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NMR Proton Relaxation in Trioxane and Trithiane

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Laboratory and rotating frame proton NMR relaxation times as well as second moments have been measured for the solids trioxane and trithiane. In both cases only evidence for rotation of the molecules about their respective three fold axes can be found. For this process the correlation times are, for trioxane

$$\tau = 1.8 \times 10^{-17} \exp(15{,}000/RT),$$

and for trithiane

$$\tau = 9.8 \times 10^{-17} \exp(21{,}400/RT).$$

(Here R is in kcal mol^{-1} K^{-1}.) The rate of this rotation is too fast, or its barrier too low, for it to be rate limiting in the solid state polymerization process.

A INTRODUCTION

Both trioxane[1] and trithiane[2] polymerize under certain conditions in the solid state; trioxane becomes polyoxymethylene. In order to assist in determining what role molecular motions may play in this polymerization, the NMR proton spin-lattice relaxation time, T_1, and the rotating frame relaxation time, $T_{1\rho}$, have been measured as functions of temperature for both solids. Previous NMR second moment studies[3,4] are used to supplement and confirm the resulting interpretation. Only rotation about the molecular three-fold axis is fast enough to affect the NMR parameters, as will be developed. No evidence for the phase transition postulated by Nadkarni and Schultz[5] to occur at 194°C for trithiane was found.

Both trioxane[6] and trithiane[7] crystallize as ferroelectric solids. Does the polymerization process spontaneously preserve the molecular polarization? Rotation about the three-fold axis preserves the orientation of the molecular electric dipole moment. If this process were the rate limiting step in polymerization, it might be supposed that mere opening of the ring would also preserve the orientation of the molecular moment, and that a polar polymer would result. It develops that a process of much rarer temporal probability must be the rate limiting step in the polymerization process, and the NMR relaxation experiment is equivocal about the ultimate formation of a polar polymer.

B EXPERIMENT

A Bruker SXP spectrometer was used. T_1 was measured using alternating $180° - \tau - 90°$ and 90° sequences repeated at times long compared to T_1; the signals from the two sequences were subtracted and the logarithm of the difference was plotted as a function of τ to obtain the relaxation time. Measurements were made at 60 MHz. $T_{1\rho}$ was measured using alternating 270°-spin lock (τ) and 90°-spin lock (τ); again the logarithm of the difference as a function of τ was used to obtain the relaxation time. The spin lock pulse was of 12 G amplitude. To obtain free induction decays for second moment determinations,[8] alternating $180° - (100\ \mu s) - 99°$ and 90° sequences were used; the logarithm of the difference was plotted as the square of the time.[8] In all cases the alternating sequences served to eliminate instrumental recovery effects; for the second moment determinations an effective pulse-plus-deadtime of 8 μs could be obtained. Temperatures were produced and controlled with the Bruker controller; accuracy is estimated as $\pm 1°$C.

C SECOND MOMENTS; EXPERIMENT

Broad line NMR studies of trioxane have been made both by Komaki and Matsumoto[3] and by Slonim *et al.*[4] Our one measurement at room temperature (7.5 G^2) agrees with the result at the same temperature of Slonim *et al.*[4] ($\sim 6.8\ G^2$) within their error limits. Their linewidth data[4] as a function of temperature have been converted, with approximation by a Gaussian line-shape, into T_2 values for comparison with our relaxation times in Figure 1. As reflected there, they observed a gradual transition, beginning at about 250 K, from the full rigid lattice second moment to a smaller, temperature independent, "quasi rigid lattice" second moment. This motional narrowing process can only be due to some rotation of the moleculae about its center of gravity, as discussed below. The second moments for the two plateaus are summarized in Table I.

