

SOLID-SOLID PHASE TRANSITIONS DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY

PART I. TETRAHEDRAL SUBSTANCES

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ABSTRACT

Although the plastic crystal phenomenon has been observed by others in such tetrahedral substances as neopentane, pentaerythrityl fluoride, tertiary butyl halides, and pentaerythritol, we have found that with few exceptions the property can be observed in compounds $CR^1R^2R^3R^4$, where R's are methyl, methylol, amino, and carboxy. Larger groups, such as ethyl, bromomethyl, iodomethyl, carboxymethyl, etc. inhibit the solid-solid transition. New enthalpy of transition data are presented for 2-hydroxymethyl-2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2,2-dimethyl-1-propanol, 2-amino-2-hydroxymethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol, 2-hydroxymethyl-2-nitro-1,3-propanediol, 2-methyl-2-nitro-1,3-propanediol, 2,2-dimethylpropionic acid, and 2,2-bis(hydroxymethyl)propionic acid. In all of these substances, the entropy of fusion is approximately equal to the communal entropy. Transition entropies, however, reflect new reorientation possibilities, often considered a property of the liquid state, but which have been demonstrated by others with the use of n.m.r. and dielectric studies to also be a property of the mesocrystalline phase. Because of the many reorientation possibilities in these substances, transition entropies may be very high, and on the basis of these data and data in the literature the following order of the contribution of various groups can be established:



Owing to the low enthalpies of fusion, traces of impurities can often significantly lower and broaden the fusion temperature, but the transition temperatures are less affected, are often very sharp, and more readily characterized the substance.

INTRODUCTION

Timmermans first observed a phenomenon that a number of molecular crystals of nearly spherical substances had unusually low entropies of fusion (less than 5 e.u.) for their homologous series¹. The solids belonging to this class are characterized by having unexpectedly high melting points, unusually high vapor pressures in the solid state, soft and waxy character, cubic crystal structures in the plastic phase, and solid-state transitions. He called these materials plastic crystals. The transition to the

plastic crystalline phase has since been shown to coincide with the onset of molecular reorientation and the low entropies of fusion of the plastic crystals have been correlated with the communal entropy (2 e.u.), which corresponds approximately to the entropy change in spherical molecules such as rare gases (3.2 e.u.). A number of experimental and theoretical investigations have contributed to an understanding of this mesocrystalline phase, and the results, including crystallographic, n.m.r., calorimetric, and dielectric constant data, have been summarized in several excellent reviews^{2,3,4}.

It has also been recognized that in addition to molecular reorientational disorder, molecular crystals in the plastic state may also have conformational disorder not present in the normal solid state. Thus, the entropy of transition, which is equal to $R \ln(A/B)$, where A and B are the statistically possible orientations in the two phases, may be much greater than the value determined by the integral symmetry numbers for the molecular reorientation. The most striking example of this effect is the 22.8-e.u. change reported for pentaerythritol⁵ in contrast to the 4.4-e.u. value reported for neopentane⁶. Attempts have been made to identify the types of conformational disorder in pentaerythritol and to correlate the disorder with entropy changes^{7,8}.

It was the purpose of this work to identify tetrahedral substances in addition to pentaerythritol that have high entropies of transition as a consequence of many possibilities for conformational disorder, and to identify, insofar as possible by the technique of differential thermal calorimetry, correlations between the heat content of the transitions and chemical structure. Attempts were also made to establish, within particular chemical series, structural changes that were permissible without inhibiting the mesocrystalline phase and to determine if a relationship existed between a structural change and a change in the transition temperature.

EXPERIMENTAL

Apparatus and procedure

All qualitative data were obtained with a DuPont 900 Differential Thermal Analyzer at a heating rate of 15°/min in an air atmosphere. The quantitative data were obtained with the Differential Scanning Calorimeter module at a heating rate of 10°/min with hermetically sealed pans. Qualitative values were determined on the basis of the temperature range of the extrapolated onset of the transition or fusion endotherm and the peak. Suitable corrections were made for the temperatures, which were determined with a chromel-alumel thermocouple.

Calibration

A calibration for the calorimeter cell was determined by constructing a smooth curve of the transition or fusion temperatures of standard substances *vs.* a calibration coefficient calculated from the heating rate, the weight of the sample, the plotted areas, and the instrument sensitivity for the x and y axes. The specific heats of the standards used in this calibration were: mercury⁹, 2.74; acetamide¹⁰, 63.5;

magnesium chloride hexahydrate¹⁰, 40.3; indium⁹, 6.79; and tin⁹, 14.2 cal/g. The maximum variation for replicate values for each point on the calibration curve was less than 5 percent.

