Proton NMR Study of Molecular Dynamics in Hydrazinium Perchlorate

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Z. Naturforsch. **45a,** 102–106 (1990); received October 17, 1989

The proton spin-lattice relaxation time T_1 (at 5.4, 10 and 15 MHz) and second moment M_2 (at 9.8 MHz) have been measured in hydrazinium perchlorate ($N_2H_5ClO_4$). The temperature dependence of T_1 shows two minima. The low temperature T_1 minimum has been explained in terms of NH_3 reorientation about the N–N axis while the high temperature minimum is attributed to the exchange of protons within the NH_2 group (180° flip about the H–N–H bisectrix). The activation energies for NH_3 and NH_2 motions are found to be 20.5 kJ mol^{-1} and 39.8 kJ mol^{-1}, respectively. The second moment variation with temperature shows two transitions around 120 K and 210 K and has been discussed in terms of NH_3/NH_2 motions.

Key words: NMR study, Molecular dynamics, Hydrazinium perchlorate.

Introduction

Hydrazinium compounds are interesting from the point of view of studying molecular dynamics as they contain symmetric mobile groups like NH_3 and NH_2 as well as hydrogen bonding connecting the hydrazinium ions in zig-zag chains. NMR study of hydrazinium perchlorate ($N_2H_5ClO_4$) has been taken up to get information about the nature of the molecular motions and to observe phase transitions which may be present. We report here the results of our measurements on proton spin-lattice relaxation time T_1 at 5.4, 10 and 15 MHz and second moment M_2 at 9.8 MHz.

Hydrazinium perchlorate, $N_2H_5ClO_4$, is monoclinic (space group C 2/C) with 8 formula units in the unit cell [1]. The unit cell dimensions are $a = 14.417$ Å, $b = 5.389$ Å, $c = 12.797$ Å and $\beta = 113.09$. The crystal consists of $N_2H_5^+$ and ClO_4^- ions. The anion is composed of a central chlorine atom surrounded by four oxygen atoms arranged at the corners of a slightly distorted tetrahedron. The cation may be thought of as a bi-tetrahedron with the two nitrogen atoms acting as centers of regular tetrahedra which are joined together at a corner. The six remaining corners are occupied by five hydrogen atoms and a lone pair of electrons. The structure may be described as a spiral column of hydrazinium ions surrounded by six columns of anion tetrahedra. The axes of the columns are parallel to the *b* axis. The hydrogen atom of the NH_2 end bonds the hydrazinium ions together in a spiral chain. The three hydrogen atoms of NH_3 are engaged in bonding the anion tetrahedron to the hydrazinium spiral chain. The remaining hydrogen atoms do not appear to be involved in bonding. The structure of hydrazinium perchlorate along the *b* axis is shown in Figure 1.

Room temperature IR absorption and a DTA study [2] are reported. IR absorption shows a band at 960 cm^{-1} due to the N–N stretching. A weakly hydrogen bonded N–H stretching is observed at 330 cm^{-1} and 620 cm^{-1}. DTA shows a melting endotherm peaking at 406 K followed by a decomposition exotherm at 420 K.

Experimental

Hydrazinium perchlorate, $N_2H_5ClO_4$ is prepared by adding stoichiometric quantities of ammonium perchlorate and hydrazine hydrate [2]. Ammonia gas liberated is removed by a pump. The solution is kept in a desiccator and evacuated till crystallites are formed. The salt is recrystallized repeatedly from absolute alcohol. The sample is dried under vacuum in a desiccator over P_2O_5. The sample is kept in an oven at 100 °C for 5 hours to dehydrate it. Since the sample is hygroscopic it had to be handled in vacuum. The sample is finely ground and packed into the sample tube. The sample tube is evacuated and sealed.

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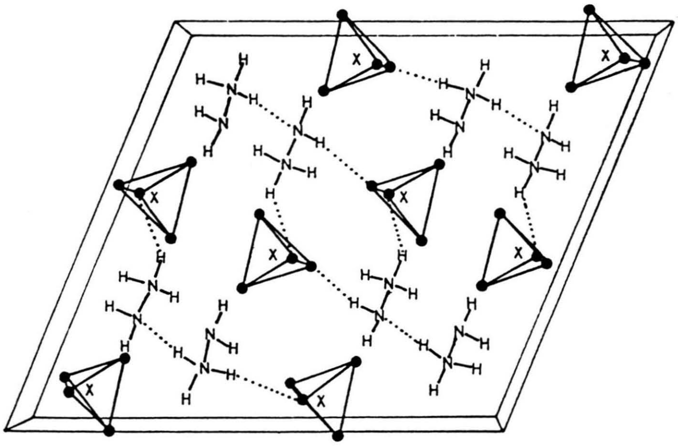

Fig. 1. A stereo view of hydrazinium perchlorate. The origin of the cell is at the lower rear right and the view is parallel to the *b* axis. The dotted lines represent the proposed hydrogen bond contacts. The symbol X represent the chlorine atom.

