Cation and Anion Reorientation at Phase Transition in Pyridinium Tetrafluoroborate

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Temperature dependences of ^{1}H and ^{19}F second moment and spin-lattice relaxation times for polycrystalline pyridinium tetrafluoroborate were measured. A phase transition was discovered at 202 K. A model of cation reorientation between inequivalent (low-temperature phase) and equivalent (high-temperature phase) equilibrium positions is proposed. Whether the anion reorients isotropically or about a symmetry axis cannot be decided. An analysis of cross-relaxation effects yielded activation parameters for cation and anion reorientation. The rotational correlation times for both ions converge just at the phase transition reaching the value of 10^{-10} s.

Key words: NMR, cross-relaxation, molecular motions, phase transitions

Introduction

In our studies of solid inter-ionic hydrogen bonded guanidinium salts by ^{1}H NMR methods we obtained information about the motion of the cation placed in various anion sublattices [1–4]. Making use of ^{1}H and ^{19}F NMR technique we also described the anion and cation motion for guanidinium tetrafluoroborate and hexafluorophosphate [3, 4]. In determining the Arrhenius activation parameters for cation and anion we discovered that the rotational correlation frequencies of both ions converge when approaching solid-liquid or solid-solid first-order phase transitions [5].

Pyridinium salts are also inter-ionic hydrogen bonded and reveal solid-solid phase transitions involving change in the cation dynamics [6, 7]. The pyridinium cation is particularly interesting because of its symmetry, planarity and aromatic character. What is more, inter-ionic hydrogen bonds can be easily formed between heteroatom and various proton donors.

For some pyridinium salts X-ray analysis revealed orientational disorder of the cation [8, 9]. Our ^{1}H NMR studies disclosed the dynamic character of this disorder [7]. In-plane 60° reorientational jumps about the pseudohexad axis overcome hindering barriers, the values of which reflect H-bonding effects.

We chose pyridinium tetrafluoroborate $C_5H_6NBF_4$ as a convenient compound for studying molecular dynamics of both ions by ^{1}H and ^{19}F NMR technique. The study was undertaken mainly to examine whether the coupling [5] of ion rotational frequencies exists in disordered crystals other than guanidinium salts.

Experimental and Results

Pyridinium tetrafluoroborate crystallizes in the trigonal space group $R\bar{3}m$, with $a = 5.626$ Å, $\alpha = 97.51°$ and $Z = 1$ [8]. The compound undergoes a phase transition at 202 K, but to our knowledge the low temperature crystal structure has not been described. The substance was obtained by allowing pyridine to react with tetrafluoroboric acid. After being thoroughly recrystallized it was used to prepare an NMR sample.

Measurements of the spin-lattice relaxation times T_1 were performed using a home-made pulse spectrometer operating at 60 MHz by a $\pi/2$-τ-$\pi/2$ pulse sequence or saturation method. The NMR second moment investigations were made with cw spectrometer operating at the Larmor frequency 28 MHz. The temperature of the sample (120–300 K) was controlled by means of a gas-flow cryostat and monitored with a Pt resistor to an accuracy of about 1 K.

The experimental results are shown in Figs. 1 and 2. The relaxation times T_1^{H} and T_1^{F} reach minima at 172 K ($T_1^{\mathrm{H}} = 166$ ms) and 182 K ($T_1^{\mathrm{F}} = 30$ ms). Both magnetization decays are nonexponential below the observed minima. In Fig. 1 only the main components

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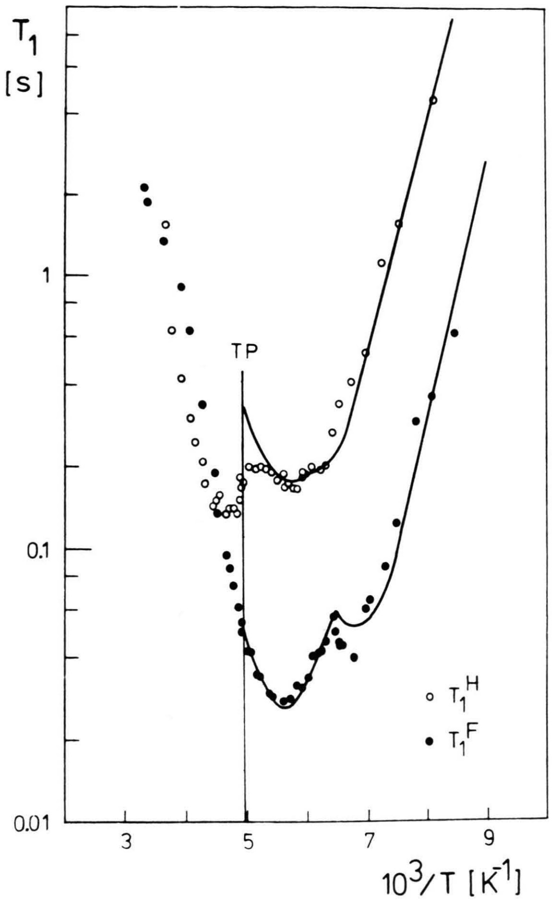

Fig. 1. Temperature dependence of spin-lattice relaxation time: T_1^H (○), T_1^F (●). Solid line: calculated.

