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THE THERMODYNAMIC PROPERTIES OF THE ESTERS OF 2,4,6-TRINITROBENZOIC ACID

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ABSTRACT

The thermodynamic properties of the esters of 2,4,6-trinitrobenzoic acid have been investigated using the techniques of hot-stage microscopy and differential scanning calorimetry. In each case an enantiotropic transition process was observed below the melting point. This transition has been explained in terms of restricted rotation and conformational freedom of the flexible alkyl chain in the crystalline solid state.

INTRODUCTION

The esters of 2,4,6-trinitrobenzoic acid (n-butyl, n-hexyl, n-octyl, n-dodecyl, n-hexadecyl, n-octadecyl) were prepared for use as surfactants to reduce the interfacial tension between paraffin wax and TNT[1]. Before these compounds are used in high explosive compositions, however, it is desirable to establish their thermal and thermodynamic properties. This becomes even more important when it is recalled that 2,4,6-trinitrotoluene exhibits polymorphism or polytypism[2–4], that 2,4,5-trinitrotoluene exhibits monotropy[5], and that a number of higher normal paraffins and their derivatives show enantiotropic transitions below their melting points[6–8]. The thermal and thermodynamic properties of the 2,4,6-trinitrobenzoate esters were therefore investigated using the techniques of hot-stage microscopy and differential scanning calorimetry (DSC).

EXPERIMENTAL

The esters of 2,4,6-trinitrobenzoic acid (n-butyl, n-hexyl, n-octyl, n-dodecyl, n-hexadecyl, n-octadecyl) were prepared by heating 2,4,6-trinitrobenzoyl chloride in the appropriate alcohol. The crude product was purified by recrystallisation twice from ethanol[9,10]. The compounds were screened using vapour phase chromatography, and shown to be pure within the scope of the instrument.

Hot-stage microscopy and differential scanning calorimetry (DSC) were used to investigate the thermal behaviour of the esters. Microscope investigations were

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restricted to temperatures above ambient, and were made using a Leitz Ortholux microscope with an attached Mettler FP2 hot-stage and polarised light. A Perkin-Elmer DSC 1B differential scanning calorimeter was used to measure the heats of fusion and transition. The samples (ca. 2.5 mg) were spread and crimped in aluminium pans, and heated in a stream of nitrogen flowing at 5×10^{-7} m^3 sec^{-1} (30 cm^3 min^{-1}). The samples were heated at a rate of 16 K min^{-1}, with an ordinate sensitivity of 2, 4 or 8 mcal sec^{-1} for full scale deflection. Both the hot-stage and the differential scanning calorimeter were used to determine the melting points and transition temperatures. All observations were made at ambient pressure.

RESULTS

No evidence was obtained for any decomposition of the 2,4,6-trinitrobenzoate esters below 420 K, and in fact thermogravimetry showed these compounds to be stable up to 470 K. However hot-stage microscopy and DSC confirmed the existence of an enantiotropic transition in addition to the fusion process. The hot-stage microscope was used to observe the transition as a discontinuous front passing through the crystals as the temperature was raised or lowered through the same transition temperature. The transition temperatures were measured within 0.5 K and the melting points within 0.1 K using the hot-stage microscope.

In addition to the normal fusion endotherm, the heating mode of the differential scanning calorimeter revealed an endotherm at the transition temperature, corresponding to the transition of the α-modification to the higher temperature β-form. Corresponding exotherms were observed for the solidification process and for the transition back to the α-form. The latent heats of fusion and transition were calculated with an accuracy of ±3% from the areas under the DSC traces.

Polymorphic transition of n-hexyl 2,4,6-trinitrobenzoate could not be detected above ambient temperature using either hot-stage microscopy or DSC. This transition was observed instead at 264 K (−9 °C) by means of DSC at reduced temperatures. The estimated error in the measurement of this transition temperature is ±1 K.