Data obtained on the basis of the experimental work with the use of this calibration curve could in some instances be compared with enthalpy data reported in literature, although not all of the reported values are of equal reliability. The values are summarized in Table I.

TABLE I

COMPARISONS OF SELECTED EXPERIMENTALLY DETERMINED HEATS OF FUSION AND TRANSITION WITH LITERATURE VALUES

Substance	Phase change	Onset temperature (°C)	ΔH (cal/g)		
			Experimental	Literature	Reference
2,2-Dimethyl-1-propanol ^a	fusion	51	11.0	12.0	11
Hexachloroethane	transition	71	6.4	8.30	12
Camphorquinone	fusion	199	8.1	9.7	13
2,2-Dimethylpropionic acid	fusion	32	5.8	7.8	13
Pentaerythritol	transition	181	72.0	77.1	5
	fusion	255	8.8	12.0	5
Ammonium nitrate	transition	127	13.2	12.62	10
	transition	88	4.21	3.998	10

^aThe reference incorrectly states the fusion temperature as -9°C .

Materials

Pentaerythritol was recrystallized from water and sublimed three times under vacuum. The purification steps did not significantly affect the heats of fusion or transition or the transition temperature, but did narrow the fusion range. Sublimation was discontinued when the fusion range was no longer narrowed, and the 266° fusion-temperature reported by Nitta⁵ could not be achieved. Unpurified 2-methyl-2-hydroxymethyl-1,3-propanediol and 2,2-dimethyl-1-propanol obtained from Aldrich Chemical Company was used. Literature values for the fusion temperatures of these two compounds are $202\text{--}203^{\circ}\text{C}$ ¹⁴ and $54.5\text{--}55.5^{\circ}\text{C}$ ¹⁵, resp. 2,2-Dimethylpropanediol was recrystallized from benzene. The reported m.p. for this substance is $126\text{--}127^{\circ}\text{C}$ ¹⁶. The 2-amino-2-hydroxymethyl-1,3-propanediol was recrystallized from dry ethanol. It is reported to melt at $169\text{--}170^{\circ}\text{C}$ ¹⁷. 2-Amino-2-methyl-1,3-propanediol, which is reported to melt at $108\text{--}110^{\circ}\text{C}$, was recrystallized five times and twice sublimed. It appeared to absorb moisture if not protected from the atmosphere. 2-Amino-2-methyl-1-propanol was redistilled twice on a 30-in spinning band column. 2-Hydroxymethyl-2-nitro-1,3-propanediol was recrystallized three times from an ethyl acetate-benzene mixture. Reported melting points for this substance include the following: 168 (dec.)¹⁸, 172 ¹⁹, 180 ²⁰, and 214°C ²⁰. 2-Methyl-2-nitro-1,3-propanediol was recrystallized four times from dry ethanol. Its reported melting points include $154\text{--}156$ ²¹ and $146\text{--}147^{\circ}\text{C}$ ¹⁸. 2,2-Bis(hydroxymethyl)propionic acid, which is reported to melt at

183²² and 192–194°C²¹, was recrystallized from water. Pivalic acid was purchased from Eastman Organic Chemicals, 2-methyl-2-nitro-1-propanol from Aldrich Chemical Company, and tetramethylammonium chloride from Fisher Scientific Company and used as received. The reported melting point for 2-methyl-2-nitro-1-propanol is 87–88°C²³ and pivalic acid, 35.5°C²⁴.

RESULTS

Experimentally determined heats of transition and fusion for substances with mesocrystalline phases are reported in Table II. The average deviation for replicate determinations in the transition values was 1.6 cal/g and in the fusion values 0.4 cal/g, the percentage error for small values being larger than for large values.

