

# Molecular Dynamics in Tetramethyl Ammonium Hexabromo Selenate $[N(CH_3)_4]_2SeBr_6$ . A Proton NMR Study

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$^1H$  spin-lattice relaxation time  $T_1$  and second moment  $M_2$  have been studied as a function of temperature over the temperature range 445 to 77 K. A discontinuous change in  $T_1$  at 365 K, indicates the presence of a phase transition, while the slope change at 152 K, is attributed to a change in the TMA ion dynamics from tumbling to torsion. The  $T_1$  results could be explained in terms of inequivalent TMA ions and their small angle torsional oscillations. A second moment ( $M_2$ ) transition occurs around 160 K and is ascribed to the freezing of TMA tumbling and  $CH_3$  reorientation.

**Key words:** Molecular dynamics; Second moment; NMR; Spin-lattice relaxation time.

## Introduction

Tetramethyl ammonium (TMA) ion dynamics in salts has been investigated, using  $^1H$  NMR, by many workers [1–3]. Generally, the activation energy for the motion of the cation was found to be smaller in  $(TMA)MX_3$ ,  $(TMA)_2MX_4$  and  $(TMA)_2MX_6$  type complexes than in simple salts. In  $(TMA)_2MCl_6$  ( $M = Pt, Sn, Te, Zr, U$ ) phase transitions have been found around 350 K and 150 K [4, 5–7, 8–10]. We have now investigated  $^1H$  NMR in  $(TMA)_2SeBr_6$  and report on the results here.

The compound was prepared following the procedure of Gütbier and Engeroff [11] and was checked by x-ray diffraction [8–10], melting temperature, specific gravity [12], IR frequencies [13] and elemental analysis. The proton  $T_1$  measurements were carried out using a home built pulsed NMR spectrometer working at 10 MHz. The second moments were calculated from the Fourier transformed FID signals. The temperature of the sample was varied using a gas flow cryostat.

## Results and Discussion

Tetramethyl ammonium ion, being tetrahedral, has 3 two-fold and 4 three-fold symmetry axes. The dom-

inant motions are the tumbling of the TMA ion and the three-fold reorientation of the methyl groups. In the model used to explain the  $^1H$  spin-lattice relaxation [1], the intra-methyl and inter-methyl dipole-dipole interactions are considered to be modulated by these motions.

### (i) Relaxation

The temperature variation of the relaxation time ( $T_1$ ) measured from 445 to 77 K is shown in Figure 1.  $T_1$  decreases from 425 K down to 365 K, where a small discontinuous decrease is observed. Above 425 K the relaxation time starts decreasing rapidly due to melting. In the temperature range 365 K to 152 K,  $T_1$  exhibits a BPP behaviour and shows a minimum of 5.4 msec at 193 K. A small change in the slope of the  $T_1$  plot is observed at 152 K. Between 130 K and 77 K,  $T_1$  follows a BPP behaviour showing a low temperature minimum of 6.3 msec at 97 K.

The small discontinuous decrease of  $T_1$  at 365 K indicates a phase transition. The activation energies above and below 365 K are found to be the same (13.8 kJ/mole). Similar phase transitions observed in  $(TMA)_2MBr_6$  ( $M = Pt, Te, Sn$ ) at slightly higher temperatures ( $\sim 400$  K) have been identified as the  $Fd\bar{3}c$  to  $Fm\bar{3}m$  transitions [3]. The observed  $T_1$  minimum of 5.4 msec at 193 K is much shorter than the expected  $T_1$  value of 9.8 msec (10 MHz) for TMA tumbling. The observed  $T_1$  behaviour could be explained by assuming an equal number of two inequivalent TMA ions (Type a and b) and equivalent methyl groups [14]. The

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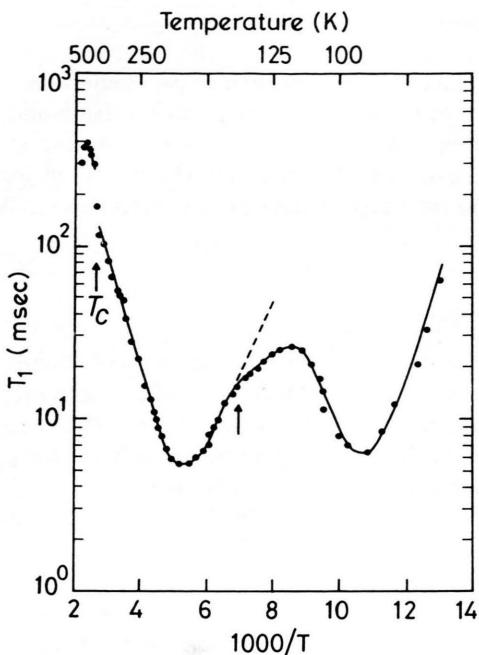


Fig. 1. Plot of relaxation time ( $T_1$ ) vs.  $1000/T$  in tetramethyl ammonium hexabromo selenate.