TABLE 1

THERMODYNAMIC PROPERTIES OF THE FUSION PROCESS

Ester	*Fusion temperature (K)*	*Heat of fusion ($kJ\ mol^{-1}$)*	*Entropy of fusion ($J\ mol^{-1}\ K^{-1}$)*
n-Octadecyl	392.3	30.02	76.52
n-Hexadecyl	393.3	29.54	75.16
n-Dodecyl	394.0	29.55	75.02
n-Octyl	396.7	29.16	73.50
n-Hexyl	402.0	32.96	82.02
n-Butyl	395.2	28.13	71.15

TABLE 2

THERMODYNAMIC PROPERTIES OF THE TRANSITION PROCESS

Ester	*Transition temperature* (*K*)	*Heat of transition* (*kJ mol*$^{-1}$)	*Entropy of transition* (*J mol*$^{-1}$ *K*$^{-1}$)
n-Octadecyl	364.1	25.40	69.74
n-Hexadecyl	349.3	18.60	53.26
n-Dodecyl	325.0	7.64	22.43
n-Octyl	312.0	2.07	6.61
n-Hexyl	264	1.70	6.44
n-Butyl	360.0	2.50	6.95

The melting points, heats of fusion and entropies of fusion of the esters of 2,4,6-trinitrobenzoic acid are given in Table 1; Table 2 contains the corresponding thermodynamic properties for the enantiotropic transitions. The variation with change of alkyl chain-length of the entropy of fusion (S_f) and the entropy of transition (S_t) are illustrated in Fig. 1 below.

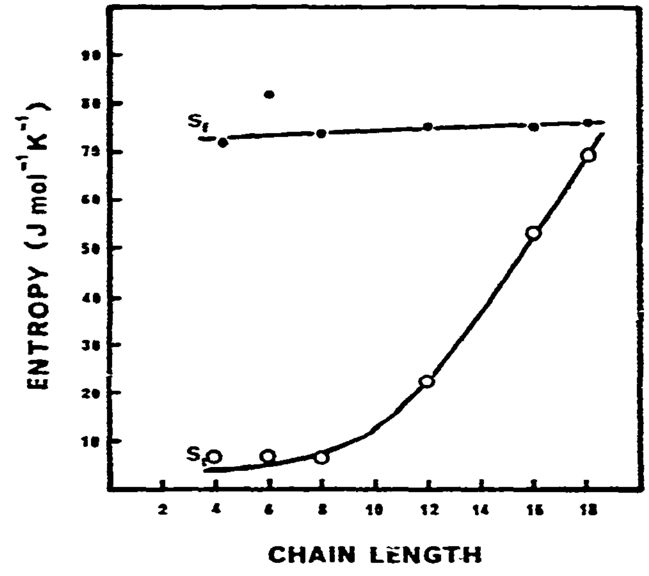

Fig. 1. Figure variation of entropies of fusion and transformation with alkyl chain-length.

DISCUSSION

The means by which a material in the ordered crystalline state increases in entropy as it passes to the more randomised melt can conveniently be reduced to a number of components. Positional disordering of the centres of gravity of the component molecules occurs in all cases, and for all except spherically symmetrical molecules orientational or rotational disordering is found. Flexible molecules such as derivatives of the longer paraffins, however, can experience an additional increase in entropy due to conformational disordering*, brought about by an increase in the number of conformations of the flexible chain accessible in the liquid state[11].

Although the different mechanisms by which entropy can be increased obviously interact to some extent, to a first approximation the total entropy of fusion (S_f) of flexible molecules can be treated as the sum of the separate contributions,

$$S_f = S_{pos} + S_{or} + S_{conf}.$$

The positional disordering of the centres of gravity of the molecule on fusion can make only a limited contribution to the total entropy of the system. Thus the entropy of fusion of the inert gases (neon, argon, krypton and xenon) lie in the range 3.25–3.40 entropy units (13.6–14.2 J mol^{-1} K^{-1})[12], while even quite large "globular" molecules (such as bicyclo[2,2,2]octane), whose repulsion envelopes are nearly spherical, have low entropies of fusion, of the order 2–3 entropy units (8.4–12.6 J mol^{-1} K^{-1})[13,14]. Similarly orientational or rotational disorder can contribute only a few entropy units, regardless of the size of the molecules. On the other hand the conformational component increases without obvious limit as the length of the flexible molecule is increased by the addition of successive structural units[11]. Thus, according to the hypothesis of Aranow et al.[15], the entropy of fusion of derivatives of the normal paraffins should increase by $R \ln 3$ for each additional methylene unit. The results obtained for the n-paraffin (odd series), n-alkylcyclohexane and n-alkylbenzene series are in good agreement with this theory[16].

From the point of view of classical thermodynamics, enantiotropic transitions may be considered exactly analogous to the fusion process, and occur when the molecules can achieve an additional degree of disorder in the solid state. Positional disorder of the cation causes polymorphism in certain silver salts such as silver iodide[17]; orientational disorder can also cause enantiotropic transitions in quasi-spherical or quasi-cylindrical molecules such as carbon tetrachloride[8] or certain derivatives of the longer normal paraffins[6–8]. Thus it might logically be supposed that enantiotropic transitions should also be possible as a consequence of conformational disordering in the solid state.

