

Pressure dependence of self diffusion in the plastic crystals hexamethylethane, norbornylene and cyclohexane

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MS received 7 February 1972

Abstract. Translational self diffusion in three molecular crystals has been studied as a function of pressure using nuclear spin-lattice relaxation time measurements. Activation volumes are obtained which are consistent with a vacancy diffusion mechanism.

Molecular crystals exhibiting a plastic crystalline phase are generally composed of globular molecules which are undergoing rapid reorientational motion. A consequence of this is that the entropies of fusion are low ($\Delta S_f \lesssim 20 \text{ eu}^\dagger$). It has been noted (eg Bladon *et al* 1971) for plastic crystals with relatively high entropies of fusion ($\Delta S_f > 17 \text{ eu}$) that the activation enthalpy for self diffusion, ΔH^* , is approximately twice the latent heat of sublimation, L_s . For these plastic crystals the activation enthalpies obtained by nuclear magnetic resonance (NMR) techniques are in good agreement with those obtained by radiotracer and creep measurements. Agreement between these techniques for materials with lower ΔS_f is not so good (Bladon *et al* 1971) and discrepancies have been tentatively attributed to relaxation around vacancies. It has been suggested (Jost 1960, Hood and Sherwood 1966a) that since L_s is a measure of the lattice energy, the observation that $\Delta H^* \simeq 2L_s$ implies a single vacancy mechanism for self diffusion. Plastic crystals with relatively low entropies of fusion ($\Delta S_f < 17 \text{ eu}$) have revealed self diffusion activation enthalpies, as determined by NMR, which are in the range $L_s < \Delta H^* \lesssim 2L_s$. This is consistent with vacancy formation parameters obtained by Baughman and Turnbull (1971) from analysis of excess heat capacity in similar systems. These authors suggest considerable vacancy relaxation may be responsible for the low vacancy formation enthalpies in the low ΔS_f materials. In the case of cyclohexane ($\Delta S_f = 9.2 \text{ eu}$) radiotracer measurements of the isotope effect have suggested that many neighbouring atoms (about twelve) are cooperatively involved in the microscopic diffusion step (Chadwick and Sherwood 1972.)

The temperature dependence of the proton spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, for hexamethylethane (Chezeau *et al* 1971), norbornylene (Folland *et al*, to be published) and cyclohexane (Roeder and Douglass 1970) has been measured under their equilibrium vapour pressures. The correlation times for translational self diffusion have been deduced for the plastic phase in each case. Self diffusion coefficients have also been determined by radiotracer studies in hexamethylethane (Lockhart and Sherwood, to be published) and cyclohexane (Hood and Sherwood 1966b). In the case of hexamethylethane ($\Delta S_f = 20 \text{ eu}$) results obtained by the two methods are in good agreement. However, for cyclohexane ($\Delta S_f = 9.2 \text{ eu}$) the activation enthalpy from radiotracer measurements ($\Delta H^* = 68.2 \text{ kJ mol}^{-1}$) differs significantly from the NMR

$\dagger 1 \text{ eu} \equiv 1 \text{ J K}^{-1} \text{ mol}^{-1}$

result ($\Delta H^* = 41.4 \text{ kJ mol}^{-1}$). At temperatures near the melting point the NMR relaxation measurements, interpreted using a vacancy diffusion model (Roeder and Douglass 1970), give values for the diffusion coefficient which are more than two orders of magnitude lower than radiotracer measurements. Tanner (private communication) has recently measured the self diffusion coefficient in cyclohexane using the pulsed field gradient NMR technique which shows good agreement with values calculated from the NMR relaxation results.

A powerful method with which to investigate the nature of the defect responsible for self diffusion in solids is to study the pressure dependence of a diffusion controlled process. Such measurements can be interpreted in terms of an activation volume, ΔV^* , for the diffusion process. In the case of metals, activation volumes are frequently found to be less than their respective molar volumes, V_m . This is taken to indicate inward relaxation of the surrounding atoms into a vacancy. Only one experimental investigation of the pressure dependence of self diffusion in organic molecular crystals has been reported previously (Anderson and Slichter 1966b). Very small activation volumes were found, with $\Delta V^*/V_m \approx 0.08-0.15$.

We have measured $T_{1\rho}$ for hexamethylethane and norbornylene at 296 K and for cyclohexane at 270 K, for hydrostatic pressures up to 2.8 kbar. Over most of this range $T_{1\rho}$ is entirely determined by modulation of intermolecular dipolar interactions by the relative translational motion of molecules. Impurity levels, estimated by vapour phase chromatography, for cyclohexane and norbornylene were less than 1000 ppm and 500 ppm respectively. The sample of hexamethylethane was that used previously (Chezeau *et al* 1971). Samples were degassed and contained in a glass cylinder sealed with a Kel-F plunger to transmit the pressure. Measurements were made at a Larmor frequency of 14.3 MHz and RF field strengths, H_1 , of 2.0 and 10.0 G. The spin-lattice relaxation times T_1 were also measured. T_1 is controlled by endospherical molecular reorientation over most of the pressure range investigated. Results for cyclohexane are shown in figure 1. The three substances chosen have different crystal structures as shown in table 1.

