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Technical Report on Contract

N6 ONR-269, T. O. III and X

by

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A STUDY OF NUCLEAR RESONANCE OF THE SUPERCOOLED ROTATIONAL

TRANSITION OF 2,3-DIMETHYLBUTANE\*†

\*Contribution from the College of Chemistry and Physics of The Pennsylvania State University †

This research was carried out under Contract N6 ONR-269 (T.O. III and X) of the U.S. Office of Naval Research

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SUMMARY

The proton magnetic resonance lines during the transition of the supercooled variety of 2,3-dimethylbutane to the normal state have been investigated. An increase in rotational characteristics is followed by an exponential decrease in peak height of the resonance line. This is interpreted in terms of a transition around Frenkel holes. An observed asymmetry in the line shape is treated mathematically on this basis.

INTRODUCTION

This work is part of a series of investigations of rotation in solid solutions. Work on the system, neohexane-cyclopentane, has already been reported.<sup>1</sup> The investigation of rotation in solid

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<sup>1</sup> J. G. Aston, B. Bolger, R. Trambarulo, H. Segall, J. Chem. Phys., 22, 460 (1954)

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2,3-dimethylbutane is the beginning of work on the system, neohexane-2,3-dimethylbutane. The results with 2,3-dimethylbutane have their own significance outside of any results of the whole phase study.

2,3-dimethylbutane exhibits one transition point of the rotational type below

its normal melting point of  $145.19^{\circ}\text{K}$ .<sup>2</sup> The ability of 2,3-dimethylbutane to supercool

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<sup>2</sup> D. R. Douslin, H. M. Huffman, J. Am. Chem. Soc., 68, 1704 (1946)

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below its transition temperature of  $136.07^{\circ}\text{K}$  has been noted previously in a series of thermal studies<sup>3</sup> and in the

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<sup>3</sup> J. Smittenberg, H. Hoog, R. A. Henkes, J. Am. Chem. Soc., 60, 17 (1938)

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determination of its Raman Spectrum 4, 5. The most reliable

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<sup>4</sup> N. Sheppard, G. J. Szasz, J. Chem. Phys., 17, 86 (1949)  
<sup>5</sup> N. Sheppard, J. K. Brown, H. Chem. Phys., 19, 976 (1951)

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determination of its heat capacity was reported without any indication of difficulties due to supercooling although difficulties due to supercooling were noted with its isomer, 3-methylpentane.<sup>2</sup>

The existence of relatively free rotation or no rotation in the solid state can be distinguished by the width of the proton resonance absorption line.<sup>6a,b</sup> A wide line (greater than about 4 gauss) which indicates no

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<sup>6a</sup> H. S. Gutowsky, G. E. Pake, J. Chem. Phys., 18, 162 (1950)      J. Chem. Phys.,  
<sup>6b</sup> H. S. Gutowsky, G. B. Kistiakowsky, G. E. Pake, E. M. Purcell, 17, 972 (1949)

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rotation, is due to the existence of internal magnetic fields produced by neighboring protons. Relatively free rotation eventually causes the internal fields to average out to zero and produces a narrow line (less than about 4 gauss).

In the present investigation we have been able to work with the supercooled rotating variety down to  $65^{\circ}\text{K}$ . and have found that it slowly loses its freedom of rotation on standing at constant temperature as well as by cooling. When this super-

cooling is removed by the occurrence of the transition to the normal state the substance warms up due to the heat of transition but does not reach the transition temperature. During the transition the adsorption line narrows from about 8 gauss to 3.5 gauss and does not broaden to the 9 gauss of the normal non-rotating variety until the transition is complete. The only conceivable explanation of this phenomenon is that the transition occurs in a labile configuration around Frenkel holes<sup>7</sup> producing a lower but constant

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<sup>7</sup> J. Frenkel, Kinetic Theory of Liquids, Chaps. I, III, Orford, Clarendon Press (1946)

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spin-lattice relaxation time and hence a higher peak height as well as a narrower line due to increased rotation. The configuration around the hole stays in this labile state until the transition is practically complete.

