW-40S spectrometer. A home-made apparatus similar to that reported previously[15] was employed for DTA experiments. Differential scanning calorimetry (DSC) was carried out by use of a Perkin–Elmer 7 Series Thermal Analysis System.

$(CH_3)_3CNH_3ClO_4$ (abbreviated to (*t*-BA)ClO$_4$) was prepared by neutralizing *t*-butylamine with perchloric acid and recrystallized twice from isopropyl alcohol. $(CH_3)_3CND_3ClO_4$ ((*t*-BA*d*$_3$)ClO$_4$) was prepared from purified (*t*-BA)ClO$_4$ by repeated crystallization three times from heavy water and was finally purified by recrystallization from CH_3OD. $(CD_3)_3CNH_3ClO_4$ ((*t*-B*d*$_9$A)ClO$_4$) was obtained from perchloric acid and $(CD_3)_3CNH_2$ purchased from MSD Isotopes and recrystallized from isopropyl alcohol. The obtained crystals were dried under high vacuum at room temperature for 24 h and then at ca. 50 °C for 24 h before elemental analysis and the measurements of NMR, DTA, and DSC. Calcd for $(CH_3)_3CNH_3ClO_4$: C, 27.67; H, 6.91; N, 8.07%. Found: C, 27.64; H, 6.82; N, 8.13%.

Results

DTA curves recorded for (*t*-BA)ClO$_4$ over the temperature range of 80—420 K are shown in Fig. 1. When the sample was heated from room temperature, three endothermic anomalies appeared at 327, 394, and

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† Deceased on 27 February, 1991.

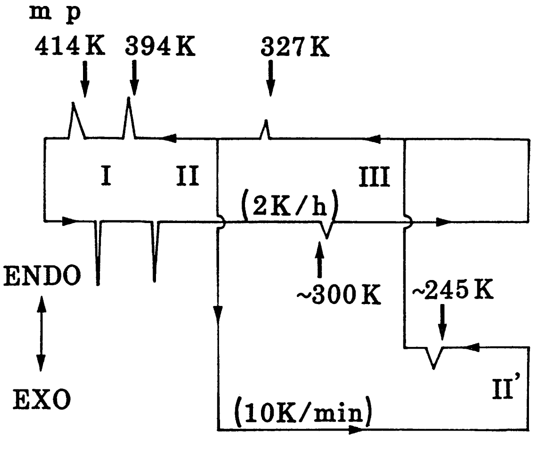

Fig. 1. DTA curves of $(CH_3)_3CNH_3ClO_4$. The cooling and heating rate is ca. 1 K min^{-1} unless otherwise noted. I, II, III, and II′ are the names of obtained solid phases.

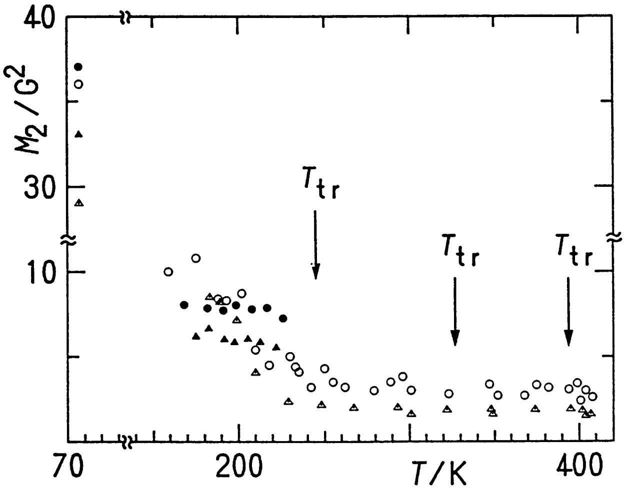

Fig. 2. Temperature dependence of the ^{1}H NMR second moment (M_2) observed for $(CH_3)_3CNH_3ClO_4$ (○ for phases I, II, and III; ● for phase II′) and $(CH_3)_3CND_3ClO_4$ (△ for I, II, and III; ▲ for II′). T_{tr}'s are transition temperatures determined for $(CH_3)_3CNH_3ClO_4$ by DTA.