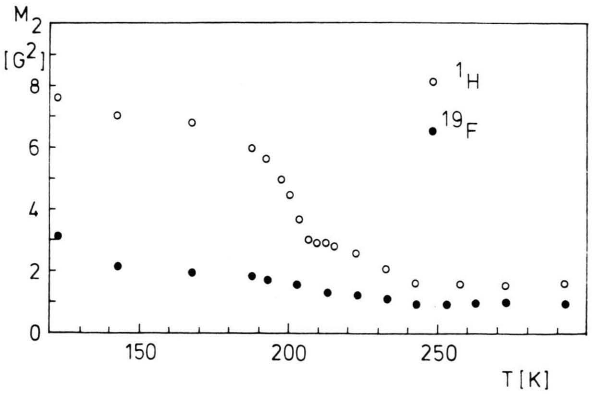

Fig. 2. Temperature dependence of proton (○) and fluorine (●) NMR second moment.

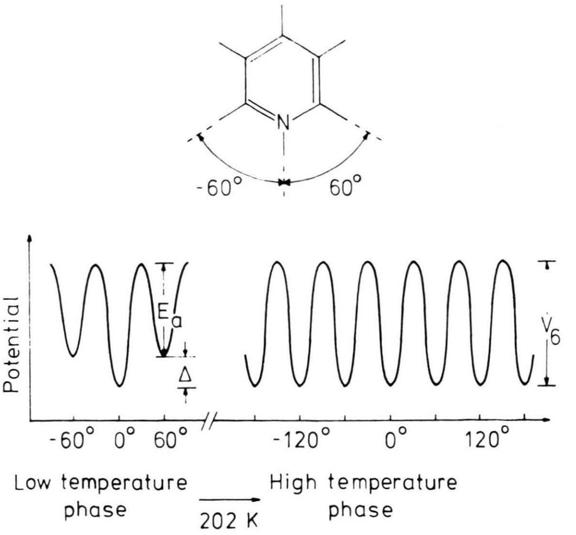

Fig. 3. The potential for reorientation of the pyridinium cation.

for the relaxation times are shown. At the transition point (202 K), T_1^H jumps from 200 to 130 ms while T_1^F shows a change in the slope. The second moment of 7.6 G^2, measured for protons at 123 K (Fig. 2), decreases at higher temperature to 3 G^2, observed immediately above the phase transition. Above 240 K the second moment reaches a plateau of 1.6 G^2. The fluorine second moment decreases gradually from 3.2 G^2 at 123 K to the plateau of 1.0 G^2, reached above 240 K.

Discussion

The temperature dependences of the second moment indicate that there are molecular reorientations of ions in both sublattices already in the low temperature phase.

Since the molecular structure of ions is not known, let us consider two models of ion motions in low temperature phase.

(1) reorientation of the pyridinium cation by 60° between inequivalent equilibrium positions (see Fig. 3) with simultaneous isotropic reorientation of BF_4 anion.

(2) reorientation of the pyridinium cation as above with simultaneous C_3 reorientation of BF_4 anion.

For isotropic anion reorientation (model (1)), agreement between experimental and calculated values of the T_1^F minimum can be obtained taking the distance

Table 1. Activation parameters for the motions considered.

	τ_0 [s]	E_a [kJ/mol]
Cation $C_5NH_6^+$	$1.5 \cdot 10^{-13}$	13.6
Anion BF_4^-	$7.1 \cdot 10^{-15}$	18.6

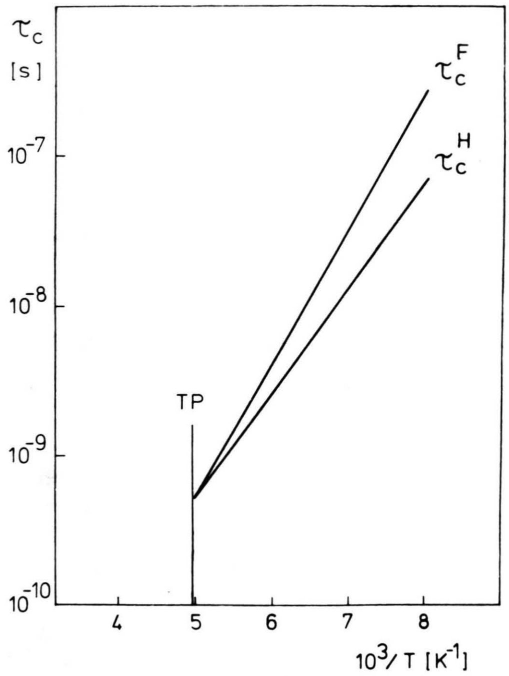

Fig. 4. Temperature dependence of rotational correlation times τ_c^H and τ_c^F for cation and anion, respectively.