The proton spin-lattice relaxation time T_1 has been measured at 5.4, 10 and 15 MHz using a home made variable frequency pulsed NMR spectrometer. Inversion recovery pulse sequence was used for T_1 values upto 500 msec while saturation burst was used for T_1 above 500 msec. Proton NMR signals were recorded using a home made Pound-Knight-Watkins (PKW) type wide-line NMR spectrometer working at 9.8 MHz. Care was taken to avoid line saturation and modulation broadening. Second moments were calculated from experimental derivative curves.

Sample temperature in the range 100 K to 300 K was varied using a gas flow cryostat. The accuracy of the temperature control/measurement was better than ± 0.5 K.

Results and Discussion

1. Spin-Lattice Relaxation Time T_1

The temperature dependence of T_1 at 5.4, 10 and 15 MHz is shown in Figure 2. Two T_1 minima are observed.

According to the BPP theory [3], the spin-lattice relaxation rate due to dipole-dipole interaction within the NH_3 group modulated by the reorientation of NH_3 about the C_3 axis can be expressed as [4]

$$\frac{1}{T_1} = \frac{9}{20} \frac{\gamma^4 \hbar^2}{r^6} \left\{ \frac{\tau_c}{1+\omega^2 \tau_c^2} + \frac{4\tau_c}{1+4\omega^2 \tau_c^2} \right\}, \quad (1)$$

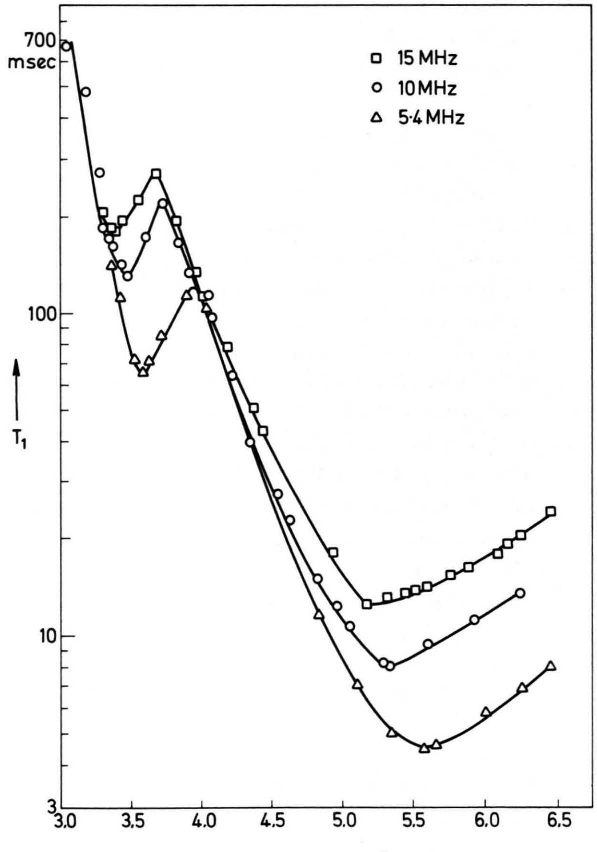

Fig. 2. T_1 versus $1000/T$ for polycrystalline $N_2H_5ClO_4$.

where

$$\tau_c = \tau_{c0} \exp(E_a/kT) . \tag{2}$$

In many hydrazinium compounds only the NH_3 group is effective in relaxation through its reorientation and the NH_2 protons are also relaxed by the NH_3 group through spin-diffusion [5]. This process has been observed in a number of hydrazinium compounds and amino acids [6–8].

The spin-lattice relaxation rate due to NH_3 reorientation including spin diffusion (to relax the NH_2 group) is given by [9]

$$\frac{1}{T_1} = \frac{3}{5}\left(\frac{1}{T_1}\right)_{NH_3} , \tag{3}$$

where $(1/T_1)_{NH_3}$ is the relaxation rate due to the reorienting NH_3 group if it has to relax its own protons.