414±1 K. The first two anomalies were attributed to solid-solid phase transitions and the last one to melting. The corresponding entropy changes determined by DSC were 6.9, 12, and 17 J K^{-1} mol^{-1}, respectively.

The phase obtained between 327 and 394 K could easily be supercooled down to ca. 100 K by cooling at a rate faster than 10 K min^{-1}. With increasing temperature of a rapidly cooled sample, an unusual exothermic anomaly appeared at ca. 245 K. The solid phases revealed by DTA are designated in the order of decreasing temperature as phases I, II, III, and II′, as shown in Fig. 1. The partially deuterated analogs, $(t\text{-BA}d_3)ClO_4$ and $(t\text{-B}d_9\text{A})ClO_4$, showed approximately the same DTA curves as in Fig. 1 and their transition temperatures are given in Figs. 4 and 5, respectively.

The temperature variation of M_2 observed for $(t\text{-BA})ClO_4$ and $(t\text{-BA}d_3)ClO_4$ between 77 and 408 K is shown in Fig. 2. The M_2 values at 77 K determined for $(t\text{-BA})ClO_4$ in phases III and II′ were 36 and 37±2 G^2 (1 G=1×10^{-4} T), respectively, while for $(t\text{-BA}d_3)ClO_4$, 33 and 29±2 G^2, they were of the same order. Between 170 and 220 K in phase II′, almost constant values of 7.8 and 5.9±0.3 G^2 were obtained for $(t\text{-BA})ClO_4$ and $(t\text{-BA}d_3)ClO_4$, respectively. Above 240 K, the M_2 values for both salts were almost constant and no remarkable change was observed at the transition points, $T_{tr}(\text{III}\rightarrow\text{II})$ and $T_{tr}(\text{II}\rightarrow\text{I})$.

The temperature dependences of ^{1}H NMR T_1 determined at 32 and 8.5 MHz are shown in Figs. 3, 4, and 5 for $(t\text{-BA})ClO_4$, $(t\text{-BA}d_3)ClO_4$, and $(t\text{-B}d_9\text{A})ClO_4$, respectively. When measured at 32 MHz, $(t\text{-BA})ClO_4$ in phase III yielded three T_1 minima of 25, 42, and 51 ms located at 172, 235, and 323 K, respectively, while $(t\text{-BA}d_3)ClO_4$ exhibited two minima of 21 and 59 ms at 169 and 317 K, respectively. Regarding $(t\text{-B}d_9\text{A})ClO_4$, a T_1 minimum of 13 ms was observed at 244 K.

$(t\text{-BA})ClO_4$ and $(t\text{-BA}d_3)ClO_4$ in phase II′ gave a broad and asymmetric T_1 minimum, considered to have resulted from superimposed two or more minima. From the T_1 data observed for $(t\text{-B}d_9\text{A})ClO_4$ at 8.5

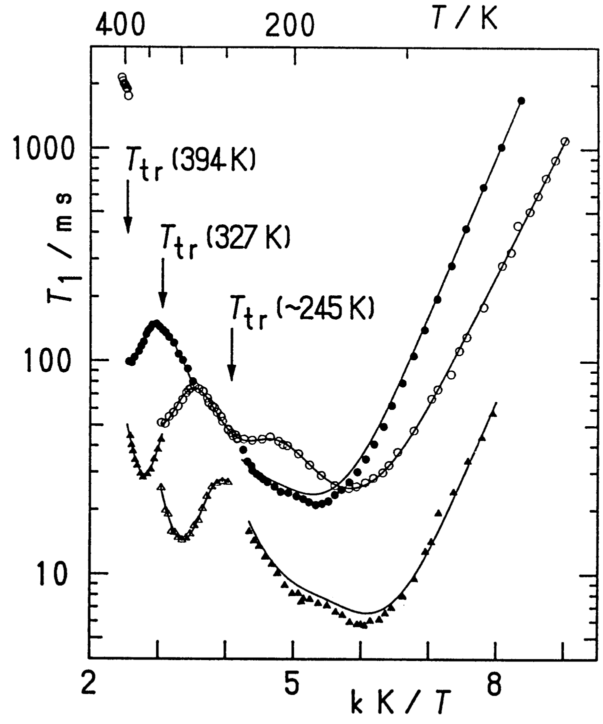

Fig. 3. Temperature dependence of the spin-lattice relaxation time (T_1) observed at 8.5 MHz (△ for phase III; ▲ for phases II and II′) and 32 MHz (○ for I and III; ● for II and II′) in $(CH_3)_3CNH_3ClO_4$. The solid lines in phases II and III indicate the best-fit theoretical values, whereas the lines in phase II′ are the calculated T_1 curves using the motional parameters determined for $(CH_3)_3CND_3ClO_4$ and $(CD_3)_3CNH_3ClO_4$.