Let us now consider the effect of increasing chain-length on the entropies of fusion and transition of the normal 2,4,6-trinitrobenzoate esters. The entropy of fusion, S_f, surprisingly increases very little with the length of the alkyl chain (0.188 J mol^{-1} K^{-1}, or 0.023 R per methylene unit), and it is apparent that conformational disordering plays no important part in the fusion process. On the other hand, although the entropy of transition, S_t, of the lower esters (n-butyl, n-hexyl, n-octyl) is small and constant within experimental error, it increases by 8.70 J mol^{-1} K^{-1} or 1.05 R per methylene unit for the higher esters. This agrees well with the value of $R \ln 3$ predicted

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*This phenomenon has occasionally been described as "configurational disordering"[11]. Throughout the present work, however, the more accurate "conformational disordering" has been used.

by Aranow et al.[15] for the contribution to the conformational entropy caused by one additional methylene unit.

While the entropy of transition of the longer esters is essentially a linearly increasing function of the alkyl chain-length, the shorter esters do not follow this pattern. A similar departure from the general trend in entropy of fusion has been observed for the lower homologues of the n-alkylbenzene and n-alkylcyclohexane series. This has been explained in terms of rotation about the axes of the short, "internally stiff" alkyl chains in the liquid state rather than the complete conformational disordering expected[16], and it is suggested that a similar phenomenon also occurs when the lower esters of 2,4,6-trinitrobenzoic acid are heated above their transition temperatures. Thus steric hindrance from the trinitrobenzoate moiety prevents the shorter hydrocarbon chains from assuming all possible conformations, and constrains the chains in the form of rigid rods which undergo restricted rotation about their own axes when the compound is heated above its transition temperature. Only when the methylene units are sufficiently removed from the nitroaromatic "head", can they assume all possible conformations and make a significant and systematic contribution to the entropy of transition of the molecule.

CONCLUSIONS

The entropies of fusion of the 2,4,6-trinitrobenzoate esters are almost independent of the alkyl chain-length, increasing only by 0.023 R per methylene unit.

However, enantiotropic transition of the esters occurs below the respective melting points. For the shorter esters (n-butyl, n-hexyl, n-octyl) steric hindrance from the 2,4,6-trinitrobenzoate moiety prevents the paraffinic chain from assuming all possible conformations, and restricted rotation of the chain about its axis occurs when the esters are heated above their transition temperatures. When they are sufficiently removed from the 2,4,6-trinitrobenzoate "head", the flexible methylene units can attain all possible conformations, and the entropy of transition of the longer esters increases by 1.05 R per methylene unit, compared with the value of $R \ln 3$ predicted for conformational disordering.

REFERENCES

1 J. Eadie and W. S. Wilson, unpublished results.
2 W. Connick, F. G. J. May and B. W. Thorpe, *Aust. J. Chem.*, 22 (1969) 2685.
3 D. G. Grabar, F. C. Rauch and A. J. Fanelli, *J. Phys. Chem.*, 73 (1969) 3514.
4 D. G. Grabar, J. P. Hession and F. C. Rauch, *The Microscope*, 18 (1970) 241.
5 M. C. Chick and B. W. Thorpe, *Aust. J. Chem.*, 24 (1971) 191.
6 A. R. Ubbelohde, *Trans. Faraday Soc.*, 34 (1938) 289.
7 V. Vand, *Acta Crystallogr.*, 6 (1953) 797.
8 D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons, New York, 1969.
9 Ming-Che Chang and C. H. Kao, *J. Chin. Chem.*, (1935) 256.
10 W. S. Wilson, *D.S.L. Technical Note, No.* 305, 1973.
11 A. R. Ubbelohde, *Melting and Crystalline Structure*, Clarendon Press, London, 1965.
12 K. Clusius and K. Wiegand, *Z. Phys. Chem. B*, 46 (1940) 1.

13 J. Pirsch, *Monatsh.*, 86 (1955) 216, 226.
14 J. Timmermans, *J. Phys. Chem. Solids*, 18 (1961) 1.
15 R. H. Aranow, L. Witten and D. H. Andrew, *J. Phys. Chem.*, 62 (1958) 812.
16 A. Bondi, *Chem. Rev.*, 67 (1967) 565.
17 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 2nd ed., 1962.