

INTERNAL MOTIONS IN CERTAIN ABX₃ COMPOUNDS

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ABSTRACT

Interesting temperature dependence of spin-lattice relaxation time was reported in tetramethylammonium CdCl₃ (TMA CdCl₃). The temperature dependence of proton SLR time has been studied in (TMA) HgCl₃, (TMA) HgBr₃ and (TMA) HgI₃ which also belong to ABX₃ type of compounds, and the motional effects observed in these compounds have been analysed on the basis of SLR models proposed for TMA compounds.

INTRODUCTION

INTERESTING motional effects due to the methyl group and the tetramethylammonium ion (TMA ion) reorientations have been reported in several TMA halides¹⁻⁹. (TMA) CdCl₃ which belongs¹⁰ to the ABX₃ type of compounds exhibits strikingly interesting motional effects and phase transitions. (TMA) trihalo mercurates have important structural features common with (TMA) CdCl₃, and are known to be ferroelectric^{11,12}. The TMA ions in (TMA) CdCl₃ occupying the space between chains of metal ions, bridged by Cl⁻ ions, are disordered at room temperature and undergo significant thermal motion, and order at lower temperatures accompanying a phase transition¹⁰. The TMA ions in (TMA) trihalo mercurates link the separate anion chains running through the crystal^{13,14}. The motional effects due to the methyl group and TMA ion reorientations, studied by proton magnetic relaxation technique in three ABX₃ type of compounds are being reported in this communication.

EXPERIMENTAL

(TMA) Hg Cl₃, (TMA) Hg Br₃, (TMA) Hg I₃ have been prepared and characterised following the methods reported in literature^{11,12}. Proton spin-lattice relaxation times (T_1) have been measured in these compounds in the temperature range 425–107 K, using a home-made spectrometer¹⁵ operating at 10 MHz. Details of the experiments are described elsewhere¹⁶.

RESULTS AND DISCUSSION

The temperature dependence of T_1 in (TMA) Hg Cl₃ and (TMA) Hg I₃ is presented in figure 1. The curve obtained for (TMA) Hg Br₃ has the same form as that of (TMA) Hg I₃. The spin-lattice relaxation model for TMA