Equations (1) to (3) describe the relaxation process. The calculated $T_{1\min}$* due to NH_3 reorientation including spin-diffusion varies from 7.2 to 10.7 msec at 15 MHz for the interproton distance ranging from 1.59 to 1.71 Å. This value is slightly smaller than the experimental one of 12.5 msec. Such discrepancies between the theoretical and experimental values are known in the literature [10–12]. Equation (1) is based only on proton-proton dipolar interactions within the NH_3 group. It does not account for the proton-nitrogen interactions or the torsional oscillations of the NH_3 group. Ratcliffe et al. [11] have shown that the inclusion of proton-nitrogen interactions may lower the calculated T_1 at the minimum by about 15%. On the other hand, Johnson [13] has shown for the CH_3 group that torsional oscillations may increase T_1 at the minimum by 14 to 22%. Kumar and Johnson [14] have shown that this leads to a smaller slope of $\ln T_1$ versus T^{-1} plots on the low temperature side than on the high temperature side of the T_1 minimum. Thus the discrepancy between the theoretical and experimental values of T_1 at the minimum and the presence of different slopes on either side of the T_1 minimum may be due to torsional oscillations.

A least squares fitting of the observed values of T_1 to the BPP model gives $C = 8.8 \times 10^9$, $\tau_{c0} = 3.6 \times 10^{-14}$ sec and $E_a = 20.5$ kJ mol^{-1}.

A value of 8.6×10^9 has been calculated for C from T_1 at the minimum. The reduction in second moment ΔM_2 (assumed to be due to the same NH_3 reorientation) calculated from the value of C is found to be 18.0 G^2, which is close to the value of 20 G^2 observed for NH_3 reorientation in hydrazinium compounds [10, 13–15].

The high temperature T_1 minimum may be interpreted as due to $-NH_2$ group reorientation about the N–N axis. A similar high temperature T_1 minimum has been observed in $LiN_2H_5SO_4$ [15] (attributed to $-NH_2$ reorientation). Also a high temperature $T_{1\varrho}$ minimum due to $-NH_2$ motion has been observed in $N_2H_5NO_3$ [10], $N_2H_5HC_2O_4$ [12] and $(N_2H_5)_2C_2O_4$ [12].

There are two possibilities for the $-NH_2$ reorientation: reorientation about the N–N direction and 180° flips about the H–N–H bisectrix. For reorientation of NH_2 about the N–N axis, the calculated T_1 at the minimum [11] is of the same order as that for NH_3. But the observed high temperature T_1 at the minimum is much higher (nearly by a factor of 20). It appears therefore that the high temperature T_1 minimum is most likely due to exchange of the protons within the NH_2 group (180° flips about the H–N–H bisectrix). This is suggested by the fact that the maximum relaxation rate due to this process is much smaller (factor of 10) than the maximum in the relaxation rate resulting from $-NH_3$ reorientation [15]. NH_2 flips have a relatively small effect on the relaxation rate because only intergroup interactions with neighboring NH_2 groups and with the $-NH_3$ part of the molecule are operative. These interactions involve relatively large interproton distances. A similar T_1 minimum observed in $LiN_2H_5SO_4$ [15] has also been attributed to this motion.

T_1 at the minimum calculated (using the O'Reilly result [16]) for NH_2 motion is 180 msec, which is in good agreement with the experimental value of 181.4 msec at 15 MHz. For NH_2 motion, a relaxation constant of 8.4×10^8 has been calculated from the observed T_1 minimum. The best fit activation energy, pre-exponential factor and relaxation constant are 39.8 kJ mol^{-1}, 5.5×10^{-15} sec and 8.5×10^8 respectively. The activation energy obtained for NH_2 reorientation in $N_2H_5ClO_4$ is slightly smaller than those obtained in other hydrazinium compounds viz., 46 kJ mol^{-1} for $N_2H_5HC_2O_4$ [12], 43.5 kJ mol^{-1} for $(N_2H_5)_2C_2O_4$ [12] and 44.8 kJ mol^{-1} for $LiN_2H_5SO_4$ [15], but it is comparable with $E_a = 39.3$ kJ mol^{-1} in $N_2H_5NO_3$ [16].

The experimental T_1 plot shows a slight frequency dependence on the high temperature side of the NH_3

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* $T_{1\min} = T_1$ at the minimum.

