An ^{1}H NMR Study on the Cationic Motion in Solid tert-Butylammonium Chloride and Bromide

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The ^{1}H spin-lattice relaxation time (T_1) in solid $(CD_3)_3CNH_3Cl$ and $(CD_3)_3CNH_3Br$ was measured above room temperature and the motional parameters for the reorientation of the NH_3^+ groups were determined. The ^{1}H NMR absorptions measured in the same temperature range for $(CH_3)_3CNH_3Cl$ and $(CH_3)_3CNH_3Br$ indicate the presence of superimposed several cationic motions commonly taking place in both compounds. From X-ray powder patterns taken at room temperature, the bromide was found to be isomorphous with the chloride.

1. Introduction

tert-Butylammonium chloride has been reported to form orthorhombic crystals belonging to the space group Pbca with $a = 17.770$, $b = 8.877$, and $c = 8.647$ Å, and $Z = 8$ at 115 K [1]. Reorientational motions of the cations in the crystals of tert-butylammonium chloride, bromide and iodide have been studied by Ratcliffe and Dunell using ^{1}H NMR techniques [2]. They have shown the occurrence of complex cationic motions consisting of C_3 reorientations of the CH_3 and NH_3^+ groups in the cation and the C_3' reorientation of the tert-butyl group in the temperature range from ca. 100 to 500 K. Motional parameters for these cationic reorientations were evaluated by analysing the ^{1}H spin-lattice relaxation times (T_1), especially the barrier to the NH_3^+ reorientation was carefully estimated by these authors. However, the parameters for this motion, indirectly derived from the data of fully protonated and partly deuterated (ND_3) salts, are less reliable than those for the other motions because the observed T_1 minima due to the tert-butyl and the NH_3^+ reorientations overlap. For the bromide, temperature dependence studies of the ^{1}H NMR second moment (M_2), T_1, and the spin-lattice relaxation time in the rotating frame ($T_{1\varrho}$) have also been reported by Konieczka and Pajak [3].

In the present investigation, we intend to measure the temperature dependence of ^{1}H T_1 for partly deuterated salts, $(CD_3)_3CNH_3Cl$ and $(CD_3)_3CNH_3Br$ in order to accurately determine the motional parameters for the reorientation of the NH_3^+ group. Measurements of M_2 of ^{1}H NMR absorptions are also carried out for $(CH_3)_3CNH_3Cl$ and $(CH_3)_3CNH_3Br$ above room temperature to confirm the existence of the complex cationic motions reported. X-ray powder diffraction patterns have been taken for $(CH_3)_3CNH_3Br$ at room temperature.

2. Experiments

$(CH_3)_3CNH_3Cl$ and $(CH_3)_3CNH_3Br$ were prepared by neutralization of tert-butylamine with hydrochloric and hydrobromic acid, respectively. The crystals were recrystallized twice from methanol. The partly deuterated salts were prepared in a similar manner using $(CD_3)_3CNH_2$ purchased from MSD Isotopes. Wide-line ^{1}H NMR measurements were performed at 40 MHz with a JEOL JNM-MW-40S spectrometer. Proton spin-lattice relaxation times were measured at

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18 and 32 MHz for the chloride and the bromide, respectively, employing a 180°–τ–90° pulse sequence by use of a pulsed spectrometer described elsewhere [4]. X-ray powder patterns were taken by means of an X-ray diffractometer from Rigaku Denki Co. equipped with a copper anticathode.

3. Results and Discussion

The powder X-ray diffraction angles (2θ) obtained at ca. 295 K for $(CH_3)_3CNH_3Br$ are shown in Table 1. The powder patterns of $(CH_3)_3CNH_3Cl$ were also recorded at the same temperature for comparison. The diffraction patterns of both salts indicate that their crystals are isomorphous. The observed diffraction angles could be well interpreted as resulting from an orthorhombic structure with lattice constants of $a = 18.31$, $b = 9.18$, and $c = 9.00$ Å.

