Thermochimica Acta, 7 (1973) 317–324
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THERMAL ANALYSIS AND SPECTROSCOPIC STUDIES OF SOME COMPLEXES OF 1,7-DIACETOXY-2,4,6-TRINITRO-2,4,6-TRIAZAHEPTANE

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(Received 11 June 1973)

ABSTRACT

Complexes of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) have been prepared with a wide range of organic solvents. The stoichiometry of the complexes was determined where possible by thermogravimetric analysis, and the mode of thermal decomposition of the complexes was studied by differential scanning calorimetry. The enthalpies of desolvation were evaluated from the thermal analysis for about half of the complexes prepared.

Infrared and Raman spectra were measured on some of the complexes in an attempt to determine the nature of the bonding, if any, taking place between the host BSX molecules and the guest solvent molecules. The spectroscopic results are discussed in terms of similar measurements for other inclusion compounds and also with reference to the detailed crystal structure of some of the BSX complexes.

INTRODUCTION

Crystallographic studies on 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX) and some of its complexes were performed by one of us several years ago and the results of this work have now been published[1]. Detailed crystal structure determinations on pure BSX and three of its solvent complexes have been carried out and will be reported in due course[2].

During this work attempts were made to prepare a complex of BSX with formamide, the existence of which had been reported recently[3]. None of these attempts, made under a wide range of experimental conditions, yielded material which differed crystallographically from pure BSX.

In view of the contradictory evidence on the existence or otherwise of the BSX–formamide complex, it was decided to reinvestigate the thermal properties of BSX grown from formamide solution.

Complexes of BSX with several other organic solvents were also prepared and investigated by differential scanning calorimetry (DSC) and by thermogravimetric analysis (TGA) where possible. Five of the solvents we used had been used previously[3] to prepare complexes for differential scanning calorimetry studies but the agreement between the two sets of results is not particularly good and it was therefore decided to present the results of these systems.

Infrared and Raman spectra were determined for some of the complexes in an attempt to see if the formation of these complexes involved specific bonding in the complexes or if the complexes were essentially clathratic in nature with the solvent molecules simply trapped in the BSX crystal lattice.

EXPERIMENTAL

Materials

The BSX for all the experimental work was a pure recrystallised sample prepared and supplied by E.R.D.E. (Waltham Abbey) and all the solvents were reagent grade chemicals which were used without further purification.

The complexes were prepared by dissolving BSX in the hot solvent and allowing to cool slowly when the crystals of the complex were deposited. The crystalline complexes were left in the presence of excess solution until required for study when the crystals were removed from the solution and dried on filter papers.

Thermal analysis

The calorimetric measurements were made using a Perkin Elmer DSC-1B differential scanning calorimeter and the thermogravimetric analyses were done with the Perkin Elmer TGS-1 Thermogravimetric Analyser. The thermograms were measured at scanning rates of either eight or sixteen K min^{-1} and the enthalpy changes were calculated after calibration of the instrument with a known weight of high-purity tin.

Infrared spectra

The infrared spectra of nujol mulls of the solid complexes were recorded on a Perkin Elmer Model 225 spectrometer. The instrument was calibrated with a polystyrene film.

Raman spectra

The Raman spectra of the solids were excited by means of the 568.2 nm line of a Coherent Radiation Laboratories Model 52K krypton laser and recorded on a Cary 81 spectrometer. The spectra were recorded using 4.5 cm^{-1} slits with an exciting power of 25 mW at the sample. The instrument was calibrated using krypton emission lines.