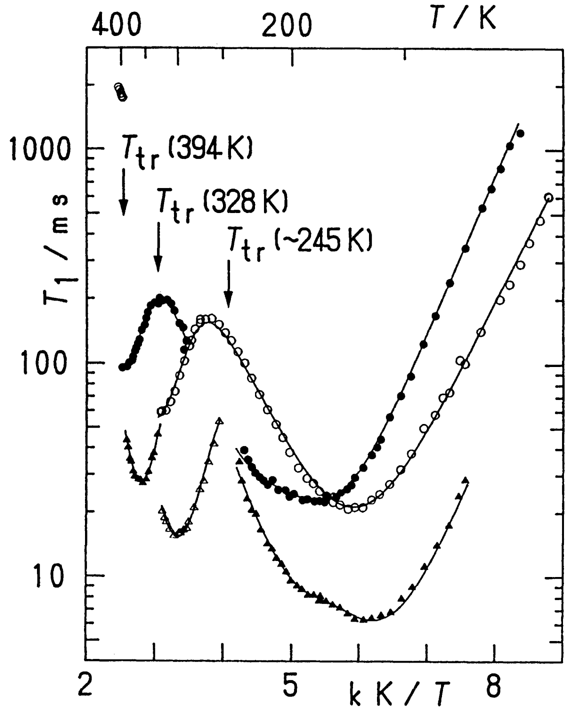

Fig. 4. Temperature dependence of the spin-lattice relaxation time (T_1) observed at 8.5 MHz (△ for phase III; ▲ for phases II and II′) and 32 MHz (○ for I and III; ● for II and II′) in $(CH_3)_3CND_3ClO_4$. T_{tr}'s are transition temperatures determined for $(CH_3)_3$-CND_3ClO_4 by DTA. The solid lines indicate the best-fit theoretical values.

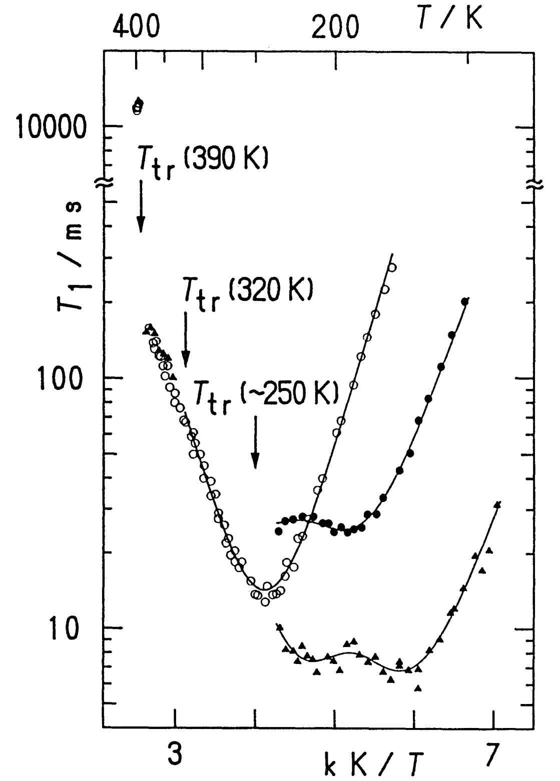

Fig. 5. Temperature dependence of the spin-lattice relaxation time (T_1) observed at 8.5 (▲) and 32 MHz (○ for phases I, II, and III; ● for phase II′) in $(CD_3)_3CNH_3ClO_4$. T_{tr}'s are transition temperatures determined for $(CD_3)_3CNH_3ClO_4$ by DTA. Solid lines indicate the best-fit theoretical values.