The proton M_2 measurements for $(CH_3)_3CNH_3Cl$ and $(CH_3)_3CNH_3Br$ in the temperature range 330–420 K provided an almost constant value 3.5 ± 0.3 G^2 for both salts. This value is very close to the theoretical M_2 of 3.84 G^2 [3, 5] calculated by assuming that the cations perform rapid C_3 reorientations of the CH_3 and NH_3^+ groups as well as C_3' reorientation of the tert-butyl group. This assignment is consistent with the results obtained from the ^1H T_1 and $T_{1\varrho}$ data [2, 3], but inconsistent with the M_2 studies by Konieczka and Pajak [3]. These authors observed M_2 values less than 1.8 G^2 above 223 K for the bromide and assigned them to quasi-isotropic overall reorientation of the cation about its center of gravity. However, no T_1 minimum corresponding to this motion was detected in the present study and also in their T_1 and $T_{1\varrho}$ measurements.

The temperature variations of ^1H T_1 observed for $(CD_3)_3CNH_3Cl$ and $(CD_3)_3CNH_3Br$ are shown in Figs. 1 and 2, respectively. ^1H T_1 in $(CD_3)_3CNH_3Cl$ determined at 18 MHz and in $(CD_3)_3CNH_3Br$ at 32 MHz yielded a minimum of 8.5 ms at 437 K and 14.5 ms at 415 K, respectively. Both minima are attributed to the C_3 reorientation of the NH_3^+ group in the cation. This is because this NH_3^+ motion gives rise to theoretical T_1 minima of 7.6 and 13.6 ms for Larmor frequencies of 18 and 32 MHz, respectively [2]. On the high-temperature side of each T_1 minimum, both salts showed somewhat non-exponential behavior of the free-induction decay signals plotted against the time interval between 180° and 90° pulses.

Table 1. Comparisons between calculated and observed 2θ values for $(CH_3)_3CNH_3Br$ at ca. 295 K ($a = 18.31$, $b = 9.18$, $c = 9.00$ Å).

h k l	Calc.	Obs.	Relative int.
2 0 0	9.66	9.67	80
2 1 0	13.66	13.66	15
1 1 1	14.61	14.62	8
0 2 0	19.34	19.38	100
4 0 0	19.39		
0 0 2	19.73	19.72	20
3 1 1	20.06	20.06	15
1 0 2	20.32	20.32	10
2 2 0	21.66	21.68	30
4 1 0	21.69		
2 0 2	22.01	22.00	8
1 2 1	22.28	22.28	10
2 2 1	23.83	23.85	60
4 1 1	23.87		
2 1 2	24.07	24.08	10
3 1 2	26.45	26.45	10
4 2 0	27.52	27.51	5
0 2 2	27.76	27.76	5
4 0 2	27.80	27.81	8
5 1 1	28.04	28.04	15
6 0 0	29.26	29.27	60
2 2 2	29.46	29.47	10
2 3 0	30.81	30.82	20
3 2 2	31.46	31.48	10
5 0 2	31.50		
1 1 3	31.76	31.77	10
6 1 1	32.48	32.47	2
5 2 1	32.83	32.81	2
3 1 3	34.72	34.73	20
4 3 0	35.28	35.27	15
6 0 2	35.54	35.53	10
1 2 3	36.10	36.09	10
4 3 1	36.71	36.72	15
2 3 2	36.85	36.84	10
3 3 2	38.51	38.51	5
3 2 3	38.77	38.78	2
8 0 0	39.37	39.36	15

The experimental T_1 values shown in the figures were evaluated from the initial linear portion of the logarithmic plots of the recovery of the magnetization.

Since the cations in the crystals are equivalent [1], the observed T_1 curves can be analyzed by a single BPP equation [6]:

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

where C, τ, and ω denote the motional constant for the NH_3^+ motion, the correlation time of the motion, and the angular resonance frequency, respectively. For an NH_3^+ group, when regarded as an isolated three-spin system, C is given by

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

where γ and r stand for the gyromagnetic ratio of a proton and the interproton distance in a NH_3^+ group,

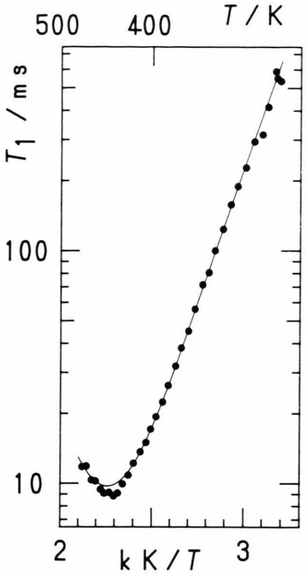

Fig. 1. Temperature dependence of ^{1}H T_1 observed at 18 MHz for $(CD_3)_3CNH_3Cl$. The best-fitted theoretical curve is shown by the solid line.