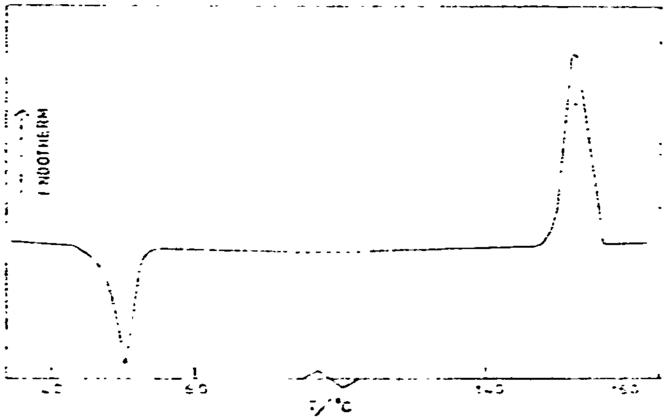
RESULTS AND DISCUSSION

Thermal analysis

Pure BSX

During the calibration experiments several thermograms were run on pure BSX in order to obtain an independent value for the heat of fusion of BSX which was found to be 38.5±2.2 kJ mol^{-1}. This is in close agreement with the value reported by Hall[3].

During these experiments it was observed that upon cooling to room temperature the melted BSX transformed to a glass-like phase and only reverted to the crystalline form on heating to about 50±5 °C. This behaviour is illustrated in Fig. 1 where the glass-crystal exotherm (−23.0±2.2 kJ mol^{-1}) can be seen in the region 45–55 °C and the crystal-liquid endotherm in the region 146–154 °C.



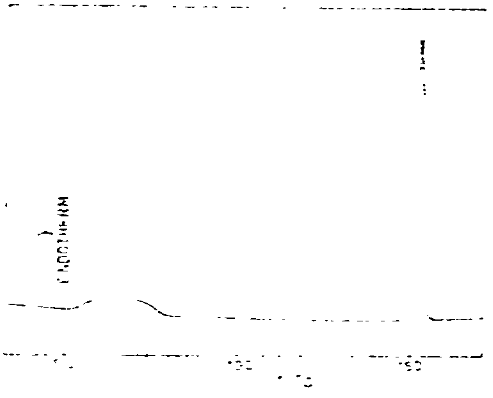


Fig. 1 (left). Thermogram for pure BSX which has been melted and supercooled to the glassy state. The peak between 40° and 60 °C is the glass-crystal exotherm and the peak between 140 and 160 °C is the crystal-liquid endotherm.

Fig. 2 (right). Thermogram for BSX–C_6H_5F complex showing the desolvation endotherm at 50–80 °C and the BSX fusion endotherm at 150 °C.

This phenomenon is quite reproducible and the glassy form of BSX is stable for several hours at temperatures below 40 °C.

BSX–solvent complexes

In discussing the thermal properties of BSX–solvent complexes it is convenient to divide them into two separate groups.

In the first group are complexes of BSX with benzene, fluorobenzene, pentafluorobenzene, hexafluorobenzene, dibromomethane, 1,4-dioxane 3-bromopyridine, acetophenone and acetonitrile. All of these complexes desolvate cleanly at relatively low temperatures and the endothermic desolvation peak is followed by a sharp BSX melting endotherm at about 150 °C. This type of behaviour is illustrated in Fig. 2 which is the thermogram for the BSX–fluorobenzene complex. In this case the fluorobenzene is lost as vapour in the region 50–80 °C, leaving behind pure BSX. A repeat run on the same sample shows that all the fluorobenzene had been removed in the first heating process. For the complexes listed in this category it is possible to calculate the enthalpy changes for the process.

$$\text{BSX–solvent(solid complex)} \rightarrow \text{BSX(solid)} + \text{solvent(vapour)}$$

Furthermore, the stoichiometry of the complexes in this category are easily determined thermogravimetrically by measuring the loss in weight when a known weight of the complex is heated beyond the temperature of desolvation.

The enthalpies of desolvation for these complexes were determined by measuring the areas under the peaks corresponding to the desolvation process and the fusion of BSX. Knowing the stoichiometry of the complex and the enthalpy of fusion of BSX, the enthalpies of desolvation are easily determined. The results obtained from thermal studies on this group of complexes are summarised in Table 1.