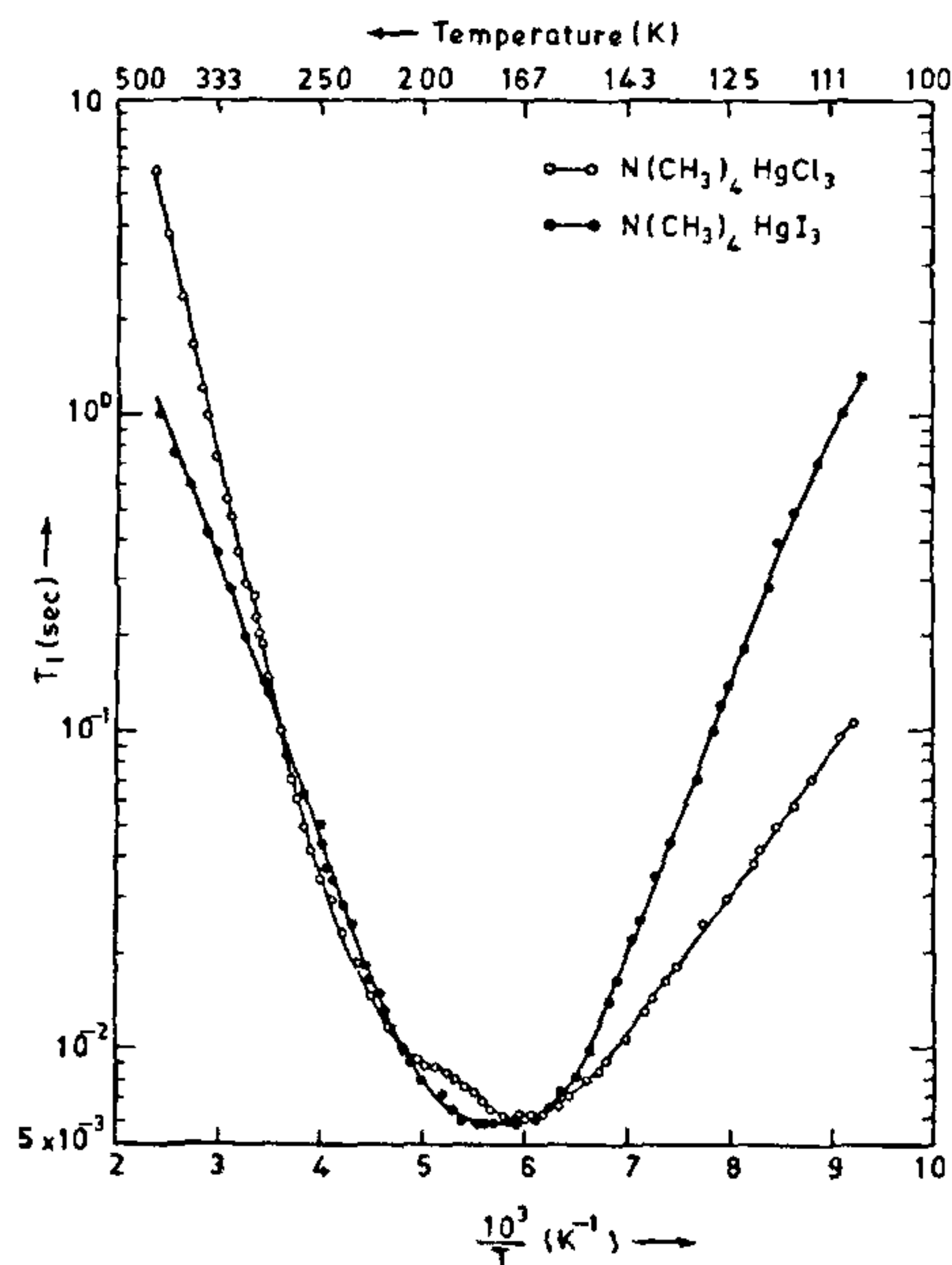


Figure 1. Temperature dependence of SLR time

halides³ explains the occurrence of two T_1 minima in the temperature dependence of T_1 in TMA compounds; the high temperature minimum being attributed to the motions of the TMA ion, and the low temperature minimum to the methyl group motion. The motion being random and thermally activated the correlation time τ_c can be expected to follow the relation

$$\tau_c = \tau_0 \exp(E_a/KT)$$

Table 1 Results of theoretical analysis of the experimental data

Compound	Activation Energy (E_a) (For TMA ion) Kcal M ⁻¹	$T_{1\text{ min}}$ (msec)	Contribution to the relaxation rate at $T_{1\text{ min}}$	
			TMA ion	CH ₃ Group
(TMA) Hg Cl ₃	6.38	5.8	0.55×10^{-2}	0.182×10^3
		8.7	0.104×10^3	0.501×10^1
(TMA) Hg Br ₃	5.56	5.4	0.504×10^1	0.182×10^3
(TMA) Hg I ₃	4.07	5.6	0.977×10^2	0.183×10^3

where E_a is the activation energy required to overcome the potential barrier hindering the motion, K is the Boltzmann constant, T is the temperature and τ_0 is a constant.

The temperature dependence of T_1 , observed in (TMA) Cd Cl₃¹⁰, being opposite to that of TMA halides³, was attributed to the non-equivalence of the correlation time of one of the methyl groups with the other three in the TMA ion.

The temperature dependence of T_1 in (TMA) Hg Cl₃ exhibits a shallow minimum in T_1 of 8.7 msec at 199.6 K and a deeper minimum of 5.8 msec at 166.4 K. The minimum at 199.6 K can be ascribed to the random reorientations of the TMA ion from the observed T_1 value of 8.7 msec which is in close agreement with the expected value of 9.6 msec at 10 MHz according to the relaxation model due to Albert *et al.*³. The deeper minimum in T_1 of 5.8 msec at 166.4 K is characteristic of the random reorientations of the methyl group.

The temperature dependence of T_1 in (TMA) Hg Br₃ shows only one minimum in T_1 of 5.42 msec around 181 K. (TMA) Hg I₃ also exhibited a single minimum in T_1 at 174.4 K of value 5.6 msec. This suggests that the correlation times corresponding to the motions of TMA ion and the methyl group in (TMA) Hg Br₃ and (TMA) Hg I₃ are close to each other, and the observed minimum in T_1 is predominantly due to the motion of the methyl group. The temperature dependence of the (TMA) Hg Cl₃ is similar to that of (TMA) halides, while that of (TMA) Hg Br₃ and (TMA) Hg I₃ is different.