TABLE II

TRANSITION AND FUSION ENTHALPY AND ENTROPY DATA FOR VARIOUS TETRAHEDRAL SUBSTANCES

Substance	Transition			Fusion		
	Temperature (cal/g)	ΔH (cal/g)	ΔS (e.u.)	Temperature (°C)	ΔH (cal/g)	ΔS (e.u.)
Pentaerythritol	182–183	72.0	21.5	258	8.9	2.3
2-Hydroxymethyl-2-methyl- 1,3-propanediol	81	46.1	15.6	197	10.7	2.7
2,2-Dimethyl-1,3-propanediol	40–43	31.3	10.3	125–126	10.8	2.8
2,2-Dimethyl-1-propanol	–31	12.1	4.4	51–54	11.0	3.0
2-Amino-2-hydroxymethyl- 1,3-propanediol	131–134	67.6	20.3	166–169	6.0	1.7
2-Amino-2-methyl-1,3- propanediol	78–80	57.3	17.2	110–112	6.8	1.9
2-Hydroxymethyl-2-nitro- 1,3-propanediol	80–82	35.5	15.2	decomposition at 184°		
2-Methyl-2-nitro-1,3- propanediol	79–80	45.5	17.5	149–153	6.8	2.2
2-Methyl-2-nitro-1-propanol	35–39	34.5	13.3	88–89	7.5	2.5
2,2-Bis(hydroxymethyl)propionic acid	152–155	68.6	21.7	194–197	6.4	1.8
2,2-Dimethylpropionic acid	7–9	20.5	7.5	32–36	5.8	1.9
Tetramethylammonium chloride	262–265	21.6	4.4	sublimation		

A large number of substances were screened qualitatively, and those listed in Table III did not exhibit a mesocrystalline phase.

Temperatures of transition and fusion are also reported in Table II. In addition, trimethylacetone exhibited a transition at –34 and a fusion at 15–20°C.

DISCUSSION

It is apparent from the data in Tables II and III that very subtle changes in molecular geometry and size can inhibit the mesocrystalline phase. Although neopentane, pentaerythrityl fluoride²⁵, and pentaerythritol have transitions, substances with larger substituent groups do not have a mesocrystalline phase. This difference was

TABLE III

TETRAHEDRAL SUBSTANCES WITHOUT SOLID-SOLID TRANSITIONS

<i>Substance</i>	<i>Temperature range examined (°C)</i>
Pentaerythrityl tetrabromide	-180 to 160
Pentaerythrityl tetraacetate	-60 to 79
Pentaerythrityl tetramethanesulfonate	-50 to 202
Tetra- <i>tert</i> -butyl thiopentaerythritol	-60 to 116
2,2-Bis(hydroxymethyl-1-butanol)	-50 to 56
Dimethylmalonic acid	-50 to 198
Tris(chloromethyl)acetic acid	-60 to 108
3-Chloro-2,2-dimethylpropionic acid	-30 to 38
Tetramethylammonium bromide	0 to 392
Trimethylacetamide	-40 to 152
2-Amino-2-methylpropionic acid	-140 to 300

identified in the tetrabromide, the tetraacetate, the tetramethanesulfonate, and the tetra-*tert*-butylthioether. It has also been reported that the tetrachloride does not have a transition²⁶ below 27°C. The inhibiting effect of halomethyl groups is also evident in failure of tris(chloromethyl)acetic acid to have a solid-state transition while pivalic acid does. Although the possible interchange of halomethyl for methyl groups in neopentane is limited to the fluoromethyl groups, all degrees of substitution of hydroxymethyl for methyl groups provide substances with mesocrystalline phases. Also, in the acid series, hydroxymethyl substitution does not suppress the solid-state transition as evidenced by 2,2-bis(hydroxymethyl)propionic acid. Very slight changes in substitution with loss of symmetry cal. also inhibit the mesocrystalline phase. For example, 2,2-bis(hydroxymethyl)-1-propanol has a solid-solid transition, 2,2-bis(hydroxymethyl)-1-butanol does not; trimethylacetic acid has a transition; trimethylacetamide does not.

The extent of functional substitution can also determine if a mesocrystalline phase occurs. Substitution of one methyl group for a carboxy group in neopentane (pivalic acid) gives a plastic crystal; the second substitution (dimethylmalonic acid) inhibits the transition. Although plastic crystalline phases were detected in 2-amino-2-hydroxymethyl-1,3-propanediol and 2-amino-2-methyl-1,3-propanediol, no phase change could be detected in 2-amino-2-methyl-1-propanol. Also, 2-amino-2-methylpropionic acid did not exhibit a transition. A single nitro group could be substituted for a methyl group in all the hydroxymethyl derivatives.