B-F equal 1.43 Å, as in $LiBF_4$ [10]. The C_3 anion reorientation (model (2)) requires three distances B-F equal 1.36 Å and one equal 1.41 Å, as in guanidinium tetrafluoroborate [3].

To interpret the temperature dependences of the relaxation times we must consider all cross-relaxation effects in the ^1H,^{19}F,^{14}N,^{11}B and ^{10}B spin system. These interactions are important in the temperature ranges in which $\omega_H \pm \omega_F \approx 1/\tau$, $\omega_F \pm \omega_B \approx 1/\tau$ and $\omega_H \pm \omega_B \approx 1/\tau$*, where τ is the correlation time for the anion or the cation reorientation. Considering thus the dipolar interactions between three unlike spins we can present the time variations of the nuclear magnetization as

$$[\dot{M}] = [R]\,[M - M_0].$$

The total relaxation matrix $[R]$ is the sum of relaxation matrices connected with the cation reorientation $[R]_H$ described by τ_H and the anion reorientation $[R]_F$ described by τ_F. The dipolar diagonal relaxation rate is

$$R_{II} = \tfrac{2}{3}\gamma_I^2\, \Delta M_2\,(I-I)\, g_1(\omega_I, \tau) + \sum_j \tfrac{1}{2}\gamma_I^2\, \Delta M_2\,(S-I)\, g_2(\omega_I, \omega_{Sj}, \tau),$$

and off-diagonal relaxation rate is

$$R_{IS} = \frac{1}{2}\gamma_S^2\, \Delta M_2\,(S-I)\, \frac{N_S}{N_I}\, g_3(\omega_I, \omega_{Sj}, \tau)$$

with

$$g_1(\omega_I, \tau) = \tau/(1+\omega_I^2\tau^2) + 4\,\tau/(1+4\,\omega_I^2\,\tau),$$

$$g_2(\omega_I, \omega_{Sj}, \tau) = \tau/[1+(\omega_I-\omega_{Sj})^2\tau^2] + 3\,\tau/(1+\omega_I^2\tau^2) + 6\,\tau/[1+(\omega_I+\omega_{Sj})^2\tau^2],$$

$$g_3(\omega_I, \omega_{Sj}, \tau) = -\tau/[1+(\omega_I-\omega_{Sj})^2\tau^2] + 6\,\tau/[1+(\omega_I+\omega_{Sj})^2\tau^2].$$

One can calculate the respective elemens of the relaxation matrices if one knows the changes of the second moment connected with the onsets of the ion reorientations. The fitting of the eigenvalues of the relaxation matrix to the experimental points gives the same activation parameters for both models of reorientation (Table 1). The additional fitting constants are $\Delta M_2\,(H-F) = 0.8\ G^2$, and the relaxation constant $C_{H-H} = 7.474 \cdot 10^8\ s^{-2}$.

With this relaxation constant it was possible to estimate the difference between adjacent minima of the potential energy $\Delta = 3.1$ kJ/mol for the cation reorientation (see Fig. 3). The activation energy of 13.6 kJ/mol determined from T_1 experiments added to Δ gives $V_6' = 16.7$ kJ/mol, slightly smaller than 17.4 kJ/mol, the activation energy V_6 for C_6 reorientation of the investigated cation in the high temperature phase. The similar model for pyridinium cation reorientation between inequivalent minima has already been considered [11–14]. The role of the cation and anion reorientation in the structural phase transitions in more complicated systems of pyridinium hexachloro- and hexabromometallates has also been discussed [15–17].

The plot of the correlation times τ_c (accuracy ±10%) versus temperature (Fig. 4) shows that the correlation times for ions of both sublattices converge just at the phase transition, reaching a value of 10^{-10} s. This correlation time behaviour is the same as that observed recently for guanidinium salts [4, 5]. The effect seems to indicate the existence of a new kind

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* In first approximation, the H-N interaction as well as small quadrupolar contributions can be neglected. Interactions with low abundant spins of ^{10}B are included in the diagonal elements of the relaxation matrix.

of coupling in a disorded ionic crystal between the stochastic reorientation motions of cations and anions. This coupling maybe drives the phase transition in which a change in hydrogen bonding may play an essential role.

The dynamics of the guanidinium cation was investigated in some halides and tetrahalocomplexes [18–20]. Conclusions about reorientations of both ions were obtained for guanidinium tetrahalocomplexes [21].

Acknowledgements

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