MHz, two minima could be distinguished at 170 and 210 K.

A sudden increase of T_1 was observed for (t-BA)ClO_4 and (t-BAd_3)ClO_4 at T_{tr}(III→II), above which temperature each salt measured at 8.5 MHz showed a minimum at almost the same temperature (360 K) in phase II. T_1 of (t-Bd_9A)ClO_4 showed no remarkable discontinuity at the transition and increased with temperature in phase II; the gradient of T_1 vs. T^{-1} plots in this phase is slightly gentler than in phase III. At T_{tr}(II→I), of all salts increased discontinuously. In phase I, T_1 of (t-BA)-ClO_4 and (t-BAd_3)ClO_4 increased with temperature, whereas a decrease of T_1 was observed for (t-Bd_9A)ClO_4. T_1 of each salt measured at 32 and 8.5 MHz gave the same values within the experimental error.

Discussion

Second Moments of ^{1}H NMR Absorptions. To interpret the M_2 values obtained for (t-BA)ClO_4 and (t-BAd_3)ClO_4, we calculated the M_2 values for the following motional states of the cation: 1) the rigid lattice, 2) the C_3 reorientations of the three CH_3 groups about the respective C–C bond axes, 3) the C_3 reorientation of the NH_3^+ group about the C–N bond axis in addition to the CH_3 reorientations, and 4) the C_3' reorientation of the t-butyl group about the C–N bond axis together with the NH_3^+ and CH_3 reorientations. Since no crystal data are available for this salt, we calculated the M_2 values arising from only intra-cationic magnetic dipole-dipole interactions. In the calculation, the bond distances of C–C, C–N, C–H, and N–H were taken to be 1.54, 1.47, 1.10, and 1.04 Å, respectively;16,17) all bond angles were assumed to be tetrahedral. The calculated values for the above-mentioned motional modes are given in Table 1 for both t-BA$^+$ and t-BAd_3^+ cations.

By comparing the observed M_2 values with the calculated ones, the cations are expected to be rigid at 77 K in phases III and II′. The differences between the

Table 1. Second Moments (M_2/G^2) of ^{1}H NMR Absorptions Calculated for $(CH_3)_3CNH_3^+$ and $(CH_3)_3CND_3^+$ Cations

	$(CH_3)_3CNH_3^+$	$(CH_3)_3CND_3^+$
Rigid	25.7	22.7
CH_3 Reorientation	12.7	6.0
CH_3 and NH_3^+ Reorientation	7.0	6.0
CH_3, NH_3^+, and t-Butyl Reorientation	3.8	2.3

observed and calculated values seem to be attributable to intermolecular contributions. The almost constant values of M_2 observed between 170 and 220 K in phase II′ can be explained by a model of the C_3 reorientations of the CH_3 and NH_3^+ groups. Above ca. 240 K, the cations are considered to undergo the C_3 reorientations of the CH_3 and NH_3^+ groups as well as the C_3' reorientation of the *t*-butyl group. The M_2 values of 3.3±0.3 and 2.0±0.2 G^2 obtained for (*t*-BA)ClO_4 and (*t*-BA*d*$_3$)ClO_4, respectively, above 240 K are, however, somewhat smaller than the calculated values for this motional model. This implies the existence of additional cationic motions which are activated even below 240 K. The large-amplitude librations of the cation about the C–C and C–N axes can be thought of as one such motional mode. In fact, a large-amplitude torsional motion of the cation about the C–N axis has been reported from an X-ray diffraction study of $(CH_3)_3CNH_3Cl$.[18] Since a ClO_4^- ion forms the hydrogen bond with a cation weaker than a Cl^- ion, it is expected that the cation in perchlorate librates more freely with a much larger amplitude.