TABLE 1

Solvent	*Desolvation temperature (°C)*	$\Delta H_{desolvation}$ *(kJ mol^{-1})*	ΔH_{vap} *of solvent (kJ mol^{-1})*	*Complex stiochiometry by TGA BSX: solvent*
benzene	60–80	30.5 ± 2.2	30.9	1:0.80
fluorobenzene	55–75	27.2	31.4	1:0.85
pentafluorobenzene	80–95	21.7	32.2	2:1.02
hexafluorobenzene	100–120	18.4	31.8	2:1.04
1,4-dioxane	80–100	32.6 (14.2)[a]	35.5	1:0.96 (1:1)[a]
dibromomethane	40–50	23.0	35.1	1:1.00
3-bromopyridine	70–90	38.0	—	2:0.90
acetophenone	45–60	39.3 (15.0)[a]	37.6	2:1.04 (2:1)[a]
acetonitrile	60–90	39.7	33.4	1:0.98

[a] The figures in brackets are taken from ref. 3.

The desolvation temperature ranges referred to throughout this paper are perhaps best described as "procedural decomposition temperatures", a term used by McAdie[4] to describe the desolvation temperatures of urea–hydrocarbon adducts. The desolvation temperatures depend therefore on factors such as sample environment, temperature scanning rate and type of instrument used and do not have any precise thermodynamic significance.

In the second group of complexes are those formed with dimethylformamide, dimethylacetamide, acetylacetone, cyclohexanone, 1,1,2,2-tetrachloroethane, pyridine, nitrobenzene, 4-hydroxybutanoic acid lactone and N-methyl-2-pyrrolidinone. The behaviour of these complexes under the conditions of heating within the DSC apparatus is characterised by the absence of a clear demarcation between the desolvation of the complex and the BSX fusion endotherm. Upon desolvation the solvent only partially escapes as vapour and some is retained in the form of a solution with BSX. Further loss of solvent vapour from the solution can occur as the temperature continues to rise but at the same time the solubility of BSX in the solvent increases and all of the BSX may consequently be in solution before the melting point is reached.

Thermograms illustrating this type of behaviour are shown in Fig. 3 for the complexes of BSX with cyclohexanone and dimethylformamide. The second part of the thermogram for BSX–cyclohexanone shows a repeat run on the same sample. It

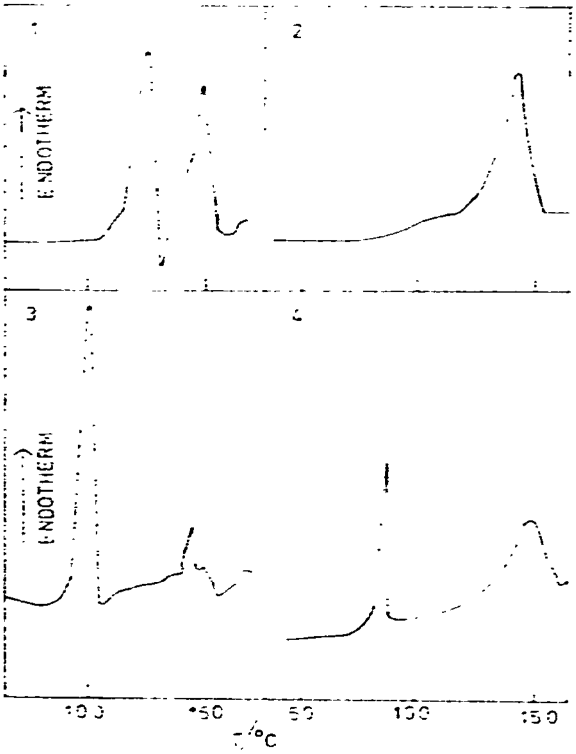


Fig. 3. (1) and (2) are the endotherms for the BSX–cyclohexanone complex. In (1) the desolvation endotherm occurs at about 130 C and merges with the BSX fusion endotherm. (2) is the thermogram obtained when the same sample used in (1) is cooled and reheated. (3) and (4) are the corresponding thermograms for the BSX–dimethylformamide complex.

can be seen that although there is no desolvation peak, the BSX melting endotherm is very broad due to residual cyclohexanone in the BSX. The BSX–dimethylformamide complex behaves similarly, the repeat run showing the desolvation endotherm reduced by about a factor of four and the BSX fusion endotherm greatly increased in size and sharpness. Further runs of the same sample enhance this effect.