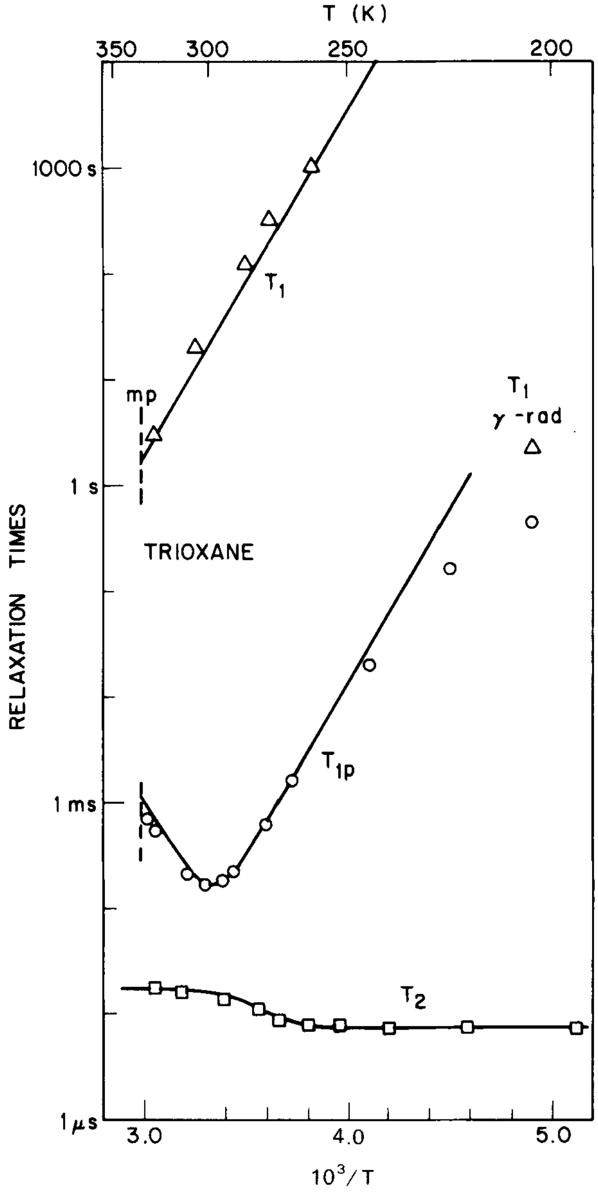

FIGURE 1 Proton relaxation times T_1, $T_{1\rho}$ and T_2 for trioxane in the solid state. The solid lines for T_1 and $T_{1\rho}$ represent the chosen fit to the data. For T_2, the solid line shows the trend of the data; the T_2 data are based on the work of Slonin (Ref. 4).

TABLE I

Second moments (in units of G^2)

	Theory		Experiment	
	Trioxane	Trithiane	Trioxane	Trithiane
A. Rigid Lattice				
Methylene pair	8.97	8.97		
Other Intramolecular	2.83	.95		
Intermolecular	4.16	2.34		
TOTAL	16.0	12.3	16.0[a], 15.2[b]	14
B. Three-Fold Axis Rotation				
Intramolecular	2.71	2.5		
Intermolecular	2.3 ± .3	1.2		
TOTAL	5.0	3.7	5 ± 1	3.3
C. Difference (A-B)	11.0	8.6	11 10.5 ± .3[c]	10.7
D. Spherical Rotation	1.6			

[a] Slonim *et al.*;[4] (preferred value).

[b] Komaki and Matsumoto;[3] recalculated by numerical integration from their figure at −48°C.

[c] Difference determined from fitting $T_{1\rho}$ minimum.[18]

We determined the second moment for trithiane at room temperature and at two temperatures close to the melting temperature, also summarized in Table I. These second moments, with the approximation of a Gaussian lineshape, were converted to T_2 for comparison with relaxation time measurements in Figure 2. Here also a linewidth transition has occurred. No change in second moment occurred at the temperature of the phase transition suggested by Nadkarni and Schultz (see Figure 2).

D SECOND MOMENT CALCULATIONS

The structure of the trioxane molecule has been well studied in the solid[1,3–6,9] and gaseous[10] states as well as in solution.[11] Thus far it has not been observed in any but the chair configuration. Clark and Hewitt[10] have used electron diffraction to give directly all the intramolecular proton-proton distances (i.e., their refinement 5) and the resulting theoretical intramolecular rigid lattice second moment[12] is listed in Table I. The crystal structure of Busetti *et al.*[6] was used to determine individual intermolecular proton separations out to a distance of 6.13 Å for the Van Vleck sums;[12] at longer distances the

