Proton spin-lattice and spin-spin relaxation times of $(N(CH_3)_3H)(I)(TCNQ)$

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Proton spin-lattice T_1 and spin-spin T_2 relaxation times are reported for $(N(CH_3)_3H)(I)(TCNQ)$ in the temperature range 150 to 500°K. The overall relaxation process of the system can be described by contributions from rotation of the $N(CH_3)_3H^+$ group about its symmetry axis, tumbling of that group, and the scalar and dipole interactions of the protons with the unpaired electron. Rotation of the trimethylammonium group leads to a minimum in T_1 at 210°K, while tumbling gives rise to another minimum at 340°K. The activation energies for the two processes are 0.064 and 0.11 eV, respectively. The overall reorientation of the $N(CH_3)_3H^+$ group, therefore, appears to dominate the T_1 process below 400°K. No direct evidence is observed in the NMR data for the reversible transition seen in the conductivity and ESR data at 160°K, however, it does appear that such a transition may influence the $N(CH_3)_3H^+$ reorientations leading to smaller activation energies for the reorientation processes.

I. INTRODUCTION

The study of linear-chain organic complexes based on 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) and inorganic complexes containing one-dimensional (1D) chains of halogen (as poly-halide) has recently received considerable attention due to their novel anisotropic properties.[1,2] One such highly conducting ternary TCNQ complex, $(N(CH_3)_3H^+)(I_3^-)_{1/3}(TCNQ^{2/3-})$, is novel in that it contains 1D chains of tri-iodide as well as 1D TCNQ chains.[3,4] In addition, x-ray work has revealed[5] a 1D superlattice ascribed to a periodic distortion in the iodine chain.

The $(N(CH_3)_3H^+)(I_3^-)_{1/3}(TCNQ^{2/3-})$ system forms highly reflecting green crystals whose four-probe room-temperature conductivity σ parallel to the TCNQ chains is ~ 20 $\Omega^{-1}cm^{-1}$. In a plot of σ versus temperature T, a weak maximum is observed at 240°K where $\sigma(240°K) = 1.08\sigma(295°K)$.[4] Below 160°K, the conductivity drops rapidly, reaching a maximum in $d(-\log_{10}\sigma)/d(1/T)$ at 150°K.[6] These results have been interpreted[6] as a reversible semiconductor-semiconductor transition at 150°K. The "metal-like" behavior above 240°K and the broad maximum in $\sigma(T)$ at 240°K have been interpreted according to the model of Epstein et al.[7-9] as a semiconductor with a strongly temperature-dependent mobility determined by interaction of charge carriers with molecular vibrations. The existence of a gap for $T > 150°K$ has been confirmed by thermoelectric-power[10] and optical[11] studies.

Electron-spin-resonance (ESR) studies[4] of $(N(CH_3)_3H)(I)(TCNQ)$ also support the existence of a reversible transition below 160°K. Between 295 and 160°K, the linewidth decreases linearly to a minimum at 160°K. Below 160°K, the linewidth increases nonlinearly, while the spin density progressively decreases as the temperature is lowered. ESR and conductivity data, therefore, suggest a reversible transition beginning at 160°K, however, no such transition is observed by differential scanning calorimetry (DSC).[4]

The $(N(CH_3)_3H)(I)(TCNQ)$ system contains protons on both the $N(CH_3)_3H^+$ cation and TCNQ. Thus, we have measured the proton spin-lattice (T_1) and spin-spin (T_2) relaxation times of $(N(CH_3)_3H)(I)(TCNQ)$ in the hope that an elucidation of the reorientational processes available to the constituent molecules would provide some insight into its physical properties.

