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SOLID-SOLID PHASE TRANSITIONS DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY

PART IV. NEW TRANSITIONS IN TETRAHEDRAL SUBSTANCES

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ABSTRACT

Data are presented to show that tris(hydroxymethyl)acetic acid, monochloropentaerythritol, monofluoropentaerythritol, difluoropentaerythritol, monoaminopentaerythritol, and diaminopentaerythritol exhibit solid-state transitions to a plastic crystalline state. Transitional enthalpies in many of these substances are lower than might be expected by analogy with related structures, suggesting that some configurational contributions to their entropy increments have been inhibited.

INTRODUCTION

In an earlier paper in this series[1], previously unreported first order solid–solid transitions were described for a number of tetrahedral substances of the type $CR^1R^2R^3R^4$; in which R's were methyl, methylol, amino, nitro, and carboxy. Substances in this class having the necessary symmetry to undergo discrete transitions (onset of reorientation freedom) and fusions (onset of translational freedom) were characterized by large transition entropies and low fusion entropies. These materials, often called plastic crystals, are sometimes defined as substances in which the fusion entropy is approximately equal to the communal entropy. The large transitional entropies require the concomitant onset of conformational disorder and reorientation freedom. Some data indicate the contribution of group efforts to the transitional entropies may be additive, but often the number of states of disorder required to satisfy the experimental entropy changes are too numerous to allow a quantitative estimate.

In order to obtain new data on the contribution of various functional groups to entropy changes in transition, as well as possible interactions between groups, compounds containing the carboxy, chloromethyl, fluoromethyl, and aminomethyl groups have been prepared and their fusion and transition temperatures and entropies determined. Six compounds with previously unreported solid-state transitions were found.

EXPERIMENTAL

All qualitative data were determined with a Du Pont 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. The procedure and calibration were described earlier[1]. The new data obtained are reported in Table I. Temperatures throughout this paper are reported in °C.

TABLE I

SUMMARY OF NEW ENTHALPY DATA FOR TRANSITIONS AND FUSIONS OF PLASTIC CRYSTALS

Compound	*Transition*			*Fusion*		
	Temp. (°C)	*ΔH (cal/g)*	*ΔS (e.u.)*	*Temp. (°C)*	*ΔH (cal/g)*	*ΔS (e.u.)*
Tris(hydroxymethyl)acetic acid	124–127	48.83	18.5	217–221	4.23	1.3
Monochloropentaerythritol	61–63	35.63	16.5	136–137	5.11	1.9
Monofluoropentaerythritol	68–72	33.28	13.5	203–207	10.68	3.1
Difluoropentaerythritol	18–20	21.37	10.3	Sublimes		
Tetrafluoropentaerythritol[a]	−29–−26	18.66	11.0	88–90	6.96	2.8
Monoaminopentaerythritol	86–91	45.86	17.3	200–208	7.87	2.3
Diaminopentaerythritol	68–73	44.20	16.6	159–160	9.34	2.9

[a] Reported[2] transition, −24°C, ΔS, 12.66 e.u.; fusion, 94°C, ΔS, 3.35 e.u.

Preparation of intermediates

Monobromopentaerythritol, m.p. 74–76° was obtained in a yield of 46% by Wawzonek's procedure[3] (Lit.[7] m.p. 75–76°). The method of Saucier[4] was employed to prepare dibromopentaerythritol, m.p. 107–110° (Lit.[4] m.p. 109–110°), and tribromopentaerythritol, m.p. 65–68° (Lit.[4] m.p. 65–68°). The yields were 45 and 51%, respectively. Issidorides's procedure[5] was followed for converting dibromopentaerythritol to 3-bromomethyl-3-hydroxymethyloxacyclobutane, b.p. 108–110° (1.6 mm), n_D^{20} 1.5093 [Lit.[5] b.p. 141–143° (1–2 mm), n_D^{20} 1.5101] in a 63% yield. Monobromopentaerythritol was similarly converted to 3,3-bis(hydroxymethyl)oxacyclobutane, m.p. 74–76°, b.p. 148–150° (0.6 mm) [Lit.[5] m.p. 84°, b.p. 128° (0.04 mm)] in a 42% yield and tribromopentaerythritol to 3,3-bis(bromomethyl)oxacyclobutane, b.p. 121–123° (19 mm), n_D^{20} 1.5409 [Lit.[7] b.p. 125° (23 mm)] in a 59% yield. All intermediates were further characterized by their infrared and n.m.r. spectra.