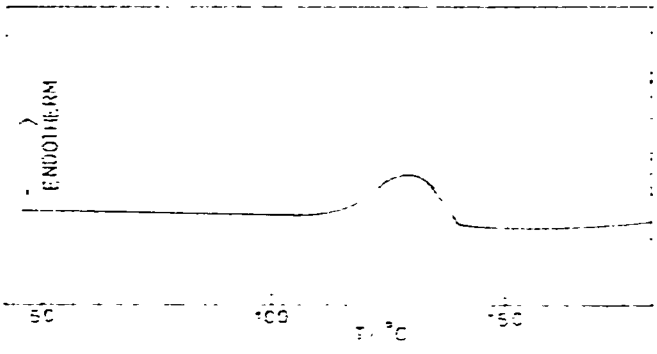


Fig. 4. Thermogram of BSX crystallised from formamide showing the solution endotherm of BSX in formamide occluded in the BSX crystal layers.

For these complexes, the process of desolvation as previously defined is inseparable from other phase changes and it is impossible to calculate the enthalpies of desolvation of such complexes from these thermograms. Thermogravimetric analyses for some of these complexes also proved impossible because of the slow release of the solvent even at temperatures as high as 150 °C. The results for this second category of complexes are given in Table 2.

TABLE 2

Solvent	*Desolvation temperature (°C)*	*Complex stoichiometry by TGA*
dimethylformamide	90–115	1:1[a] (1:1)[b]
dimethylacetamide	60–70	1:1[a]
acetylacetone	70–80	3:1[a]
cyclohexanone	105–120	2:1.00 (1:1)[b]
tetrachloroethane	120–130	2:0.90 (1:1)[b]
pyridine	40–50	1:1.10
nitrobenzene	75–85	1:0.97
4-hydroxybutanoic acid lactone	70–90	—
N-methyl-2-pyrrolidinone	50–65	1:1[a]

[a] The results are only approximate as thermogravimetric analysis did not furnish good results for these systems. [b] The figures in brackets are taken from ref. 3.

The BSX–formamide system

Crystals of BSX grown from formamide were found to be plates, like those of pure BSX whereas all the other BSX complexes were needle-like in crystal form. On examination of the BSX grown from formamide, the thermogram showed an endotherm in the region 110–140 °C in apparent agreement with the desolvation endotherm reported by Hall[3] for this system. It can be seen from Fig. 4 that on heating beyond 140 °C, no BSX fusion endotherm is observed even up to 200 °C when thermal decomposition of BSX occurs. A sample of the BSX–formamide "complex" was then examined in an unsealed pan covered with a thin glass slide when it would be seen that at temperatures above 110 °C the BSX dissolved rapidly in formamide which was trapped between the plates of BSX crystals. It appears, therefore, that BSX grown from formamide is not a complex for crystallographic evidence shows that it is identical with pure BSX, but free liquid formamide does appear to be occluded in some way between layers of the BSX crystals. Attempts to analyse the BSX–formamide mixture by thermogravimetric analysis proved inconclusive and it was found that the amount of formamide decreased rapidly as the crystals were crushed and dried between filter papers.

Spectroscopic and crystallographic analyses

The crystal structures of BSX and its complexes with dimethyl formamide, 4-hydroxy-butanoic acid lactone and 1,4-dioxane have been determined and these results will be reported elsewhere[2]. It is found that in pure crystalline BSX each molecule exists in a monomeric form and that both carbonyl groups in each BSX molecule occupy crystallographically equivalent positions. This is confirmed by the infrared and Raman spectra of BSX which show only one band for the carbonyl stretching mode at 1745 cm^{-1}.