II. EXPERIMENTAL

The $(N(CH_3)_3H)(I)(TCNQ)$ was synthesized from gradient-sublimed TCNQ as previously reported.[3] A sample was placed in a 7-mm (o.d.) NMR tube, degassed and sealed under a vacuum of $\sim 10^{-5}$ Torr. The proton relaxation times were obtained on a Bruker SXP NMR spectrometer operated at 90 MHz. The spin-lattice relaxation times were measured by the 180°-t-90° pulse technique. The 90° pulse length was 2.5 μsec and the recovery time of the receiver was 6 μsec. The spin-lattice relaxation time T_1 was obtained from the slope of plots of $\ln[M(\infty)-M(t)]$ versus time, where $M(t)$ is the amplitude of the free-induction decay (FID) following the 90° pulse and $M(\infty)$ is the value of $M(t)$ for an infinite time interval between the 180° and 90° pulses. No deviations from exponential behavior were observed. Spin-spin relaxation times T_2 were obtained from the FID following the 90° pulse and T_2 was taken as $t_{1/2}/\ln2$ where $t_{1/2}$ is the time for the magnetization to decay to one-half its original value.
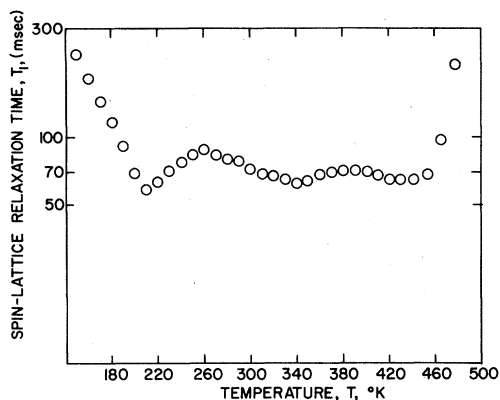
FIG. 1. Temperature dependence of proton spin-lattice relaxation time T_1 for $(N(CH_3)_3H^+)(I_3^-)_{1/3}(TCNQ^{2/3-})$.

III. RESULTS AND DISCUSSION

Plots of T_1 and T_2 versus temperature for $(N(CH_3)_3H)(I)(TCNQ)$ are given in Figs. 1 and 2, respectively. The T_1 data exhibits two well-defined minima of equal intensity at 210 and 340 °K. There is also evidence of a leveling of T_1 in the 430 °K range. However, before this process proceeds to a sufficient extent to unequivocally identify it as a leveling of the T_1 or the beginning of another minimum, dramatic increases in T_1 and T_2 begin to take place at 450 °K. These increases at 450 °K may be associated with the decomposition of the material. At these temperatures, there is evidence of the deposition of material at the top of the NMR tube. Similarly, the T_2 plot shows two transitions. At the low-temperature transition (180 °K), T_2 increases by almost a factor of 3. The higher-temperature transition (340 °K) is much less intense and T_2 increases by only 3 μsec through this transition. With the breakdown of the material, T_2 increases dramatically at 450 °K and
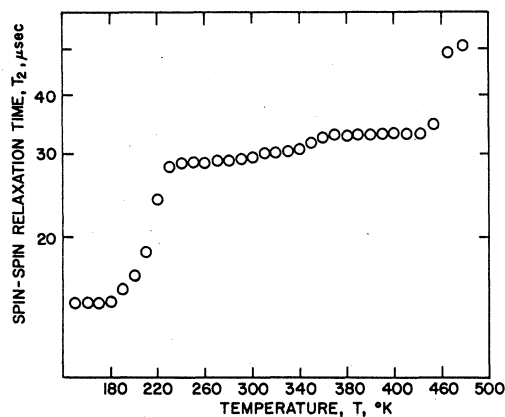

FIG. 2. Temperature dependences of proton spin-spin relaxation time T_2 for $(N(CH_3)_3H^+)(I_3^-)_{1/3}(TCNQ^{2/3-})$.

the FID becomes nonexponential, reflecting at least two components.