Tetrafluoropentaerythritol

Tetrabromopentaerythritol was converted by Gryszkiewicz-Trochimowski's procedure[8] to tetrafluoropentaerythritol in an 8% yield. After the tetrafluoropentaerythritol was distilled at 114–115°, sublimation gave a pure product, m.p. 88–90° (Lit.[8] b.p. 110–110.2°, m.p. 92°).

Difluoropentaerythritol

3,3-Bis(fluoromethyl)oxacyclobutane was prepared from 10.0 g (0.041 mole) 3,3-bis(bromomethyl)oxacyclobutane by Sorenson's method[9] and used without purification. After the 3,3-bis(fluoromethyl)oxacyclobutane was treated with a drop of sulfuric acid, refluxed 6 h, neutralized with 10% barium hydroxide, and extracted with ether, the ether extract was dried, evaporated, and the residue was sublimed. Difluoropentaerythritol (1.3 g, 21%) was obtained, after recrystallization from toluene and two sublimations under vacuum.

Monofluoropentaerythritol

3-Bromoethyl-3-hydroxymethyloxacyclobutane was converted to 3-fluoromethyl-3-hydroxymethyloxacyclobutane in the manner described for the preparation of 3,3-bis(fluoromethyl)oxacyclobutane except that a reaction temperature of 150° was used. The 3-fluoromethyl-3-hydroxymethyloxacylobutane was similarlyhydrolyzed to monofluoropentaerythritol in a 76% yield. In the procedure the crude product was extracted with ethyl acetate as well as with ether. After a crystallization from ethyl acetate and one sublimation, the pure product, m.p. 203–207° was obtained.

Monochloropentaerythritol

A mixture of 4.0 g (0.034 mole) of 3,3-bis(hydroxymethyl)oxacyclobutane in 40 ml of 36% aqueous hydrochloric acid was refluxed for 2 h, cooled, and mixed with 100 ml of saturated sodium chloride solution, then the mixture was extracted continuously for 38 h with ether. Evaporation of the ether and sublimation of the residue gave a solid, which upon recrystallization from ethyl acetate–chloroform afforded 3.2 g (62%) of monochloropentaerythritol, m.p. 138–139° (Lit.[10] m.p. 141°).

Monoaminopentaerythritol

Govaert's procedure[11] was employed to obtain monoaminopentaerythritol carbonate from 3,3-bis(hydroxymethyl)oxacyclobutane in a 64% yield. Sublimation of the carbonate gave monoaminopentaerythritol, m.p. 200–209° (Lit.[11] m.p. 207°).

Diaminopentaerythritol

After 100 ml of 50% aqueous ethyl alcohol saturated with ammonia at 0° and 10.0 g (0.055 mole) of 3-bromomethyl-3-hydroxymethyloxacyclobutane were heated in an autoclave at 190° for 22 h, the ethyl alcohol was distilled off. The residue in 50 ml of anhydrous ethyl alcohol was treated with dry ice until no more amine carbonate precipitated. When 2.1 g of amine carbonate was thermally decomposed and sublimed at 160° (0.2 mm), reprecipitated with dry ice, and resublimed, 0.8 g (11%) of diaminopentaerythritol, m.p. 159–160°, was obtained.

Tris(hydroxymethyl)acetic acid

Kutchen's procedure[12] gave 24% of tris(hydroxymethyl)acetic acid, m.p. 217–221° after recrystallization from ethyl alcohol (Lit.[12] m.p. 202–205°, and[13] 210–213°) from tris(chloromethyl)acetic acid.