In the case of the BSX complexes for which the structures have been determined, it is found that the BSX molecules exist in centrosymmetric pairs in the crystal structure with the two BSX carbonyl groups now in non-equivalent positions. The oxygen atom of one of the carbonyl groups is found to be relatively close (between 2.95 and 3.11 Å) to two nitro-nitrogen atoms in an adjacent BSX molecule while the carbonyl oxygen at the other end of the BSX molecule is not in close proximity to any nitro-nitrogen atoms. The guest solvent molecule is found to lie in such a position that a solvent oxygen atom is again close to two nitro-nitrogen atoms in a BSX molecule.

The Raman spectrum of the BSX–DMF complex also indicates that the two carbonyl groups in BSX are in non-equivalent positions, producing two bands at 1751 and 1761 cm^{-1}. The DMF carbonyl stretching band occurs in the complex at 1666 cm^{-1} in both the infrared and Raman spectra, compared with a vapour phase value[5] of 1716 cm^{-1} thereby confirming that the DMF molecule is bonding to the BSX molecules in the complex.

In the Raman spectrum of the 4-hydroxy-butanoic acid lactone complex, the carbonyl band of the solvent is centred at about 1755 cm^{-1} and overlaps the BSX carbonyl bands so that it is not possible to confirm that there are two separate BSX carbonyl bands. The vapour phase carbonyl stretching band in 4-hydroxy-butanoic acid lactone[6] occurs at 1814 cm^{-1} and it is concluded that bonding occurs between the 4-hydroxy-butanoic acid lactone molecules and the BSX molecules in the complex.

No spectroscopic information was found for the interactions present in the BSX–1,4-dioxane complex, but the crystallographic results show that one of the ring oxygen atoms is again interacting with two nitro-nitrogen atoms on a BSX molecule.

It is concluded that complexes of BSX with solvents containing carbonyl or ether oxygen atoms, involve strong specific interactions between nitro-nitrogen atoms of the BSX molecules and the oxygen atoms of the solvents. It is not possible at present to attempt any quantitative correlations between structural and spectroscopic results on the one hand and the enthalpies of desolvation on the other for the thermal analysis does not prove to be a suitable method for obtaining the heats of desolvation of most of these complexes.

Raman spectra have also been measured on complexes of BSX with benzene and acetonitrile and in both cases a single BSX carbonyl band is found at 1752 cm^{-1}, indicating that carbonyl oxygen to nitro-nitrogen interactions are weaker in this type of complex. The cyanide stretching mode of acetonitrile in its BSX complex gives two Raman bands at 2251 and 2295 cm^{-1} which are similar to the values of 2261 and 2297 cm^{-1} for acetonitrile[7] as a guest molecule in a β-quinol clathrate, indicating that very little if any interaction occurs between acetonitrile molecules and BSX molecules. Similar conclusions can be drawn for the BSX–benzene complex and it is possible that complexes in this category are clathrate-like in nature. It has not yet been possible to prepare a crystal of any of the complexes like the BSX–benzene complex which are suitable for a full crystal structure determination and it is therefore not possible to say if these complexes are true clathrates or not.

REFERENCES

1 G. F. Claringbull and R. W. H. Small, *Acta Crystallogr.*, B27 (1971) 863.
2 R. E. Cobbledick and R. W. H. Small, to be published.
3 P. G. Hall, *J. Chem. Soc. (A)*, (1970) 3137.
4 H. G. McAdie, *Can. J. Chem.*, (1962) 2195.
5 L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, 55 (1959) 14.
6 D. Welti and R. Stephany, *Appl. Spectrosc.*, 22 (1968) 678.
7 J. E. D. Davies, *JCS Dalton*, (1972) 1182.