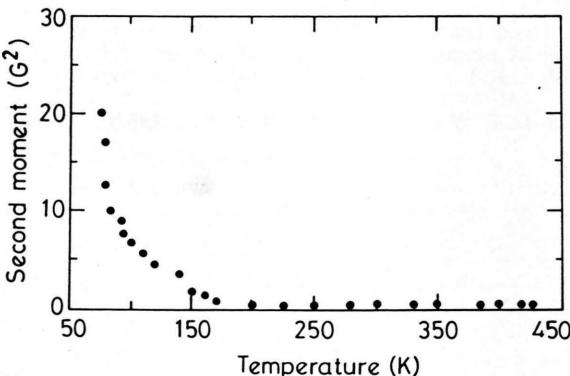


Fig. 2. Temperature variation of second moment in tetramethyl ammonium hexabromo selenate.

activation energies and the pre-exponential factors for the tumbling motion of the a and b type TMA ions are 13.8 and 12.6 kJ/mole with  $1.5 \times 10^{-12}$  and  $7.8 \times 10^{-12}$  sec, respectively. These activation energies are much smaller than the corresponding values in simple compounds like TMA halides [1], indicating a large freedom for the TMA ions in the present compounds. The slope change observed at 152 K is ascribed to changes in TMA dynamics from tumbling to small angle tor-

Table 1. Activation energies and phase transition temperatures ( $T_c$ ) in tetramethyl ammonium hexabromo metallaes.

$(TMA)_2MBr_6$	Activation energy (kJ/mole)	Motional mode	Phase transition temperatures $T_c$ (K)	Ref.
$PtBr_6$	18.4	$CH_3$ reorientation	367, 123, 97	[3]
	18.7	Over all tumbling		
	8.5	Small angle $CH_3$ torsion		
$TeBr_6$	17.8	$CH_3$ reorientation	362, 84	[3]
	19.2	Over all tumbling		
	7.7	Small angle $CH_3$ torsion		
$SnBr_6$	15.4	$CH_3$ reorientation	371, 90	[3]
	23.2	Over all tumbling		
	9.4	Small angle $CH_3$ torsion		
$SeBr_6$	11.3	$CH_3$ reorientation	365	present work
	13.8(a)	Over all tumbling		
	12.6(b)	Over all tumbling of b ion		
	3.8	Small angle TMA torsion		

sional oscillation (as the slope change occurs at a higher temperature than the methyl  $T_1$  minimum, it can not be due to small angle torsion of the methyl groups). Following Woessner [15] the amplitude of the torsional oscillations ( $\theta$ ), the correlation time  $\tau_0$  and the activation energy are obtained as  $12^\circ$ ,  $1.2 \times 10^{-12}$  sec and 3.8 kJ/mole, respectively. The second minimum of 6.3 msec, observed at 92.5 K, is ascribed to TMA torsional oscillations and  $C_3$  reorientation of the methyl groups with corresponding activation energy and pre-exponential factor of 11.3 kJ/mole and  $5.5 \times 10^{-15}$  sec, respectively. A comparison of motional parameters and phase transition temperatures  $T_c$  with other members of the  $(TMA)_2MBr_6$  group is given in Table 1.

### (ii) Second Moment

The temperature variation of the second moment in  $(TMA)_2SeBr_6$  is shown in Figure 2. The second moment remains nearly constant at a value of  $0.45 G^2$  from 430 K to 160 K. Below 160 K it steadily increases and reaches  $23 G^2$  at 77 K. The small second moment of  $0.45 G^2$  observed above 160 K can be explained in terms of TMA and  $CH_3$  reorientations.

Since only a single step  $M_2$  transition is observed, it appears that TMA and the  $\text{CH}_3$  reorientations become effective in line narrowing around the same temperature. This is reasonable in view of the comparable activation energies for the two types of motions as seen from the  $T_1$  data. Below this temperature, the slowing down of the TMA and  $\text{CH}_3$  motions gives rise to a steady increase of the second moment.

Similar  $M_2$  behaviour (0.6  $\text{G}^2$  above 150 K, and 24  $\text{G}^2$  around 77 K) has been observed in  $(\text{TMA})_2\text{MX}_6$  ( $\text{M} = \text{Pt, Te, Sn; X} = \text{Cl, Br}$ ) by Prabhumirashi *et al.* [2], and by Sato *et al.* [3]. They have also explained the  $M_2$  behaviour (above 160 K) in terms of the isotropic reorientation of the cation and the  $\text{CH}_3$  groups while that around 77 K as due to the freezing of the TMA and methyl groups.

## Conclusions

The  $T_1$  data show the presence of two inequivalent tumbling TMA ions, TMA small angle torsion and methyl group reorientation. The phase transition at 365 K, appears to be the  $\text{Fd}3\text{c}$  to  $\text{Fm}3\text{m}$  transition, as reported in the other  $(\text{TMA})_2\text{MX}_6$  compounds.

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