Molecular Motion in Solid Tetrapropylammonium Bromide and Iodide

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The proton NMR second moment and spin-lattice relaxation time for tetrapropylammonium bromide and iodide have been measured over a wide temperature range. A solid-solid phase transition related to the onset of cation tumbling was found for both salts and confirmed by DTA. In the low temperature phases methyl group reorientation was evidenced. For iodide a dynamic nonequivalence of the methyl groups and the onset of ethyl groups motion was also discovered.

Key words: NMR, Molecular motions, Phase transitions

Introduction

Investigations of the molecular motion in tetraalkylammonium salts using NMR technique revealed methyl group reorientations and cation tumbling in solid tetramethyl-, -ethyl- and -butylammonium compounds [1–12]. In this work we have examined the molecular reorientations of the tetrapropylammonium cation. The published data concerning the spin-lattice relaxation time for tetrapropylammonium iodide are incomplete [7]. Therefore we have undertaken a DTA and NMR study of M_2 and T_1 for tetrapropylammonium bromide [TPABr] and iodide [TPAI]. The main aim of this study was an analysis of the expected motions and a comparison of the motional behaviour of smaller and larger molecular cations.

Experimental

Polycrystalline samples of tetrapropylammonium bromide TPABr and iodide TPAI (puriss Fluka AG), recrystallized from anhydrous ethanol, were evacuated for several hours and sealed under vacuum in glass tubes. Using a home-made NMR spectrometer operating at a Larmor frequency of 28 MHz, proton broadline measurements were carried out. The second moments were calculated from the first derivatives of the absorption lines with an accuracy of about 10%.

The spin-lattice relaxation times of the ^{1}H resonance were measured at 38.2 MHz using a home-made pulse spectrometer. The temperature of the samples was stabilized to within 1 K by a gas-flow cryostat. Differential thermal analysis was made with a Derivatograph Unipan (typ DSC 605 M).

Results

a) Second Moment

The temperature dependences of M_2 of proton magnetic resonance lines for TPABr and TPAI are shown in Figure 1. For TPABr one observes a plateau of M_2 of about 19.0 G^2. At 378 K M_2 drops abruptly to 0.8 G^2. This value remains constant to 443 K (m.p. 553 K). Our DTA study shows a heat capacity transition at 381 K. For TPAI, M_2 decreases from a constant value of about 19.0 G^2 between 130 and 233 K to 10.6 G^2 at 333 K and then remains constant up to about 373 K, where it starts to decrease again. At about 411 K M_2 decreases abruptly to 0.6 G^2. This value remains constant to 473 K (m.p. 553 K). The DTA curve exhibits a heat capacity transition at 417 K.

b) Spin-Lattice Relaxation Times

The temperature dependences of T_1 are shown in Figure 2. For TPABr the V-shaped curve shows a sharp minimum of 47 ms at 154 K. At about 378 K a considerable jump to lower values of T_1 takes place. Above 378 K one observes linear increase of T_1. For TPAI the T_1 plot shows a minimum of 78 ms also at

Fig. 1. Temperature dependences of second moments for TPABr (o) and TPAI (●).
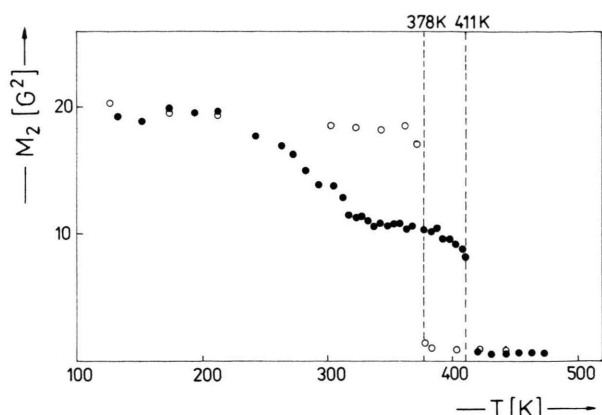

Fig. 2. Temperature dependences of spin-lattice relaxation times for TPABr (o) and TPAI (●).

about 154 K and a shoulder at lower temperature. Above room temperature T_1 starts to decrease sharply up to 410 K where it jumps to slightly lower value and thereafter increases linearly with temperature.