For the semiconducting paramagnetic materials, such as the alkali-TCNQ salts, T_1 decreases with increasing temperature, becoming temperature-independent above room temperature. Here, the relaxation of the TCNQ protons is predominantly due to their interaction with the unpaired electrons of the paramagnetic species.[12] For the ammonium-TCNQ salt, there is an additional relaxation at low temperature due to reorientation of the NH_4 cation.[13] Below room temperature, the spin-lattice relaxation in ammonium-TCNQ is dominated by the cation reorientation with some contribution to its relaxation from the dipolar interaction with the unpaired electron of the TCNQ moiety.[13] Above room temperature, the overall proton relaxation is governed by contributions from scalar interactions of the TCNQ protons with the unpaired electron. At these temperatures, there is also a finite contribution from the reorientation of the NH_4^+ ion.[13] A frequency-dependent study of the proton T_1 shows that on the low-temperature side of the minimum due to NH_4 reorientation, T_1 is frequency dependent. However, at temperatures above the minimum, T_1 is independent of frequency.[13] This is consistent with the intramolecular dipole-dipole mechanism, which is dominant as a result of NH_4^+ reorientation, and which requires that at temperatures below the T_1 minimum $\omega^2\tau_c^2 \gg 1$ and above the minimum $\omega^2\tau_c^2 \ll 1$. Several ammonium halides have also been examined by NMR relaxation techniques. Methylammonium chloride exhibits relaxations due to $-CH_3-$ and $-NH_3-$ rotations. The activation energies obtained from the experimental data are strongly dependent on the morphology of the phases present.[14] Similar studies on tetramethylammonium halides reveal two relaxations due to the rotating of the methyl group and the tumbling of the tetramethylammonium cation. The activation energies for both processes decrease with increasing size of the anion.[15]

A comparison of the T_1 data of $(N(CH_3)_3H)(I)(TCNQ)$ with other TCNQ systems reveals that below 400 °K the overall T_1 behavior is dominated by the reorientational processes of the $N(CH_3)_3H^+$ species. We utilize the model of Dunn and McDowell[16] for reorientation of the trimethylammonium unit undergoing the composite motion of rotation of the $-CH_3-$ group about its threefold axis, rotation of the $-N(CH_3)_3-$ group about its threefold axis and isotropic tumbling of the whole unit. The expression derived for the spin-lattice relaxation time is given by[16]

$$\frac{1}{T_1} = \frac{9}{80}\frac{\gamma^4\hbar^2}{r^6}[Af(\tau_{c1}) + Bf(\tau_{c3}) + Cf(\tau_{c4}) + Df(\tau_{c5})], \quad (1)$$

where we have

$$f(\tau) = \tau/(1 + \omega^2\tau^2) + 4\tau/(1 + 4\omega^2\tau^2)$$

and

$$A = \tfrac{1}{3}(1 - 3\cos^2\delta)^2, \quad B = \tfrac{3}{2}\sin^4\delta,$$

$$C = \sin^2 2\delta + \sin^4\delta, \quad D = \tfrac{1}{2}(8 - 3\sin^4\delta).$$

Here δ is the angle between the $C-N$ bond and the symmetry axis of the whole unit. The τ's are sums of the correlation times for the specific motions, r is the interproton distance within a methyl group, $\hbar$ is Planck's constant divided by 2π, and δ is the gyromagnetic ratio for the protons.

Rotation of the $-CH_3-$ group about its threefold axis would, in spite of neglecting intermethyl and intermolecular effects, lead to T_1 values which are much lower than those observed. However, there is good agreement between the experimental T_1 minima at 210 °K (59 msec) and the calculated value for rotation of the $N(CH_3)_3H$ unit about its symmetry axis (~55 msec), assuming a δ of 75°. The T_1 minimum at 210 °K does not exhibit a corresponding T_2 transition within the accessible temperature range. The T_1 minimum occurs when the reorientational frequency is of the order of 10^8 Hz. The corresponding T_2 transition is observed at a frequency of 10^4–10^5 Hz. For thermally activated processes, therefore, the corresponding T_2 transition would occur at a much lower temperature than the T_1 minimum, beyond that accessible by the instrument used. However, if an estimate is made of the activation energy for the reorientation process from the slope of the straight-line portion of the $\log_{10}T_1$-versus-temperature plot, one obtains a value of 0.064 eV (1.5 kcal/mole) for rotation of the $N(CH_3)_3H^+$ unit about its symmetry axis. This is in agreement with the value for rotation of the methylammonium ion in the corresponding chloride.[14] The reorientation process, therefore, may very well involve both rotation of the methyl group and rotation of the trimethylammonium unit as a whole about their symmetry axes. This reorientation process may correspond to an anomaly observed in the Young's modulus[17] and the microwave dielectric constant[18] of $(N(CH_3)_3H)(I)(TCNQ)$ at 89 °K.