The observed entropy changes (ΔS_{tr}) at T_{tr}(III→II) and T_{tr}(II→I) were considerably large, and the sum of the two ΔS_{tr} (ca. 19 J K^{-1} mol^{-1}) was comparable with each ΔS_{tr} value at the two transitions reported for $CH_3NH_3ClO_4$.[3] This salt undergoes two solid–solid phase transitions at 321 K (ΔS_{tr}=20.9 J K^{-1} mol^{-1}) and 451 K (ΔS_{tr}=16.9 J K^{-1} mol^{-1}) and then transforms into a plastic phase in which both cations and anions are freely movable, like in liquid phase. It has been revealed that, at both low- and high-temperature transitions, the anions and the cations, respectively, acquire the greatest part of their motional freedom.[1–5,19] One might expect, accordingly, that the cations and/or the anions in (*t*-BA)ClO_4 also obtain motional freedom to a similar extent through these two transitions. Since the motional state of the *t*-BA^+ cations is thought to be little affected at both transitions, where no marked decrease in M_2 was observed, the increase in motional freedom probably occurs only in the anions and, hence, the isotropic rotation of the anions is expected in phase I.

Room-Temperature Phase (III). Referring to the above discussion on M_2, we can assign the T_1 minimum at 240 K observed for (*t*-B*d*$_9$A)ClO_4 to the C_3 reorientation of the NH_3^+ group. For this motion, ^1H T_1 can be expressed as[20]

$$T_1^{-1} = Cf(\tau), \tag{1}$$

$$C = (9/20)\gamma^4\hbar^2 r^{-6} \tag{2}$$

and

$$f(\tau) = \tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2). \tag{3}$$

Here, γ, r, τ, and ω denote the gyromagnetic ratio of a proton, the inter-proton distance in the NH_3^+ group, the correlation time of the motion, and the angular resonance frequency, respectively. Assuming an Arrhenius-type relationship between τ and the activation energy (E_a) for the reorientation process, one obtains

$$\tau = \tau_0 \exp(E_a/RT), \tag{4}$$

where τ_0 is the correlation time at infinite temperature. Eqs. 1—4 were fitted to the T_1 data obtained for (*t*-B*d*$_9$A)ClO_4 using a least-squares method. The optimum values of E_a, τ_0, and C obtained are listed in Table 2.

Table 2. Motional Parameters of *t*-Butylammonium Ions in $(CH_3)_3CNH_3ClO_4$, $(CH_3)_3CND_3ClO_4$, and $(CD_3)_3CNH_3ClO_4$

Compound	E_a/kJ mol^{-1}	$\tau_0/10^{-13}$ s	$C/10^9$ s^{-2}	Reorienting group
$(CH_3)_3CNH_3ClO_4$				
Phase I	17.3±0.5	—	—	*t*-Butyl
Phase II	41.1±0.5	0.12±0.03	1.1±0.1	*t*-Butyl(1)
	14.9±0.2	—	—	*t*-Butyl(2) and NH_3^+
Phase III	12.1±0.1	6.2 ±0.2	5.5±0.1	CH_3
	21.8±0.4	0.53±0.10	2.1±0.1	NH_3^+
	32.3±0.4	0.26±0.04	2.4±0.2	*t*-Butyl
Phase II′	14.6±0.5	—	—	CH_3 and NH_3^+
$(CH_3)_3CND_3ClO_4$				
Phase I	17.3±0.5	—	—	*t*-Butyl
Phase II	44.1±0.7	0.05±0.01	1.3±0.1	*t*-Butyl(1)
	15.3±0.5	—	—	*t*-Butyl(2)
Phase III	12.0±0.1	6.0 ±0.3	6.6±0.1	CH_3
	32.4±0.4	0.26±0.05	2.4±0.3	*t*-Butyl
Phase II′	14.1±0.1	2.6 ±0.3	5.4±0.1	CH_3(1)
	17.3±0.5	2.7 ±0.7	2.7±0.1	CH_3(2)
$(CD_3)_3CNH_3ClO_4$				
Phase II	14.8±0.8	—	—	NH_3^+
Phase III	20.1±0.2	1.5 ±0.2	9.9±0.2	NH_3^+
Phase II′	16.1±0.3	1.3 ±0.3	5.0±0.2	NH_3^+(1)
	19.6±1.0	2.2 ±0.2	4.1±0.2	NH_3^+(2)