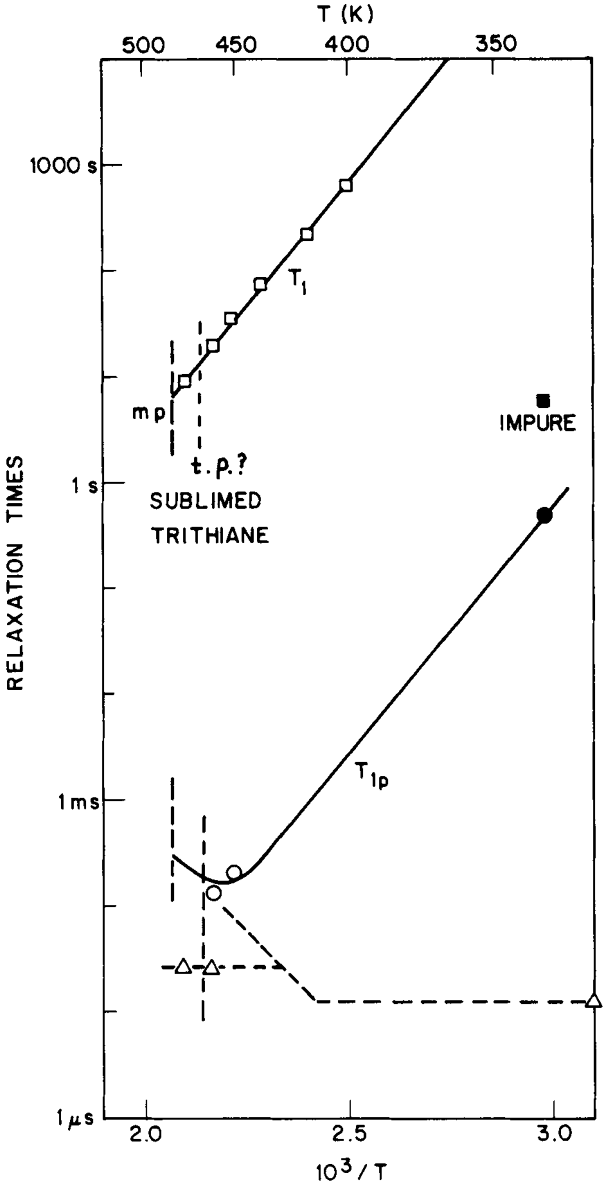

FIGURE 2 Proton relaxation times T_1, $T_{1\rho}$ and T_2 for solid trithiane. The solid lines represent the best fit to the data. The filled points refer to the as received specimen. The dashed lines for the T_2 data indicate the temperature at which a line width transition is expected.

sums were approximated by an integral in which the crystal dimensions[6] were used to calculate the proton density. With this intermolecular contribution a total second moment of 16 G^2 is calculated, in agreement with experiment. Slonim *et al.*[4] pointed out that a second moment calculated solely on the basis of hydrogen positions in the crystal as assigned by Busetti *et al.*[6] is too large. Thus, the recent electron diffraction inter-proton distances[10] relieve this discrepancy. Clearly, below 250 K the full rigid lattice second moment of trioxane has been attained, and a search for further linewidth transitions at still lower temperatures must prove fruitless.

We have found no estimates of proton positions in trithiane; therefore the rigid lattice second moment was calculated as follows. The methylene pair contribution was kept the same as for trioxane. The other intramolecular contributions were scaled with those of trioxane in the ratio of the reciprocal sixth powers of the respective molecular carbon-carbon distances.[6,7] The intermolecular contribution was scaled with that of trioxane in the ratio of the square of the respective proton densities.[6,7] The result (Table I) is somewhat smaller than the experimental value. Because of the dominance of the methylene pair contribution, this result suggests a smaller intramethylene proton-proton distance for trithiane than for trioxane (if all the excess of experiment over theory is added to the methylene contribution, the resulting 10.7 G^2 second moment leads to an interproton distance of 1.80 Å for trithiane; cf. 1.849 Å for trioxane[10]). We conclude that at room temperature and below the full rigid lattice second moment is in effect for trithiane.