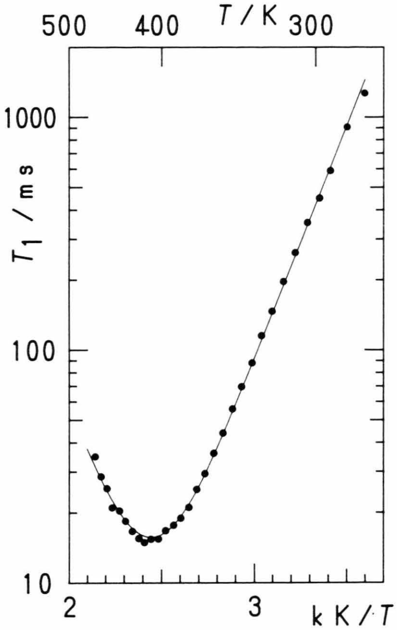

Fig. 2. Temperature dependence of ^{1}H T_1 observed at 32 MHz for $(CD_3)_3CNH_3Br$. The best-fitted theoretical curve is shown by the solid line.

Table 2. Motional parameters for the C_3 reorientation of the NH_3^+ group in tert-butylammonium ions; activation energies E_a, correlation times τ_0 at the limit of infinite temperature, and motional constants C in $(CD_3)_3CNH_3Cl$ and $(CD_3)_3CNH_3Br$ crystals.

	E_a/kJ mol^{-1}	$\tau_0/10^{-14}$ s	$C/10^9$ s^{-2}
$(CD_3)_3CNH_3Cl$	44.2 ± 0.4	3.4 ± 0.4	8.5 ± 0.2
$(CD_3)_3CNH_3Br$	38.5 ± 0.3	3.7 ± 0.3	9.0 ± 0.2

respectively. The correlation time can be related to the activation energy E_a for the motion by assuming an Arrhenius-type relationship

$$\tau = \tau_0 \exp(E_a/RT)\,. \tag{3}$$

The motional parameters E_a, τ_0, and C were obtained by a least-squares fitting of (1) and (3) to the observed T_1 data. The results are shown in Table 2.

Considerably large activation energies of 44.2 and 38.5 kJ mol^{-1} were determined for the chloride and the bromide, respectively. These values are larger than 38.9 and 32.6 kJ mol^{-1} reported for the reorientation of bulky tert-butyl groups in $(CH_3)_3CND_3Cl$ and $(CH_3)_3CND_3Br$, respectively [2]. This result indicates that strong hydrogen bonds N−H−X (X=Cl, Br) exist in the salts. Ratcliffe and Dunell calculated the activation energies for the NH_3^+ reorientation from the T_1 data of $(CH_3)_3CNH_3X$ and $(CH_3)_3CND_3X$ (X=Cl, Br, I) by considering that the observed T_1 can be expressed by the sum of BPP equations originating from NH_3^+ and tert-butyl reorientations. The estimated values of 37.5 and 33.2 kJ mol^{-1} for the chloride and bromide, respectively, in their study are smaller than those in the present study. This discrepancy indicates the difficulty in separating the NH_3^+ contribution to T_1 from the experimental T_1 in the fully protonated salts when the T_1 minima due to the NH_3^+ and tert-butyl reorientations overlap.

It is noteworthy that the motional constants C of the NH_3^+ reorientation given in Table 2 are smaller than 11.99×10^9 s^{-2} calculated according to (2) using $r = 1.666$ Å, where we assume the N−H distance and HNH angle to be 1.020 Å and tetrahedral, respectively. This implies that the dipolar interaction associated with the C_3 reorientation of the NH_3^+ group is partly averaged out at lower temperatures by some other motional modes. A large-amplitude libration of the cation can be thought as one of possible motional modes [7]. This is supported by the fact that a large internal torsional motion about the $C-NH_3^+$ bond has been found by the X-ray diffraction study on the chloride [1].

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