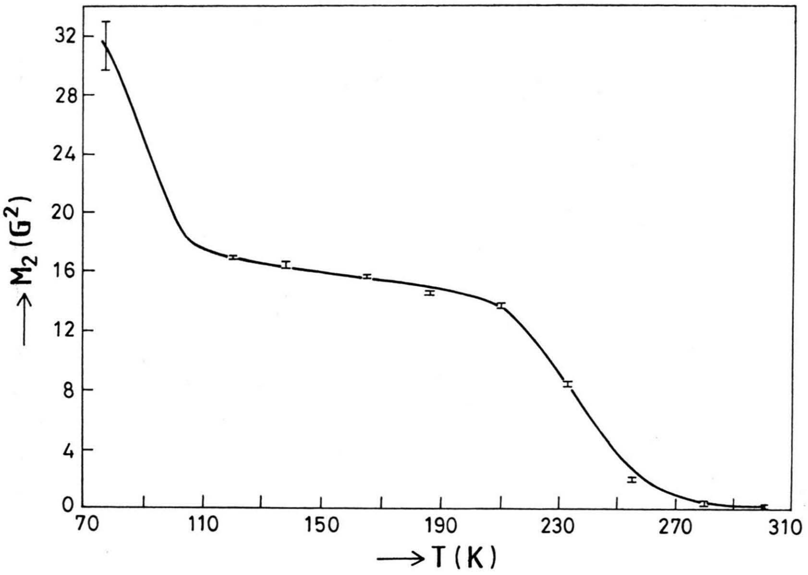

Fig. 3. Second moment versus temperature for $N_2H_5ClO_4$.

minimum but from the BPP expression (which is valid for a single type of motion) no such frequency dispersion is to be expected. The experimental T_1 behaviour in the temperature range 150–200 K may be attributed to NH_3 reorientation and in the high temperature range (250–330 K) to NH_2 motion. In the temperature range between the T_1 minima (250–200 K) both NH_3 and NH_2 motions are operative, the frequency dependent T_1 due to NH_2 being superimposed on the frequency independent T_1 due to NH_3. Consequently a slight frequency dependence is observed. This has been checked by computer simulation of the BPP expression in the presence of the NH_3 and NH_2 motions separately and also in the presence of both motions. If only one type of motion is present, the T_1 plot is frequency independent on the high temperature side but when both motions are taken into account, the curve shows a frequency dependence, as observed in our experiments.

From the knowledge of the temperatures at which the T_1 minima are observed for two Larmor frequencies, the activation energy of the reorienting group can be calculated. The low temperature T_1 minimum is observed at 193 K, 188 K and 179 K for 15, 10 and 5.4 MHz, respectively. The average activation energy calculated using two frequencies at a time is 21.8 kJ mol^{-1}, which is in good agreement with that obtained by computer fitting the data at a single Larmor frequency as a function of temperature. For the high temperature minimum the average activation energy is 39.8 kJ mol^{-1}, which is in good agreement with the best fit value.

2. *Second Moment M_2*

The proton NMR signal at room temperature is narrow with a peak-to-peak line width of 0.5 G. As the sample is cooled, the peak-peak intensity decreases with increase in line width and second moment. At 77 K, the signal has a peak-to-peak line width of 8.9 G.

The temperature dependence of experimental second moment is shown in Figure 3. The room temperature second moment is 0.27 ± 0.02 G^2. As the sample is cooled, the second moment increases gradually and around 250 K a second moment transition occurs. In the range 210 to 120 K, the second moment is almost constant giving a broad plateau region. Below 120 K, another transition in M_2 occurs, and at 77 K, $N_2H_5ClO_4$ has a second moment of 31.3 ± 1.7 G^2.

A rigid NH_2–NH_3 ion has a second moment of 40.2 G^2 [17]. For a rotating NH_3 and a rigid NH_2, the calculated second moment is 17 G^2 [17]. If NH_2 is also reorienting about the N–N bond, this would lower the second moment by 8 G^2 [17]. Even at 77 K, the second moment in $N_2H_5ClO_4$ has not reached the rigid lattice value of 40 G^2. However, the drop in the second moment from 77 K to 120 K is most likely due to the onset of NH_3 reorientation about the 3-fold axis. Above 210 K, the decrease in M_2 may be attributed to the onset of NH_2 motion about the N–N bond. The low value of the second moment near room temperature indicates reorientation of the hydrazinium ion as a whole as well as diffusion. Such a low value of the second moment ($<1\ G^2$) has been observed in $LiN_2H_5SO_4$ around 480 K [18], which has been interpreted as due to the tumbling and diffusion of the hydrazinium ions.

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