The broader T_1 minimum at 340 °K has its corresponding T_2 transition at 180 °K. This transition is of intensity equal to the low-temperature minimum and may very well result from isotropic tumbling of the whole $(CH_3)_3NH$ unit. From the expression for T_1 above, the tumbling should give a minimum of approximately 48 msec. Since this relaxation includes contributions from the rotation of the unit, an estimate of the activation energy for the process can be obtained from the straight-line

portion of the sides of the minimum after subtraction of the contribution from the rotation process. Such an operation yields an activation energy of ~0.11 eV (2.6 kcal/mole). This value is lower than that obtained for tumbling of the $(CH_3)_4N$ cation in tetramethylammonium halides. In that system, the energy values found for methyl rotation are also larger than those found for such motions in methylammonium chloride, where both methyl and CH_3NH_3 rotation energies are observed to be strongly dependent upon the morphology of the crystal phase examined.[14] It has been further established that in the tetramethylammonium halides, the activation energies decrease monotonically with increasing size of the anion for both the CH_3 group rotation and the overall cation tumbling. Such changes in the barrier heights may reflect the distortion of the methyl groups by their interaction with the halide ion. The amount of distortion is probably proportional to the electrostatic interactions which influence the overall tumbling. Such factors amplified by the large sizes of both the triiodide ion and the TCNQ moieties may account for the small activation energies observed in the $N(CH_3)_3H^+$ reorientations in this study.

Above the 340 °K minimum, the T_1 relaxation is dominated by the scalar interaction of TCNQ protons with the unpaired electrons in a manner similar to that observed for $K^+(TCNQ)^-$ and $NH_4(TCNQ)$.[12, 13] However, as has been demonstrated for the ammonium TCNQ case,[13] there is still a substantial contribution from the reorientation of the $N(CH_3)_3H^+$ ion, lowering the overall T_1 below that expected for the simple alkali TCNQ salts. At 340 °K, there is another T_2 transition whose corresponding T_1 minimum probably begins to emerge at 430 °K. Before the minimum completely emerges, decomposition is evident. At this time, it is difficult to assign this high-temperature process, which is unobserved in other measurements.

The reversible transition that is observed in the conductivity[4, 6] and ESR[4] data beginning at 160 °K, is not observed in the NMR data. This occurs because the transition is associated with the TCNQ portion of the molecule and the NMR data, as we have shown, is dominated by the $N(CH_3)_3H^+$ group reorientation throughout the temperature range studied. The transition that takes place in the TCNQ stacks, therefore, is not of sufficient magnitude to perturb the $N(CH_3)_3H^+$ reorientation in order to be reflected as a discontinuous or sharp transition in the proton relaxation data. The lack of such a transition in the DSC data[4] indicates that it is not a detectable first-order transition. However, the transition in the TCNQ stacks may be indirectly felt through the $N(CH_3)_3H^+$ reorientations

and may also contribute to the lowering of the activation energies involved for $N(CH_3)_3H^+$ reorientation. Selective deuteration of both TCNQ and $N(CH_3)_3H^+$ moieties should aid in the further understanding of this reversible transition observed by ESR and conductivity data.

In summary, T_1 and T_2 measurements on $(N(CH_3)_3H^+)(I_3^-)(TCNQ^{2/3-})$ reveal two relaxations which are attributed to rotation of the $N(CH_3)_3H^+$

group about its symmetry axis and isotropic tumbling of the unit as a whole. These two processes dominate the overall proton spin-lattice relaxation behavior up to temperatures approaching 400 °K. Above this temperature, scalar interaction of the TCNQ protons with the unpaired electron becomes relatively more important. Activation energies of 1.5 and 2.6 kcal/mole are determined for the rotation and tumbling processes.

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