#### EXPERIMENTAL

The nuclear magnetic resonance apparatus, permanent magnet, and cryostat have been described previously.<sup>1</sup> The resonance absorption occurred at 23.592 magacycles in a field of 5541 gauss. All the line shapes were recorded after passage through a lock-in amplifier whose output is proportional to the first derivative of the absorption line. The width of the line was taken as the width in gauss between the maximum and minimum of the derivative curve. The sample of 2,3-dimethylbutane, with less than 0.1 mole percent impurity, was prepared and purified by fractional melting.

#### RESULTS

The existence of the "supercooled rotating" state was first noticed when a sudden rise of 17° occurred in the afterdrift of a rough heat capacity point. It was simultaneously noticed, with surprise, that the proton absorption line had narrowed during the period of heat evolution and subsequently widened to approximately the original width. The experiment was repeated three times with consistent results.

During the first run the temperature of the sample of 2,3-dimethylbutane was lowered to 60°K. The line width narrowed slightly from 8.29 gauss at 60.2°K. to 7.14 gauss at 88.0°K. on warming. After the sample was warmed a few degrees further the irreversible transition to the normal non-rotating crystalline state started at 102.9°K. During the temperature rise to about 119°K, due to heat evolution, a narrow line width of 4.04 gauss was recorded at 103.3°K. The start and end of the rapid temperature rise were taken as the start and end of the transition. The sample was allowed to cool slightly after the transition and a broad line width of 8.55 gauss was recorded at 115.6°K. A second run was made to confirm the narrowing of the line during the transition period. The temperature was lowered to 64°K in this case and a broad line 8.15 gauss wide persisted after warming to 79.2°K. The irreversible transition began at roughly 86°K and ended at 110.2°K. During this period a narrow line of 3.83 gauss was recorded at 89.9°K. and second one 3.41 gauss wide at 105.1°K. A broad line 9.21 gauss wide at 108.7°K. was recorded for the normal state after the transition.

The next two runs were made to confirm the suspicion that the "supercooled rotating" state existed in two forms. In the third run the sample was cooled to only 102°K, and allowed to drift without being heated or cooled. In this run the absorption line never broadened to more than 3.4 gauss before the transition. The transition started at 101.9°K. and finished at 124.7°K. The line widths taken during the transition were 3.36 gauss at 104.0°K. and 3.43 gauss at 122.3°K. The fourth run was made under conditions similar to those of the third run except that the lowest temperature was 87.7°K. and the run ended at 104.2°K. Once again the line never broadened before the transition. The line during the transition was 3.73 gauss wide at 88.3°K. and then broadened to 9.56 gauss at 102.7°K. after slight cooling following the transition. Then the sample was cooled to 86.0°K. where the absorption line for the normal state broadened to 12.38 gauss.

The above data has been selected to compare the line widths of the different varieties or states of 2,3-dimethylbutane at certain chosen temperatures. The comparison in groups close to the temperatures of 89°K, 103°K and 115°K is clearly

shown in table 1. Line widths at other temperatures have been included for comparison. The sample is said to be in the "supercooled rotating" state before the irreversible transition has occurred, in the transition state during the transition and in the non-rotating or normal state after the transition. It will be noticed that all three states have been observed at 89°K and 103°K in the course of the four runs. The group of data at 88°K show a width of 7.14 gauss for the "supercooled rotating" variety from run 1 compared with widths of 3.83 and 3.78 during transition in runs 2 and 4 respectively. Thus the narrowing during transition cannot be due to the spontaneous change of temperature.

A typical curve of line width vs. temperature is shown in more detail for run 2 in fig. 1. The actual line shape derivatives before, during and after the irreversible transition in run 2 are shown in fig. 2. The temperature change during the recording of one line width was 0.2° during the ordinary part of the warming curve. The temperature rose as much as two degrees while taking the line widths in the irreversible transition period due to the rapid rise in temperature.