For rigid molecules such as trioxane and trithiane the possible causes of motional narrowing are molecular self diffusion,[13] molecular rotation over a sphere,[13] or rotation about an axis.[14] Self-diffusion requires[13] that at high temperatures there should be an exponential growth of T_2 with negative reciprocal temperature, which is not observed. Rotation over a sphere would require a high temperature second moment for trioxane of ca. 1.6 G^2,[15] which is less than observed (5 G^2). Reneker *et al.*[9] have shown from dielectric loss measurements that there is no molecular motion in trioxane whereby the molecular dipole moment is reoriented. Rotation about the molecular three fold axis will not reorient the molecular dipole, which lies parallel to this axis. For rotation about this axis, the angles between the interproton vectors and the rotation axis are such (90°, 35.3°, and 66°) as to reduce the intramolecular second moment to almost exactly one fourth of its full rigid lattice value.[16] The intermolecular contribution was estimated (using Dereppe's Eq. (5)[16,17]), to fall to about half of its rigid lattice value. (The value in Table I is approximate because only a representative 15% of the pair wise interactions were actually computed.) The total second moment for three-fold axis rotation agrees well with experiment—5 G^2 in both instances. For trithiane the second moment for three-fold axis rotation was again obtained by scaling the trioxane values; the result agrees rather well with experiment (Table I).

E RELAXATION TIMES

The second moment study indicates that both trioxane and trithiane rotate rapidly about their three-fold axes at temperatures close to the melting point. The relaxation times support this interpretation and furnish estimates of the time between molecular jumps, τ, and the temperature dependence of τ.

The spin-lattice relaxation time, T_1, data for both trioxane (Figure 1) and trithiane (Figure 2) immediately below their respective melting points are clearly such that $\omega_0 \tau > 1$ at all temperature investigated. Thus

$$T_1 = 3\omega_0 \tau / 4\sigma_0^2 \tag{1}$$

where ω_0 is the resonance frequency and σ_0^2 is the difference in second moments between the rigid lattice and motionally narrowed conditions[13,18] (in frequency units). For spin lattice relaxation in the rotating frame we have[18]

$$T_{1\rho} = (1 + 4\omega_1^2 \tau^2)/\sigma_0^2 \tau \tag{2}$$

where $\omega_1 = \gamma H_1$, H_1 being the strength of radio frequency magnetic field along which the magnetization is locked and in which relaxation occurs. Note that possible anisotropies[19] in T_1 and $T_{1\rho}$ are ignored in Eqs. (1) and (2).

For trioxane, the value of the second moment difference calculated from the $T_{1\rho}$ minimum value via (2) is entered in Table I as 10.5 G^2 (Row C), in essential agreement with the theoretical prediction and the result of the second moment study. This confirms that the motional process responsible for $T_{1\rho}$ is the same as that for the second moment decrease in trioxane. The solid lines accompanying the T_1 and $T_{1\rho}$ curves for trioxane in Figure 1 were calculated from the equations (1) or (2) and the parameter set in Table II. The Arrhenius law for the jump time was assumed:

$$\tau = \tau_0 \exp(H_{\text{act}}/RT) \tag{3}$$

$$\tau_0 = \nu^{-1} \exp(-S_{\text{act}}/R) \tag{4}$$

$$\nu = (3/2\pi)(H_{\text{act}}/2I)^{1/2}$$

where I is the moment of inertia about the three-fold axis[20] and ν is the libration frequency in the three-fold potential well. The adjustable parameters τ_0 and H_{act} were chosen to give a reasonably close fit to the data of Figure 1.

For trithiane, σ_0^2 was taken from the second moment study; via Eq. (1) values of τ_0 and H_{act} were chosen, and the solid curves for T_1 and $T_{1\rho}$ were

TABLE II

Relaxation time parameters

	Trioxane	Trithiane
Second moment (s^{-2})	7.54×10^{9}	7.54×10^{9}
H_{act}(kcal/mol)	15.0	21.4
τ_0(s)	1.8×10^{-17}	9.8×10^{-17}
ν(s^{-1})	2.0×10^{12}	1.7×10^{12}
S_{act}(cal deg^{-1}mol^{-1})	20.35	17.31
I (g cm^2)	3.02×10^{-38}	5.95×10^{-38}

obtained. Agreement of the predicted $T_{1\rho}$ values with experiment proves the consistency of the interpretation for trithiane in terms of three-fold axis rotation. The parameter set is assembled in Table II. Nadkarni and Schultz[5] find a small endotherm at 467 K in trithiane, which suggests a phase transition. Ordinarily T_1 is a very sensitive indicator of such transitions; as it is unlikely that the molecular jump time would be the same in both phases, a discontinuity should result. Figure 2, however, shows no indication of a phase change in trithiane.