Table 1. Comparison of activation volumes ΔV^* with molar volumes V_m

	Crystal structure	ΔV^* ml mol ⁻¹	V_m ml mol ⁻¹	$\frac{\Delta V^*}{V_m}$	ΔH^* kJ mol ⁻¹	ΔS_f J K ⁻¹ mol ⁻¹
Hexamethylethane	BCC ^a $a_0 = 7.69 \text{ \AA}$	164	137	1.20	82.0 ^d	20.0 ^e
Norbornylene	HCP ^b $a = 6.08 \text{ \AA}$ $c = 9.81 \text{ \AA}$	86.4	94.6	0.90	48.9 ^e	10.1 ^h
Cyclohexane	FCC ^c $a_0 = 8.76 \text{ \AA}$	71.1	101	0.70	41.4 ^f	9.2 ⁱ

^a West (1934)

^b Jackson and Strange (1972)

^c Hassel and Sommerfeldt (1938)

^d Chezeau *et al* (1971)

^e Folland *et al* (1972, to be published)

^f Roeder and Douglass (1970)

^g Scott *et al* (1952)

^h Westrum (1969)

ⁱ Staveley (1962)

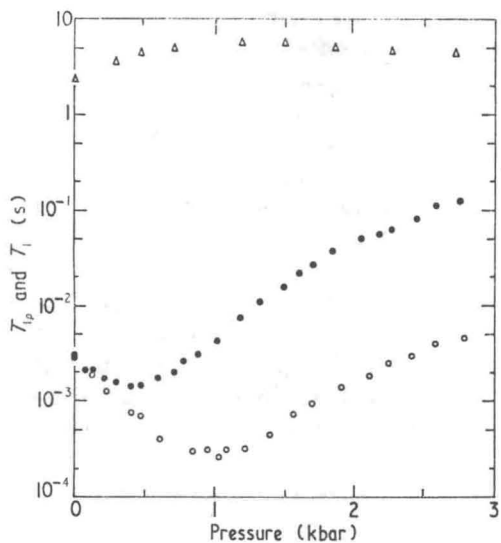


Figure 1. The experimental proton $T_{1\rho}$ and T_1 results for cyclohexane at 270 K plotted as a function of hydrostatic pressure. ● $T_{1\rho}$ at $H_1 = 10.0$ G; ○ $T_{1\rho}$ at $H_1 = 2.0$ G; △ T_1 .

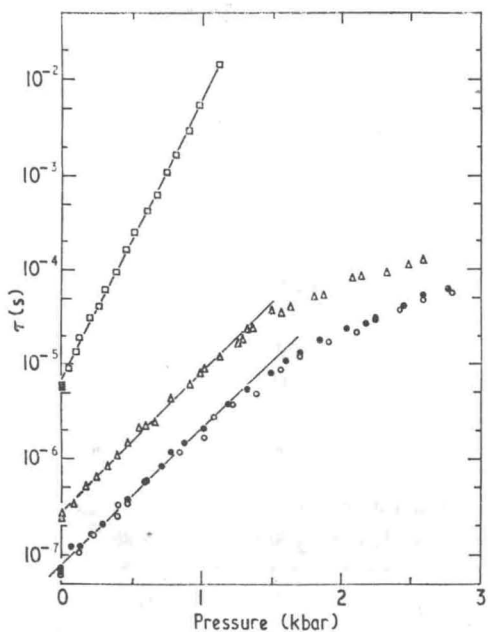


Figure 2. The translational correlation times τ for self diffusion plotted as a function of hydrostatic pressure. □ Hexamethylethane; △ Norbornylene; ○ cyclohexane ($H_1 = 2.0$ G); ● cyclohexane ($H_1 = 10.0$ G).

Measurements of the temperature dependence of $T_{1\rho}$ in these materials have previously been interpreted using a weak collision theory (Jones 1966) and correlation functions appropriate to a random walk model for self diffusion (Resing and Torrey 1963) with an average molecular jump time τ . Analysing our values of $T_{1\rho}$ in the same manner, we obtain τ as a function of pressure for each material, figure 2. In our analysis it is assumed that the strength of the intermolecular nuclear dipolar interaction is not pressure dependent. If the bulk compressibility is similar to that of comparable plastic crystals (Breitling *et al* 1971) the change in the strength of this interaction is unlikely to exceed 20% over the pressure range studied, whereas τ changes by two to three orders of magnitude. In the case of cyclohexane and norbornylene $T_{1\rho}$ passes through a minimum with increasing pressure. Since the depth of these minima is the same as the depth of minima obtained in temperature dependence studies at low pressure no significant change in this interaction had occurred. The values of τ obtained for cyclohexane from measurements at two different H_1 intensities are consistent (figure 2), thereby giving a useful check on our analysis.