TABLE II

ELEMENTAL ANALYSES OF COMPOUNDS

Compound	*Calc. for*	*Elemental analysis*[a] (%)				
		C	*H*	*Cl*	*F*	*N*
Tris(hydroxymethyl)acetic acid	$C_5H_{10}O_5$	39.89 (40.00)	6.65 (6.71)			
Monochloropentaerythritol	$C_5H_{11}ClO_3$	38.73 (38.84)	7.10 (7.17)	22.96 (22.94)		
Monofluoropentaerythritol	$C_5H_{11}FO_3$	43.54 (43.47)	7.67 (8.03)		13.52 (13.75)	
Difluoropentaerythritol	$C_5H_{10}F_2O_2$	42.80 (42.85)	7.12 (7.19)		26.97 (27.12)	
Tetrafluoropentaerythritol	$C_4H_8F_4$				52.44 (52.74)	
Monoaminopentaerythritol	$C_5H_{13}NO_3$	44.16 (44.43)	8.95 (9.69)			9.84 (10.37)
Diaminopentaerythritol	$C_5H_{14}N_2O_2$	44.64 (44.75)	10.27 (10.52)			20.69 (20.88)

[a] Percentages found with calculated values in parentheses.

Compound purity

Compound purities as assessed by elemental analyses are reported in Table II.

DISCUSSION

Considerable evidence was accrued that complexity of substitution could result in chemical interactions that prevent the estimation of functional group contributions to transitional entropies. The data do not allow an inference that the anomalies can be attributed to such chemical effects as hydrogen bonding or to steric crowding, but does clearly imply that with certain combinations of groups all configuration possibilities within functional groups do not occur.

In the substitution of a hydroxymethyl group for a methyl group within a series, an increase in the entropy of transition and fusion would be predicted. Contrary to expectations, the entropy transition values actually decrease in comparing 2,2-bis(hydroxymethyl)propionic acid[1] ($T_{tr} = 152$–$155°$, $\Delta S_{tr} = 21.7$ e.u., $T_f = 194$–$197°$) with tris(hydroxymethyl)acetic acid ($T_{tr} = 124$–$127°$, $\Delta S_{tr} = 18.5$ e.u., $T_f = 217$–$221°$). This comparison contrasts for example with a substantial increase between 2-hydroxymethyl-2-methyl-1,3-propanediol[1] ($T_{tr} = 81°$, $\Delta S_{tr} = 15.6$ e.u., $T_f = 197°$) and pentaerythritol[1] ($T_{tr} = 182$–$183°$, $\Delta S_{tr} = 21.5$ e.u., $T_i = 258°$). A similar restriction in new conformational disorder has been observed in comparing 2-methyl-2-nitro-1,3-propanediol ($T_{tr} = 79$–$80°$, $\Delta S_{tr} = 17.5$ e.u.) and 2-hydroxymethyl-2-nitro-1,3-propanediol[1] ($T_{tr} = 78$–$80°$, $\Delta S_{tr} = 15.5$ e.u.). These restrictions in conformational disorder can probably be attributed to steric hindrance.

If the possible new conformational states alone were effective in determining changes in entropy increments in comparing two structurally similar compounds, the aminopentaerythritols should have entropy increments at least as large as the pentaerythritols, but such was not the case in the two compounds examined in this series.

The halogen substituted pentaerythritols also showed lower than expected values, particularly those for the fluorine derivative in which polar effects may inhibit some conformational states. For example, the transition temperature and entropies for monofluoropentaerythritol and difluoropentaerythritol were lower than would be expected from interpolations based on values for pentaerythritol and tetrafluoropentaerythritol. It is particularly noteworthy that values for difluoropentaerythritol and tetrafluoropentaerythritol are about the same. The entropy of transition of monochloropentaerythritol exceeds the transitional entropy of monofluoropentaerythritol, despite the large size of the chlorine which should have a greater tendency to inhibit orientational freedom, but is not significantly greater than 2-hydroxymethyl-2-methyl-1,3-propanediol.

CONCLUSIONS

Taken as a whole, these results demonstrate that the total possible configurational contributions to entropy increments of solid–solid transitions cannot be assumed to be effective in determining entropy changes in complex molecules. The correlation of entropy of phase change in transition with the number of alternate non-equivalent positions that can be occupied at random by the molecule has been demonstrated in simple molecules, for example for 2-methyl-2-propanethiol[14]. Intramolecular chemical effects in these complex molecules, possibly either hydrogen bonding or steric effects, inhibit at least a portion of the states of disorder leading to lower entropy changes than might be estimated on the basis of group effects.

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