The T_1 vs $10^3/T$ curves obtained for (TMA) Hg Br₃ and (TMA) Hg I₃ can be considered as due to the superposition of two symmetrical curves, one for the reorientations of the TMA ion and the other due to the reorientations of the methyl group. The values of the activation energies and the pre-exponential factor τ_0 , for the TMA ion and the methyl group obtained from the linear portions of the high and low-temperature regions of the T_1 vs $10^3/T$ curves respectively, are

useful to evaluate the contributions from TMA and CH₃ motions to the relaxation rate at T_1 minimum. The values of E_a so computed by least-squares fitting of the experimental data¹⁶, and the contributions to the relaxation rate at $T_{1\text{ min}}$, are shown in table 1. It can be seen that when the $T_{1\text{ min}}$ is predominantly due to CH₃ motions, the contribution from CH₃ motion to the relaxation rate at $T_{1\text{ min}}$ is equal to 0.182×10^3 , and the contribution from TMA motion at $T_{1\text{ min}}$ dominated by TMA motion is 104. The fast methyl group reorientations might be hindered mostly from the interactions within the TMA ion, while the slower tumbling motions of the TMA ion are hindered by the inter-ionic forces. Hence the contribution to relaxation rate at $T_{1\text{ min}}$ of the methyl group does not seem to be affected by halogen substitution, while the contribution of TMA ion varies with the substituent. The values of E_a obtained for the TMA ion indicate increased freedom for the reorientation of the TMA ion with substitution, in the order of Cl, Br and I.

The present study does not indicate the existence of phase transitions involving protons in the temperature range of the investigations.

Thus the substitution of Cd by Hg in (TMA) Cd Cl₃ and replacement of Cl by Br and I in (TMA) Hg Cl₃ is seen to have a profound influence on the internal motions of the TMA ion and the methyl group.

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EFFICACY OF HUMAN CHORIONIC GONADOTROPHIN (HCG) ON THE MAINTENANCE OF PREGNANCY IN BARBITURATE TREATED RATS

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INTRODUCTION

BARBITURATES block ovulation by inhibiting the preovulatory LH surge which can be prevented by the administration of progesterone, in adult cycling rats. As Pituitary LH is essential to stimulate the progesterone synthesis during day 8–12 of pregnancy, administration of phenobarbital or barbital sodium during this period interrupts gestation. Therefore, in this experiment, attempt has been made to maintain the pregnancy in barbiturate treated rats by the administration of HCG on day 8, 8 to 9 or 8 to 10 of pregnancy as HCG is having long LH-like activities. The results indicate that the foetal survival is reduced in these barbiturates treated HCG administered rats as the duration of HCG treatment is increased. This failure of pregnancy maintenance may be due to the luteolytic action of HCG, as high dose or prolonged treatment of HCG is known to be deleterious to gestation.

Administration of pheno- or pentobarbital prevents ovulation for one day if administered on any day of estrous cycle prior to so called 'critical period', in adult rats and also in pregnant mare serum gonadotrophin (PMSG) primed immature rats¹⁻⁵. This blockade of ovulation is due to inhibition of preovulatory LH-

surge which is responsible for the maintenance of progesterone levels necessary for ovulation. Therefore, barbiturate induced blockade of ovulation can be prevented by the administration of progesterone before the pheno- or pentobarbital treatment^{2,6}. Administration of phenobarbital or barbital sodium from day 8–12 of pregnancy interrupts gestation which may be due to inhibition brought in the release of pituitary LH, as neutralization of endogenous LH or hypophysectomy during this period causes foetal resorption or abortion in rats¹¹⁻¹⁴. Therefore the present investigation is taken up to test the efficacy of human chorionic gonadotrophin (HCG) on the maintenance of pregnancy in phenobarbital and barbital sodium treated rats, as HCG has a long acting LH-like activities⁷⁻¹⁰.

MATERIALS AND METHODS

Nulliparous rats of Holtzman's strain weighing 140–180 g, 80–90 days old were caged with proven males at proestrus or estrus. The rats showing sperms in the vaginal smears on the subsequent day were selected for experimentation and the day was de-