A thermodynamic treatment of self diffusion (Shewmon 1963) provides an expression for the self diffusion coefficient

$$D = \gamma a_0^2 \nu \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (1)$$

where γ is a geometric factor, ν is the lattice vibration frequency, ΔG^* is the free energy of activation and a_0 is the lattice parameter. When self diffusion proceeds by molecular jumps of uniform distance a the self diffusion coefficient is related to τ by

$$D = a^2/6\tau \quad (2)$$

Therefore

$$\tau = \frac{a^2}{6\gamma a_0^2 \nu} \exp\left(\frac{\Delta G^*}{RT}\right) \quad (3)$$

The activation volume is defined as $\Delta V^* = [\partial(\Delta G^*)/\partial P]_T$ so that, using equation 3, ΔV^* is given by

$$\Delta V^* = RT \left(\frac{\partial \ln \tau}{\partial P} + \frac{\partial \ln \nu}{\partial P} \right)_T \quad (4)$$

Only the term $[\partial(\ln \tau)/\partial P]_T$ in equation 4 is determined from our experiment. Unfortunately, for these plastic crystals, data enabling calculation of $[\partial \ln \nu / \partial P]_T$ are not available. We estimate, using data for similar plastic crystals (Breitling *et al* 1971), that this term is unlikely to exceed 10% of ΔV^* . The tabulated values of ΔV^* represent only the first term in equation 4.

At pressures below 1.4 kbar $\ln \tau$ shows a linear dependence on pressure from which ΔV^* in the table is calculated. It can be seen that the ratios $\Delta V^*/V_m$ are of the order of unity suggesting a vacancy mechanism for self diffusion in these solids. The ratio is lower than unity for the two compounds with low ΔS_m . It is very similar to those found for close packed metals where single vacancy mechanisms and inward relaxation of surrounding molecules into a vacancy are generally accepted. For hexamethylethane (bcc) the ratio of 1.2 is significantly greater than the values ($\lesssim 0.5$) found for bcc metals.

Our value of ΔV^* , 71 ml mol⁻¹, for cyclohexane is considerably greater than the value 13 ml mol⁻¹ previously reported (Anderson and Slichter 1966b). This earlier value was obtained by measurement of the spin-spin relaxation time T_2 on unpurified reagent

grade cyclohexane. In addition to the fact that $T_{1\rho}$ allows measurement of much slower diffusion rates than is possible by measuring T_2 , we note that the previous T_2 measurement at atmospheric pressure and 257 K was 300 ms compared with later measurements on purified samples (Roeder and Douglass 1970) which gave $T_{1\rho} \approx 1.0$ ms. ($T_{1\rho}$ for low H_1 and T_2 should be equal at this temperature.) Our atmospheric pressure data agree with the more recent $T_{1\rho}$ data.

Rice and Nachtrieb (1959) have proposed a law of corresponding states which, in the low pressure limit, has the form $\ln D \propto T_f/T$ and which leads to the relation,

$$\frac{\Delta V^*}{\Delta H^*} = \frac{1}{T_f} \frac{dT_f}{dP} = \frac{\Delta V_f}{\Delta H_f}$$

The subscript f refers to the fusion parameters. This relationship holds well for metals and for the plastic crystal, white phosphorus (Nachtrieb and Handler 1955) In the case of cyclohexane the pressure dependence of the melting point is known (Babb 1963) enabling this relationship to be tested for an organic plastic crystal. Our measurements give $\Delta V^*/\Delta H^* = 1.82 \text{ ml kJ}^{-1}$ which compares well with $(1/T_f)(dT_f/dP) = 1.72 \text{ ml kJ}^{-1}$ at zero pressure. The value $\Delta H^* = 41.4 \text{ kJ mol}^{-1}$ obtained by NMR is used in preference to the radiotracer value.

For pressures above 1.4 kbar $\ln \tau$ does not vary linearly with pressure for cyclohexane and norbornylene. Further experiments are in progress to elucidate this apparent anomaly and will be discussed with a more detailed account of these experiments elsewhere.

The endospherical molecular reorientation, detected by its influence on T_1 , is relatively insensitive to changes in pressure. The activation volumes which can be associated with this motion are 5.3 ml mol^{-1} for hexamethylethane, 4.1 ml mol^{-1} for norbornylene and 3.2 ml mol^{-1} for cyclohexane. These values are of the same order of magnitude as found in other molecular crystals (Anderson and Slichter 1966).

We tentatively conclude that in these three plastic molecular crystals, a single vacancy diffusion mechanism is dominant. Some inward relaxation of surrounding molecules is indicated in cyclohexane and norbornylene which have a low entropy of fusion and a close packed structure, but apparently not in hexamethylethane.

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