Discussion

a) Second Moment

The theoretical value of M_2 for a rigid lattice structure of a polycrystalline sample can be calculated using the Van Vleck formula [13]

$$M_2 = 358\,(1/N) \sum_{i,j} r_{ij}^{-6}, \qquad (1)$$

where N is the number of interacting protons and r_{ij} is the interproton distance. The rigid lattice value of M_2 for tetrapropylammonium ion is a sum of intra- and interionic contributions. The intraionic part of M_2 can be calculated as [14]

$$M_{2\,\text{intra}} = (2 \cdot 4/28)\,[M_2^{\text{I}}(\text{CH}_2) + M_2^{\text{II}}(\text{CH}_2)] \\ + (3 \cdot 4/28)\,M_2(\text{CH}_3), \qquad (2)$$

where $M_2^{\text{I}}(\text{CH}_2)$ includes the interaction of protons of the four CH_2 groups nearest to the nitrogen atom; $M_2^{\text{II}}(\text{CH}_2)$ describes the interaction of protons attached to the second carbon atom in the propyl chain and $M_2(\text{CH}_3)$ includes the interaction of protons of the four CH_3 groups. Calculation was performed assuming that the nitrogen atom is at the centre of a regular tetrahedron, the C–N–C and H–C–H angles are 109.47 °, the N–C bonds lengths 1.49 Å and the
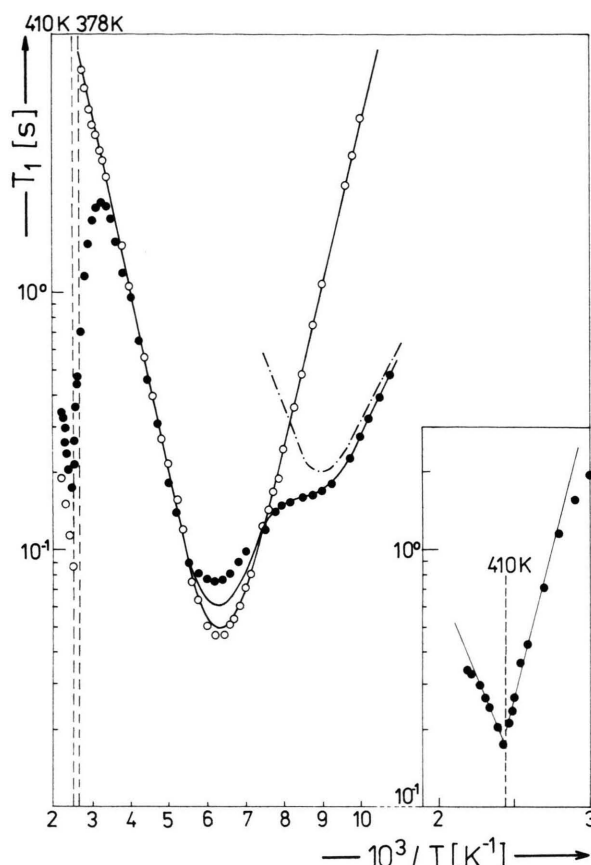
C–C and C–H bond lengths 1.54 Å and 1.09 Å, respectively. The interionic part $M_{2\,\text{inter}}$ of M_2 was estimated to be 1.0 G^2 only, like that assumed for tetraethyl- or tetrabutylammonium salts [9, 11, 12]. Thus, the total rigid lattice value of M_2 is at least 26.2 G^2 (Table 1). At low temperatures the experimental values of M_2 are much lower than the rigid-lattice values calculated for both halides. This means that the cations undergo reorientations which significantly reduce their second moments. Molecular reorientation reduces M_2 by a factor

$$\varrho = \tfrac{1}{4}\,(1 - 3\,\cos^2\theta)^2, \qquad (3)$$

where θ is the angle between the respective interproton vector and the axis of reorientation. The calculations of the reduced second moment were performed for models with consecutive onsets of reorientations of the one, two, three and four methyl groups about their

Table 1. The calculated second moment [G^2].

Type of reorientation	$M_{2\,intra}$	$M_{2\,inter}$	$M_{2\,total}$
Rigid structure	25.5	1.0	26.2
1 methyl group	23.3	1.0	24.3
2 methyl groups	21.6	1.0	22.6
3 methyl groups	19.9	0.8	20.7
4 methyl groups	18.1	0.8	18.9
4 ethyl groups	10.2	0.6	10.8
Cation tumbling	0	0.6	0.6

Table 2. The calculated minima of the relaxation times [ms].

Type of reorientation	$T_{1\,min}$
1 methyl group	202
2 methyl groups	101
3 methyl groups	67
4 methyl groups	50

Table 3. The best fitted activation parameters for C_3 methyl group reorientations.

Type of motion	TPABr		TPAI	
	E_a [kJ/mol]	τ_0 [s]	E_a [kJ/mol]	τ_0 [s]
Four CH$_3$	13.0	$1.1 \cdot 10^{-13}$		
One CH$_3$			7.5	$3.2 \cdot 10^{-13}$
Three CH$_3$			13.0	$1.5 \cdot 10^{-13}$

C_3 symmetry axes, ethyl groups reorientation and the cation reorientation around its centre of gravity. The obtained values of M_2 are given in Table 1.