The T_1 minimum at 172 K observed for $(t\text{-BA}d_3)ClO_4$ is attributable to the C_3 reorientation of all CH_3 groups in the cation, and the T_1 minima around 310 K observed at 8.5 and 32 MHz to the C_3' reorientation of the *t*-butyl group from the above discussion on M_2. Since the T_1 minima arising from the reorientations of the CH_3 and *t*-butyl groups are well separated, the correlation time (τ_1) for the CH_3 group motion is considered to be much shorter than that (τ_2) for the *t*-butyl group, i.e., $\tau_1 \ll \tau_2$. Thus, assuming that all CH_3 groups in this phase are crystallographically equivalent, we can express ^1H T_1 for these two motions by the sum of the two BBP equations associated with the CH_3 and the *t*-butyl group motions:[10,21,22]

$$T_1^{-1} = C(\text{Me})f(\tau_1) + C(\text{Bu})f(\tau_2), \tag{5}$$

$$C(\text{Me}) = (9/80)\gamma^4\hbar^2 r^{-6}\{(3/2)\sin^4\delta + (1/2)(8-3\sin^4\delta)\}, \tag{6a}$$

and

$$C(\text{Bu}) = \gamma^4\hbar^2\{(9/80)\,r^{-6}(\sin^2 2\delta + \sin^4\delta) + (27/20)R^{-6}\}. \tag{6b}$$

Here, C(Me) and C(Bu), r, R, and δ are the motional constants, the interproton distance in a CH_3 group, the distance between the centers of three protons in each CH_3 group, and the angle between C–C and C–N bonds, respectively. Employing an Arrhenius-type relationship as given by Eq. 4 for these two motions, the activation energies, the correlation times at infinite temperature, and the motional constants could be obtained for $(t\text{-BA}d_3)ClO_4$ by a fitting calculation of Eqs. 5 and 6 to the observed T_1 data. The best-fit motional parameters are listed in Table 2. Good agreement between the observed and calculated T_1 was obtained, as shown in Fig. 4.

From the above discussion on the two deuterated analogs, three well separated T_1 minima of $(t\text{-BA})ClO_4$ located at 172, 235, and 323 K can be assigned to the reorientations of the CH_3, NH_3^+, and *t*-butyl groups, respectively. T_1 for $(t\text{-BA})ClO_4$ can be expressed as

$$T_1^{-1} = (3/4)\{T_1(t\text{-BA}d_3)\}^{-1} + (1/4)\{T_1(t\text{-B}d_9\text{A})\}^{-1}, \tag{7}$$

where $T_1(t\text{-BA}d_3)$ and $T_1(t\text{-B}d_9\text{A})$ are given by Eqs. 5 and 1, respectively. A fitting calculation to the T_1 data of $(t\text{-BA})ClO_4$ was carried out using Eqs. 4 and 7. The results are given in Table 2.

The large activation energy (32.3 kJ mol^{-1}) obtained for the *t*-butyl reorientation implies that the cations were tightly packed in the crystal. Comparable activation energies of 26.9—32.6 kJ mol^{-1} were reported for *t*-BA bromide and iodide.[10,11] This result is reasonable in view of these three kinds of anions with about the same size and shape. E_a=12.1 kJ mol^{-1} for the CH_3 reorientation is also comparable with 9.8—11.7 kJ mol^{-1} for the less hindered CH_3 groups in the *t*-BA cation in halides.[10,11] E_a=21.8 kJ mol^{-1} for the NH_3^+ group, on the other hand, is considerably smaller than 27.3[23]—44.2 kJ mol^{-1} for the same motion in halides.[10,12] This is explainable in terms of a weak hydrogen bond of the N–H···O type formed in perchlorate; E_a in the present perchlorate, however, is much larger than 2—5 and 2—3 kJ mol^{-1} for the NH_3^+ reorientation in $CH_3NH_3ClO_4$[2—4] and for the NH_4^+ reorientation in NH_4ClO_4,[24—26] respectively, the values of which are regarded as being typical examples for perchlorates containing very weak hydrogen bonds. Accordingly, we suppose in the present salt, besides the hydrogen bonding, interionic steric interactions due to tightly packed cations and anions also give a considerable contribution to the barrier for NH_3^+ rotation.