A heat of transition of 1350 ± 200 cal./mol was estimated from run 3 in which the fore and afterdrifts of temperature were most favorable for estimating the start and end of the transition. That this compares well with the reversible calorimetric value of 1552 cal./mol at 136.07°K.<sup>2</sup> establishes that the entire rotational transition was being observed. The total time of the transition varied from 6 to 16 minutes in the four runs.

The end of the transition was marked by a sharp change in the line shape in runs 1 and 2. This can be seen from fig. 2 where the transition ends in the middle of the <sup>next to the</sup> last trace as was evident from the temperature reading. A discontinuity in the slope of the trace is noticed. The end occurred between recordings in runs 3 and 4.

In run 3 it was possible to estimate the manner in which the peak height decreased during the transition because three absorption line derivatives were recorded. Assuming that the transition around the Frenkel holes, involving nearest and second

nearest neighbors (and perhaps others also), involves a state of constant spin-lattice relaxation time, this decrease in peak height could be used to evaluate a first order rate constant for the phenomenon occurring around the hole. Since it takes approximately three minutes to record a line shape, the shape of the line is a function of this rate constant and could be evaluated if the rate constant were known and the spin-lattice relaxation time were constant. It therefore seemed best to group together the line shape and rate of decay and work out the theory of the effect on the basis of the above assumptions.

The line shapes during the transition can be quantitatively accounted for by assuming that the peak height of a gaussian shaped "line" decays exponentially with time during the recording of the derivative. The absorption line has the form

$$g(\nu) = Ae^{-mt'} e^{-2\pi^2 (\nu - \nu_0)^2 T_2} \quad (1)$$

where

$t'$  = time in seconds during transition,  $A$  = normalization constant when  $m = 0$  and  $m$  is the specific decay constant associated with the transition around the "Frenkel holes" and the other terms have their usual meaning. The frequency is changed linearly with time by a clock motor on the tuning condenser so that we may replace  $2\pi^2 (\nu - \nu_0)^2 T_2$  by  $(T' - T_0)^2 / 2b^2$  where  $t_0$  is the time at which  $\nu = \nu_0$ .

$$\text{Then } g(t) = Ae^{-mt_0} e^{-mt} e^{-t^2 / 2b^2} \quad \text{where } t = t' - t_0 \quad (2)$$

By a straight forward calculation the slopes at the inflection points are given by

$$g'(t)_{\pm} = \mp Ab^{-1} \exp(-mt_m) \exp \left[ -(1 + 3m^2 b^2 \pm 4mb) / 2 \right] \quad (3)$$

$t_m$  is the time of the observed maximum in  $g(t)$  and equals  $t_0 + m b^2$

The average of the absolute values of the two slopes is given by

$$g'(\nu) = \frac{g'(\nu) - g'(\nu)}{\nu} + = Ke^{-mt_m} \quad (4)$$

where  $K$  is a function of the constant,  $A$ ,  $m$  and  $b$ .

The ratio of the slopes for a given line is

$$R = \left| \frac{g'(\nu) -}{g'(\nu) +} \right| = e^{4mb} \quad (5)$$

which means that the line shape derivative should be asymmetrical.

In order to test equations (3) and (4) the logarithm of the slope was plotted for run 3 against  $t_{m\lambda}$  as shown in fig. 3. The squares represent  $\log_e g' (t)$  for each line slope recorded during the transition while the closed and open circles represent  $\log_e g' (t)_-$  and  $\log_e g' (t)_+$  respectively. The linear relationship with the same slope in each case is quite evident. The least square value of m is  $(1.01 \pm 0.01) \times 10^{-3} \text{ sec}^{-1}$ . Corresponding to a half life of 11.4 minutes, a rate constant m was also calculated for runs 2 and 4 even though only two lines were recorded during the transition in each run. In run 2,  $m = 15 \times 10^{-3} \text{ sec}^{-1}$  while  $m = 3.1 \times 10^{-3} \text{ sec}^{-1}$  in run 4. A fifth run was made to determine m from a large number of recordings during the transition. The least square method for 6 points in this run gives  $m = 1.25 \times 10^{-3} \text{ sec}^{-1}$ .