One purpose of the relaxation time measurements was the determination of appropriate conditions under which a solid state ^{13}C NMR study of chemical shift tensors might be made.[21] As Figures 1 and 2 show, the relaxation times T_1, which govern the repetition period of such experiments, become of the order of an hour under conditions in which the rigid lattice chemical shift tensor might be studied.[21] As Figure 1 shows, γ radiation (~ 1 *MR*) produces a sufficient number of paramagnetic centers to lower[22] T_1 sufficiently for such spectroscopic studies. The relaxation time for trithiane in the impure (i.e. as received) state is, however, sufficiently short. As we have ruled out any other possible motions of the trithiane molecule, the lowering of T_1 must be due to the motion of the impurity, in analogy with the relaxation caused by the diffusion of water impurities in hexamethylenetetramine.[23]

F DISCUSSION

At this time the experimental and theoretical findings for the NMR behaviors of trioxane and trithiane provide a self consistent picture. The only molecular motion necessary to explain the data suite in each case is activated jumping of the respective molecule about its three-fold axis of symmetry. Before discussing our resulting picture further, some comments about the earlier NMR studies and conclusions are required.

Komaki and Matsumoto[3] found a strong narrow NMR line in trioxane as the melting temperature was approached which they suggested might be due to molecules in the boat configuration undergoing rotation about the erstwhile three-fold axis. Slonim *et al.*[4] showed however that this narrow line did not occur in a powder obtained by freshly crushing a single crystal, and that it would develop with subsequent fusion; therefore they attributed this line to an impurity effect. Hamman *et al.*[24] accepted the original interpretation of molecular motion, however, to rationalize a phase transition they observed in trioxane at high pressures in terms of molecular flattening. Such flattening may indeed occur, but as yet NMR results cannot be called upon in support of the idea.

Slonim *et al.*,[4] in order to account for their linewidth data, developed a motional narrowing model involving librational amplitudes which increase strongly with temperature. The data in no way require such a model, as the more usual activated jumping mechanism readily accounts for relaxation and line narrowing. The development of such large amplitudes as the model would require is precluded both by X-ray evidence and the height of the rotational barrier.

There is nothing extraordinary about the values of activation enthalpy and entropy necessary to fit the data in comparison to those found for other systems. And their calculation in terms of interatomic potentials is beyond the scope of this paper. What we wish to compare are the rotational barrier and the activation enthalpy for polymerization, as determined by Sagu *et al.*[25] for trioxane. They found a value of 40 kcal/mol, almost three times the barrier for rotation, which indicates that molecular rotation, at least that about the three-fold axis, cannot be rate limiting in the polymerization process.

This problem of rate limitation can be examined directly in terms of the actual rate of molecular rotation, which at 50°C is about 4×10^6 jumps per second. Suppose a growing fiber attached one monomeric unit each time a monomer adjacent to the growing end achieved a favorable orientation within the range of $\pm 60^\circ$ about the three-fold axis from its rest position, i.e., every 2×10^{-7} second. Then fibers would propagate at a rate of about one cm per second. As polymerization times are measured in hours, such a propagation rate seems several orders of magnitude too fast.

We have established that the only motion observable in trioxane by the various NMR techniques is rotation about the molecular three-fold axis for which the barrier is 15 kcal/mol. Any other motional process which would have large NMR effects, such as boat-chair interconversion, self diffusion, or rotation by π about an axis in the molecular plane, must have a higher activation barrier, i.e. a much lower jump probability per unit time. The essential point here is that this last mentioned process, rotation of the moleculae by π about an axis in the molecular plane, would have the effect of inverting the molecule, i.e. the molecular electric dipole moment. Therefore, if the activation energy for polymerization were less than 15 kcal/mol it would be highly probable that the orientation of the molecular electric dipole moment would be preserved in the polymerization process and that each microcrystal of trioxane would result in a ferroelectric "region" of the resulting delrin polymer. Since the activation energy for polymerization is much higher than 15 kcal/mol we can not foretell the orientation of the molecular electric dipole moment after polymerization. That process which is able to reorient the moment may have an activation energy H such that $15 < H \leq 40$ kcal/mole, and the orientation of the moment may be randomized before or during the ring opening step.

In conclusion, then, we have determined the rates of rotational jumping for trioxane and trithiane about their respective three-fold axis, and we point out that this molecular rotation process observed via NMR is not rate limiting in the solid state polymerization.

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