Metastable Phase (II′). The T_1 minima observed for $(t\text{-B}d_9\text{A})ClO_4$ can be attributed to the C_3 reorientation of the NH_3^+ group. Since the two T_1 minima having almost the same values were obtained at 8.5 MHz, it is expected that there exist two crystallographically nonequivalent cations in this phase with an abundance ratio of 1 : 1. ^1H T_1 for the present motion can be expressed by superimposed two BPP equations, as

$$T_1^{-1} = C_1 f(\tau_1) + C_2 f(\tau_2). \tag{8}$$

A fitting calculation was made by use of Eqs. 8 and 4, and the results are shown in Table 2.

The broad and asymmetric T_1 minimum of $(t\text{-BA}d_3)ClO_4$ can be explained in terms of the C_3 reorientation of the nonequivalent CH_3 groups by referring to the M_2 results. When we assume two kinds of CH_3 groups in this phase, an equation similar to Eq. 8 can be used to analyze the T_1 data. A fitting calculation using this equation was successful as is shown in Fig. 4; its results are listed in Table 2. We obtained $C_1=5.4\times10^9$ and $C_2=2.7\times10^9$ s^{-2} as the optimum values for the motional constants; this implies that the nonequivalent CH_3 groups can be classified into two groups with an abundance ratio of 2 : 1. Since two kinds of cations have been revealed to exist in phase II′ from the results of $(t\text{-B}d_9\text{A})ClO_4$, the above results can be interpreted in terms of one of the following two models: 1) each cation includes two kinds of nonequivalent CH_3 groups, and 2) one cation contains three equivalent CH_3 groups, while the other has nonequivalent CH_3 groups (2 : 1), one of which is embedded in almost the same circumstance as the former three CH_3 groups.

From the results of the partially deuterated analogs, the broad T_1 minimum in $(t\text{-BA})ClO_4$ is considered as resulting from at least four T_1 successively overlapped minima, two of which are attributed to CH_3 motions and the other two to NH_3^+ motions. Thus, T_1 of $(t\text{-BA})ClO_4$ can be written using a formula similar to Eq. 7, where both $T_1(t\text{-BA}d_3)$ and $T_1(t\text{-B}d_9\text{A})$ consist of two BBP equations as given by Eq. 8. Since it is difficult to fit this equation to the present data owing to too many adjustable parameters, we only evaluated the activation energy for the CH_3 and NH_3^+ reorientations from the slope of ln T_1 vs. T^{-1} plots below 150 K. In Fig. 3, the calculated T_1 curves using Eq. 7 by substituting the parameters obtained for (t-BAd_3)ClO$_4$ and (t-Bd_9A)ClO$_4$ are shown. The agreement between the experimental and calculated T_1 is satisfactory.

It is interesting to compare the activation energies for the CH$_3$ and NH$_3^+$ groups in phase II′ with those in phase III. Table 2 shows that the activation energies of the CH$_3$ groups in the metastable phase (phase II′) are higher than that in the stable phase (phase III), whereas those of NH$_3^+$ are lower in phase II′ than in phase III. The same relation of the activation energies between metastable and stable phases is found in t-BA nitrate, where three solid phases (one stable and two metastable) exist below 254 K, between 95 and 350 K, and below 235 K, respectively.[13)]

Intermediate Phase(II). The T_1 increase of (t-Bd_9A)-ClO$_4$ with temperature in phase II is attributed to the NH$_3^+$ reorientation, the activation energy of which evaluated from the slope of T_1 curve is smaller than that in phase III. Since no discontinuous change in T_1 of (t-Bd_9A)ClO$_4$ was observed at T_{tr}(III→II) determined by DTA, the reorientation of the NH$_3^+$ group is little affected at this transition.

On the other hand, (t-BAd_3)ClO$_4$ showed a sudden increase of T_1 at T_{tr}(III→II), above which temperature this salt yielded a T_1 maximum and a minimum at 32 MHz; measurements at 8.5 MHz gave only a minimum in phase II. From these results, we can expect the presence of the following two kinds of cationic motions which contribute to in T_1 in this phase of (t-BAd_3)ClO$_4$: 1) the motion assignable to the T_1 minima observed at 32 and 8.5 MHz, and 2) the other contributing to T_1 at 32 MHz, mainly in the low-temperature range of the T_1 maximum. Referring to the M_2 results, both of these motions can be regarded as the t-butyl reorientation, since the CH$_3$ group motion is considered to be too frequent to affect T_1 in this phase as predicted from the T_1 results in phase III. This means that there exist two kinds of t-butyl groups, or two kinds of cations; the T_1 minimum can be attributed to one of the two kinds of t-butyl groups and the T_1 decrease observed in the high-temperature side of the maximum to the motion of the other. This interpretation is supported by the fact that the minimum value of 28 ms observed at 8.5 MHz in this phase is almost twice as large as that of 15 ms in phase III; this minimum was assigned to the motions of all t-butyl groups in the crystal.