The value of b is determined from the half width which should be constant for all the lines during the transition.  $b = 1/2 \Delta H$  (6)

Experimentally we have from run 3

$$\Delta H = 3.37 \pm 0.03 \text{ gauss}$$
$$\text{or } b = 21.5 \pm 0.2 \text{ sec}$$

since the radio frequency spectrometer was changed at the rate of 0.07819 gauss/sec. The other runs confirmed this value of b.

The asymmetry ratio  $\nu$  was calculated from equation (5) and compared with the experimental value for the 3 lines as shown below

$$\nu \text{ (calc.)} = 1.091$$
$$\nu_1 = 1.105$$
$$\nu_2 = 1.082$$
$$\nu_3 = 1.102$$

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$$\text{average } \nu_{exp} = 1.096$$

The small discrepancy between observed and calculated values can be accounted for by the uncertainty in the position of the base line of the derivative curves.

This exponential decrease in peak height is not to be confused with the change in

peak height that is used to make an absolute determination of the spin-lattice relaxation time  $T_1$ .<sup>8</sup>

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<sup>8</sup> M. Bloembergen, E. M. Purcell, R. V. Pound, Phys. Rev., 73, 679 (1948)

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#### DISCUSSION

It is generally expected that a solid which is supercooled below its transition point will maintain roughly the same amount of rotation as it normally has above the transition point. In 2,3-dimethylbutane it has been found possible to remove that rotation in the "supercooled rotating" state without going to the normal state by cooling to 64°K. Somewhere near this temperature the rotation of the molecules apparently becomes "locked-in" by some interaction. This is clearly shown by the fact that rotation persists in the "supercooled rotating" state if the sample is only cooled to 87°K.

As the sample, whose molecules are "locked-in", warms up an irreversible transition occurs to the normal state below the 136°K. transition point. As part of this irreversible transition the structure apparently loosens up before going to its final form so that the molecules are free to rotate in this intermediate state. The rotation is shown by the temporary narrowing of the proton absorption line which occurred in runs 1 and 2. This loosening up of the structure evidently starts with the neighbors of "Frenkel holes".<sup>7</sup> The ability to observe these Frenkel holes is dependent on the existence of the molecules in the "locked-in" state. To start rotating and under go the transition, a molecule moves into a hole leaving another hole. In run 2, at about 90°K, the intensity of the resonance absorption increased about 50% at the start of the transition; it then fell off exponentially as in a first order reaction but the line width stayed constant. This subsequent decrease in intensity is due to the decrease in the concentration of Frenkel holes about which the transition has not yet occurred. The transition can be expected to be of the first order since

the rate of decrease of Frenkel holes can be expected to be proportional to the number of holes.

It should be noticed that in the transition region in the above treatment, experimentally there is no room for a contribution to the absorption line, by the new (stable) phase into which the compound is changing. The results indicate no contribution to the resonance absorption by this phase until the transition is over. This is undoubtedly connected with the fact that, during the transition, some of the molecules are rotating with the period of the Larmor precession as they pass into the non-rotating form. The resulting coupling can produce great broadening of the line of the non-rotating forms or perhaps even saturate it. Either effect would reduce the intensity of adsorption.

The rate constant would be characteristic of the transition if the initial and final products were thermodynamically stable. Since the supercooled state is not stable the variation in the rate constant for different runs will indicate whether there is a tendency for a metastable or a randomly unstable state to occur in the supercooled solid. The fact that three determinations of the rate constant agree within a factor of 3 tends to indicate a metastable supercooled state. The fourth determination is off by an additional factor of 4 but this value of  $m$  is not too reliable since it was calculated from only two points. There is no trend in the values of  $m$  which indicate any temperature dependence. It is therefore to be concluded that the energy of activation is small.