Proton NMR Study of Molecular Dynamics in Hydrazinium Perchlorate

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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 $NH_3$ group ($180^\circ$ 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 $NH_2NH_3$ 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 C2/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 $\beta = 113.09^\circ$. 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.
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]

$$
\frac{1}{T_1} = \frac{9}{20} \gamma^2 h^2 \left\{ \frac{\tau_{c}}{1 + \omega^2 \tau_{c}^2} + \frac{4 \tau_{c}}{1 + 4 \omega^2 \tau_{c}^2} \right\}, \quad (1)
$$

![Fig. 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.](image)

![Fig. 2. $T_1$ versus 1000/T for polycrystalline N$_2$H$_5$ClO$_4$.](image)
where
\[ \tau_e = \tau_{e0} \exp\left(\frac{E_a}{kT}\right). \] (2)

In many hydrazinium compounds only the NH₃ group is effective in relaxation through its reorientation and the NH₂ protons are also relaxed by the NH₃ 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 NH₃ reorientation including spin diffusion (to relax the NH₂ group) is given by [9]
\[ \frac{1}{T_1} = \frac{3}{5} \left( \frac{1}{T_{1\text{NH}_3}} \right), \] (3)
where \( (1/T_1)_{\text{NH}_3} \) is the relaxation rate due to the reorienting NH₃ group if it has to relax its own protons.

Equations (1) to (3) describe the relaxation process. The calculated \( T_{1\text{min}} \) due to NH₃ 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 NH₃ group. It does not account for the proton-nitrogen interactions or the torsional oscillations of the NH₃ 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 CH₃ 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 \( C = 8.8 \times 10^9, \tau_{e0} = 3.6 \times 10^{-14} \) sec and \( E_a = 20.5 \) kJ mol⁻¹.

A value of \( 8.6 \times 10^9 \) has been calculated for \( C \) from \( T_1 \) at the minimum. The reduction in second moment \( \Delta M_2 \) (assumed to be due to the same NH₃ reorienta-

\* \( T_{1\text{min}} = T_1 \) at the minimum.
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 $0.27 \pm 0.02$ 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$_2$H$_5$ClO$_4$ has a second moment of $31.3 \pm 1.7$ G$^2$.

A rigid NH$_3$–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$_2$H$_5$ClO$_4$ 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 attrib-
uted 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$_2$H$_5$SO$_4$ around 480 K [18], which has been interpreted as due to the tumbling and diffusion of the hydrazinium ions.