It was unexpected that tetramethylammonium chloride has a transition while tetramethylammonium bromide does not, at least within the temperature range examined. The transition should be wholly attributed to the reorientation of the cation, which is the same in both substances. The larger molecular size of the anion may lower the energy requirement for reorientation sufficiently that its onset may occur below the temperature range examined.

If the fusion temperatures of pentaerythritol, 2-hydroxymethyl-2-methyl-1,3-

propanediol, 2,2-dimethyl-1,3-propanediol, and 2,2-dimethylpropanol are plotted against the extent of hydroxymethyl substitution and the line is extrapolated to neopentane (no hydroxymethyl substitution), the point is found to coincide with the reported value for the fusion of neopentane⁶, -17°C . Since all of these substances are in a similar state at the fusion temperature, that is, only communal entropy is to be gained, it is not surprising that the contribution of the hydroxymethyl groups to the cohesive energy stabilizing the mesocrystalline state is additive.

This observation is useful in predicting transition temperatures and predicting the existence of a mesocrystalline phase in substances not yet examined. The correlation between extent of substitution and transition temperatures is not exact, but does approximate a straight line. If the fusion temperatures of pivalic acid and 2,2-bis-(hydroxymethyl)propionic acid are plotted against extent of hydroxymethylation, a fusion temperature of 114°C would be predicted for 2-hydroxymethyl-2-methylpropionic acid. The value reported in the literature for this compound is 123°C ²⁷. A plot of the transition temperatures indicates that a transition should occur at about 78°C . A similar extrapolation predicts a fusion temperature of 276°C for tris(hydroxymethyl)acetic acid, but the literature value is $210\text{--}213^{\circ}\text{C}$ ²⁸, indicating that the substance may not have a mesocrystalline phase. A plot of the values for 2-hydroxymethyl-2-nitro-1,3-propanediol, 2-methyl-2-nitro-1,3-propanediol, and 2-methyl-2-nitro-1-propanol predict a fusion temperature for 2-methyl-2-nitropropane of 23°C , which is the reported value²⁹. Extrapolated transition temperatures predict a value of -6°C *vs.* the reported -15°C . The fusion temperature obtained for 2-hydroxymethyl-2-nitro-1,3-propanediol is 213°C by extrapolation. After numerous purifications of this substance in this work, the best value that could be obtained was a 184°C with decomposition. However, it is interesting that a 214°C fusion temperature is reported for this substance²⁰, although many lower values are also reported. The transition temperature observed for this substance in this work also occurs at a much lower-than-expected value.

Entropies of fusion approximated the 2-e.u. value associated with the communal entropy. High transitional entropies were found for substances with many possible conformational orientations. Some of the values were nearly as large as the value for pentaerythritol.