The small interionic contribution depends only slightly on molecular reorientations, as in the hexamethyldisilane [15] and in tetraethyl- and tetrabutyl-ammonium salts [9, 11, 12]. Our calculated value of M_2 for the structure with reorientating four methyl groups is in good agreement with the observed low temperature plateaux of about 19 G^2 for both halides. For the case of superposed reorientations of the methyl and ethyl groups calculations performed (Table 1) give an M_2 reduced to about 11 G^2. In our experiment the plateau of this value is observed for TPAI, only. Using the Waugh-Fiedin expression [16], the activation energy for the ethyl groups reorientation was estimated as about 42 kJ/mol.

For TPABr one can mention a beginning of a next motion before 378 K, where a phase transition takes place.

The estimated activation energy for this motion (probably molecular tumbling) is about 59 kJ/mol.

For TPAI one can also observe an onset of the next motion (probably molecular tumbling) with an activation energy of about 60 kJ/mol. For the structure with the cation reorienting about its centre of gravity, the intraionic contribution to M_2 reduces to zero. The interionic part, calculated following Smith [17] agrees well with the experimental value, which lies below 1 G^2 for both investigated compounds and is typical for this kind of motion in regular structures. Thus it follows that in both halides one observes molecular tumbling of the cation in the high temperature phase.

b) Spin-Lattice Relaxation Times

The relaxation rate for four different molecular groups CH$_3$ of cation TPA can be expressed as [18]

$$\frac{1}{T_1} = \frac{3}{28} \sum_{i=1}^{4} n_i \frac{1}{T_{1i}}, \tag{4}$$

where n_i is the number of equivalent CH$_3$ groups,

$$\frac{1}{T_{1i}} = \frac{9}{20} \frac{\gamma^4 \hbar^2}{\omega_0 r^6} g(\omega_0, \tau_{ci}) \tag{5}$$

and

$$g(\omega_0, \tau_{ci}) = \frac{\omega_0 \tau_{ci}}{1 + \omega_0^2 \tau_{ci}^2} + \frac{4\omega_0 \tau_{ci}}{1 + 4\omega_0^2 \tau_{ci}^2}. \tag{6}$$

τ_{ci} is described by the Arrhenius equation

$$\tau_{ci} = \tau_{0i} \exp(E_{ai}/RT), \tag{7}$$

where τ_{0i} is an inverse frequency factor and E_{ai} the activation energy for reorientation.

The theoretically calculated value of $T_{1\,min}$ for a structure with four methyl groups reorienting about their C_3 symmetry axes (Table 2) is in very good agreement with the experimental value $T_1 = 47$ ms for TPABr. This means that in TPABr all four methyl groups are dynamically equivalent, in accordance with X-ray data [19]. The strikingly different behaviour of T_1 for TPAI points to a more complicated motion during the relaxation. In Fig. 2 we show T_1 values (dash-dotted line) calculated as difference in relaxation rates of the two halides. The obtained minimum of $T_1 = 200$ ms corresponds very well to the calculated value for only one methyl group reorienting in TPA cation. This means that in TPAI the methyl groups are not dynamically equivalent – our preliminary X-ray data show that the crystal structures of the two halides are different. The fittings of T_1 for two models: with equivalent (TPABr) and nonequivalent

(TPAI) CH_3 groups, are shown by solid lines in Figure 2. The best fitted activation parameters shown in Table 3 lie within the limits of the values characteristic for the ion motions considered [8]. Our measurements of M_2 corroborate the model of reorientation discussed. The rigid lattice second moment is visibly reduced by reorientation of all four methyl groups. The onset of the earlier reorientation of the one unequivalent methyl group in TPAI should be observed at about 50 K below our experimental conditions.

The higher temperature behaviour of T_1 in TPAI points clearly to the existence of another motional mechanism dominating relaxation. Since the relaxation dependence undergoes a discontinuity before reaching the second minimum (see insert in Fig. 2) it is not possible to obtain unambiguous information on the nature of its mechanism. It might consists in ethyl groups reorientation with an activation energy of about 42 kJ/mol, favoured by results of our second moment analysis. For high temperature phases of both halides the activation energy of molecular tumbling determined from the slope of T_1 vs. $1/T$ amounts to about 50 kJ/mol.

Summarizing, we found solid-solid phase transitions for both halides (at 378 K for the bromide and at 410 K for the iodide), similar to salts with smaller tetraethyl- or larger tetrabutylammonium cations. With increase of cation size the transition appears at lower temperatures. In both halides one observes molecular tumbling at higher temperatures with activation energies close to those observed for tetramethyl-, -ethyl- or -butylammonium salts [1–12]. This means that the size of cation does not affect markedly the potential hindering this motion. The activation energies for the reorientation of methyl groups are similar to those determined for tetraethyl- and tetrabutylammonium halides (13 kJ/mol) though the energies found for tetramethylammonium halides are about two times higher, due to evident steric hindrances in these cations.

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