When the motion of one of the t-butyl groups contributing to T_1 at the high temperature range in phase II is sufficiently fast to allow the narrowing limit $\omega\tau_f \ll 1$, where τ_f is the correlation time for this motion, T_1 can be expressed by modifying the Eq. 8 as

$$T_1^{-1} = C_s f(\tau_s) + 5C_f\tau_f. \qquad (9)$$

Here, τ_s, C_s, and C_f are the correlation time for the motion yielding the T_1 minimum, the motional constant for this motion, and that for the fast motion, respectively. Assuming an Arrhenius relationship, like that given by Eq. 4, for the two motions, we calculated the motional parameters for (t-BAd_3)ClO$_4$ listed in Table 2 by fitting Eqs. 4 and 9 to the observed T_1 data. It is interesting to note that at T_{tr}(III→II) the cations considered to be equivalent in phase III become nonequivalent and that the C_3' reorientation of half the t-butyl groups is slowed down while the other half is accelerated. Further, the cations in phase II seem to be disordered statically rather than dynamically. Even if the cations are dynamically disordered, the jumping rate between the disordered sites of the cations is much slower than the ^{1}H NMR frequency.

The T_1 minimum of (t-BA)ClO$_4$ can be assigned to the reorientation of one of the two kinds of t-butyl groups in accordance with the results regarding its partially deuterated analogs. T_1 in the high-temperature side of the T_1 maximum observed at 32 MHz is attributable to the reorientations of the other t-butyl group and the NH$_3^+$ group. Parameters for these motions were obtained by a fitting calculation using an equation such as that given by Eq. 9.

High-Temperature Phase (I). At T_{tr}(II→I), T_1 of all salts increased discontinuously. Since no marked change in M_2 was observed around this temperature, the discontinuous increase of T_1 is ascribable to sudden decreases in the correlation times of the NH$_3^+$ and t-butyl groups. In phase I of (t-BA)ClO$_4$ and (t-BAd_3)ClO$_4$, the t-butyl motion is considered to be a dominant relaxation process. The activation energies for this motion in both salts were estimated as 17.3 kJ mol^{-1} from the slope of the ln T_1 *vs.* T^{-1} curves. This value is quite small as compared with that in t-BA halides, indicating that the cation is loosely packed in this phase.

T_1 of (t-Bd_9A)ClO$_4$ in phase I is very long and decreases with increasing temperature. This implies that the motion of the NH$_3^+$ group is too fast to have any discernible influence on T_1, and that another relaxation process is dominant in this region. Since no marked frequency dependence of T_1 was observed, one of the possible processes is a spin-rotation interaction[24,27—29)] due to rapid rotation of the NH$_3^+$ group.

It is somewhat surprising that the onset of the isotropic rotation of the cation is hindered even in the highest-temperature phase, although the t-BA$^+$ cations packed with globular ClO$_4^-$ anions are expected to be easily rotatable due to their sphere-like shape. In the highest-temperature phase of (t-BA)NO$_3$ crystals involving non-spherical anions, on the contrary, the cations are revealed to perform isotropic rotation and translational self-diffusion.[13)]

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23) This activation energy for the NH_3^+ reorientation evaluated from the T_1 data of (t-BA)I and (t-BAd_3)I by Ratcliffe and Dunell¹⁰⁾ is considered to be underestimated because it is difficult to evaluate accurately the activation energy from overlapped T_1 minima due to the t-butyl and NH_3^+ reorientations as tried by these authors. A discussion about this was made in our previous paper(12) where the E_a values for the NH_3^+ group in t-butylammonium chloride and bromide were determined directly from the T_1 data of (t-Bd_9A)Cl and (t-Bd_9A)Br.

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