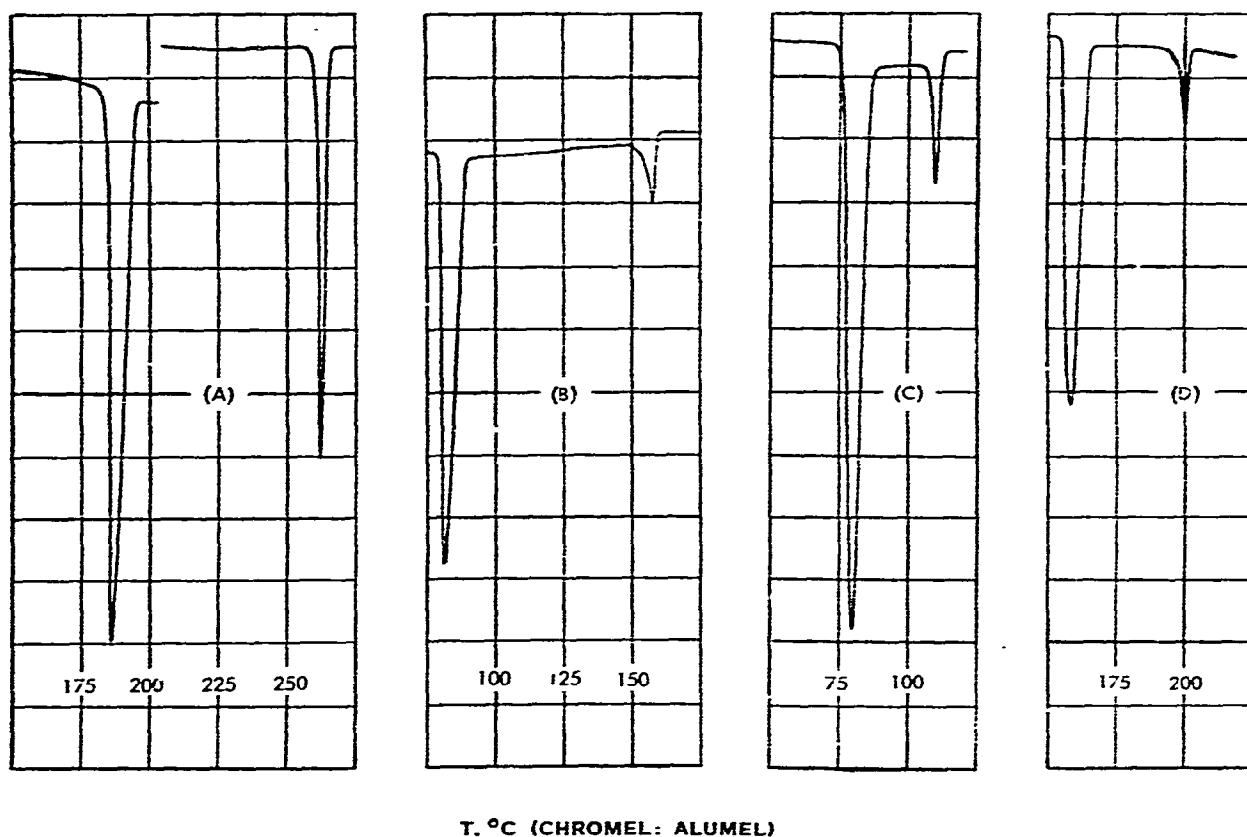
In the series pentaerythritol, 2-hydroxymethyl-2-methyl-1,3-propanediol, 2,2-dimethylpropanediol, 2,2-dimethyl-1-propanol, the substitution of a hydroxymethyl group for a methyl group increased the entropy increment by 5 e.u. indicating an equal number of new conformational possibilities is effective each time the substitution is made. The entropy increments are not so regular when other functional groups, the amine, nitro, and carboxy, are present. One observation that cannot be easily rationalized is that the transitional entropy for 2,2-dimethyl-1-propanol (4.4 e.u.) is the same as the reported transitional entropy for neopentane (4.4 e.u.)⁶. The good agreement between the reported value for neopentane and the isoelectronic and isosteric tetramethylammonium cation in tetramethylammonium chloride (4.4 e.u.) tends to confirm the literature value for neopentane.

Of particular interest is the unexpectedly low value for the transitional entropy for 2-hydroxymethyl-2-nitro-1,3-propanediol (15.2 e.u.), both in comparison with 2-methyl-2-nitro-1,3-propanediol (17.2 e.u.) and 2-amino-2-hydroxymethyl-1,3-propanediol (20.3 e.u.). The most probable explanation for the low value is steric restriction of conformational states in the presence of the large nitro group.

Taking into account literature values for pentaerythrityl fluoride (12.7 e.u.), neopentane (4.4 e.u.), carbon tetrachloride (4.9 e.u.), and carbon tetrabromide (4.4 e.u.), as well as the data in Table II, the following order of the contribution of various groups to the transitional entropies of tetrahedral substances can be established:



Transitions are often phenomenologically differentiated as first or second order depending on whether or not the transition occurs at a single temperature or over a range of temperatures. Since differential thermal analysis is a dynamic method rather than an equilibrium method, the method cannot differentiate transition order. There was no apparent difference in the sharpness of the endotherms, except when impurities



T. °C (CHROMEL: ALUMEL)

Fig. 1. Typical differential thermal analysis traces showing transition and fusion endotherms: (A) pentaerythritol (fusion determined at twice the sensitivity as the transition); (B) 2-methyl-2-nitro-1,3-propanediol; (C) 2-methyl-2-amino-1,3-propanediol; (D) 2,2-bis(hydroxymethyl)propionic acid.

were present, and under this circumstance, the fusion range was broadened. Several representative differential thermal analysis traces are reproduced in Fig. 1. Sample purification seldom had a marked effect on transition temperature, but could markedly narrow the fusion range and increase the fusion temperature. Such an effect is not unexpected since the extent of melting point depression can be predicted to be inversely proportional in the molar heat of fusion according to the Clausius-Clapeyron equation.

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