

THERMAL INVESTIGATION OF ORGANIC CRYSTALLINE COMPLEXES. II. THERMAL BEHAVIOUR OF THE COMPLEXES DURING HEATING

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ABSTRACT

A number of crystalline charge-transfer complexes of polynuclear aromatic hydrocarbons with 2,4,6-trinitrotoluene (TNT) and picric acid were investigated by differential thermal analysis. It was found that the thermal behaviour of each complex during heating is different and depends mainly on its thermal stability. The temperatures, enthalpies and entropies of polymorphic transitions, and the melting points of eutectic mixtures were determined. It is suggested that every thermal investigation of the complexes should be based on other additional investigations such as thermal stability and solid–liquid phase diagrams.

INTRODUCTION

During the determination of the enthalpies of fusion of various charge-transfer complexes by the DTA method, other peaks were noted below the temperature of melting of the complexes [1]. These peaks often changed during the subsequent cycles of heating. Similar peaks were also reported by other authors [2–4] who pointed out that they may really provide useful information about the thermal stability of the complexes. The present paper is devoted to this type of investigation.

A survey of the available literature shows that during the investigation of solid complexes by the DTA method some difficulties were encountered in the interpretation of the peaks below their melting points. All the authors agree on one point, namely the interpretation of peaks associated with the melting points of the complexes [2–9]. There are also serious discrepancies in the opinions on the thermal stability of the complexes in the liquid and solid states.

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EXPERIMENTAL

The apparatus, materials and method of synthesis of the complexes are described in a previous work [10]. The measurements and the calculations of transition enthalpies for peaks on thermograms have also been described there [10]. Besides preliminary fusion of a sample, two cycles of heating A and B were applied. Further cycles of heating did not provide significant information.

RESULTS

The differential thermal analysis (DTA) curves obtained for the complexes investigated may be divided into three groups according to the number, shape and magnitude of the peaks. Selected examples of the complexes belonging to each group are described below.

The first group displays a single endothermic peak on thermograms in both cycles of heating; the magnitude of the peak is the same in subsequent cycles. The typical shape of a DTA curve is presented for naphthalene in Fig. 1. Complexes belonging to the first group are as follows: picric acid complexes with acenaphthene, naphthalene, 2-methylnaphthalene, 1,8-dimethylnaphthalene, 9-methylantracene, and TNT complexes with acenaphthene, phenanthrene, fluorene, naphthalene, 2-methylnaphthalene, 1,8-, 1,6-, 1,4-, 2,6-dimethylnaphthalenes, 9-methylantracene.

In the second group of complexes consisting of only 2,3-dimethylnaphthalene (Fig. 2) and 2,6-dimethylnaphthalene with picric acid, a single peak appears in the A cycle of heating. Then in the B cycle of heating an additional small peak below the melting point of the complex is observed. The enthalpies for the main peaks on thermograms are nearly the same for both complexes.

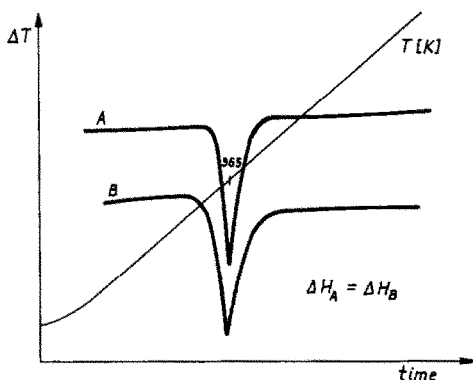


Fig. 1. Thermogram of TNT complex with naphthalene.

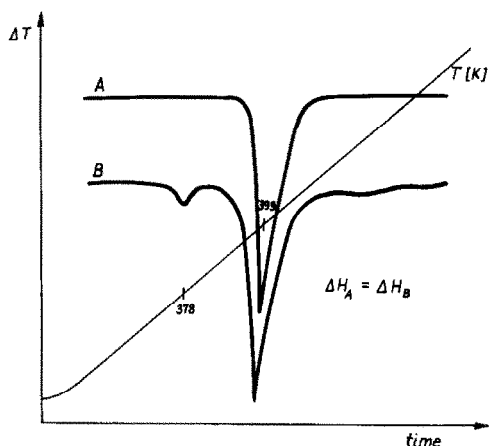


Fig. 2. Thermogram of picric acid complex with 2,3-dimethylnaphthalene.

In the third (most numerous) group of complexes, two or more endothermic peaks, which change in the subsequent cycles of heating, occur on the DTA curve during heating in A and B cycles. For complexes of anthracene (Fig. 3), 1-methylnaphthalene, 1,3-, 1,5-dimethylnaphthalenes with TNT, and for complexes of 1-methylnaphthalene and 1,3-, 1,4-, 1,5- and 1,6-dimethylnaphthalenes with picric acid, the enthalpy for the first peak (I) in the A cycle of heating is smaller than that in the B cycle of heating. In the case of the second peak (II), the value of enthalpy is greater in the A cycle than in the B cycle. For fluorene and phenanthrene complexes with picric acid, and the fluoranthene complex with TNT (Fig. 4), the magnitude of the first peak decreases, while that of the second peak increases in the B cycle of heating. For pyrene and fluoranthene (Fig. 5) with picric acid, and for pyrene with TNT, the enthalpy for the peaks in all the cycles of heating is constant.

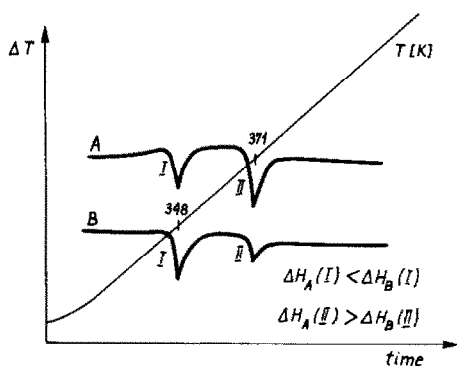


Fig. 3. Thermogram of TNT complex with anthracene.

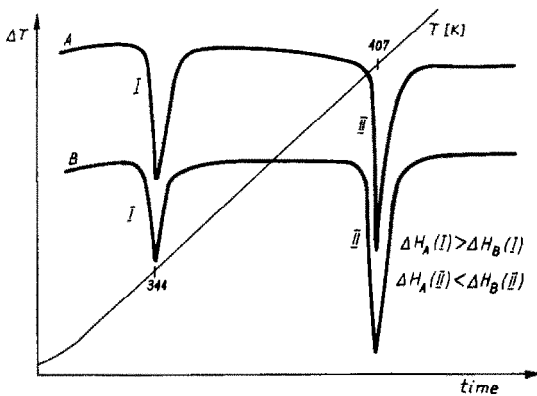


Fig. 4. Thermogram of TNT complex with fluoranthene.

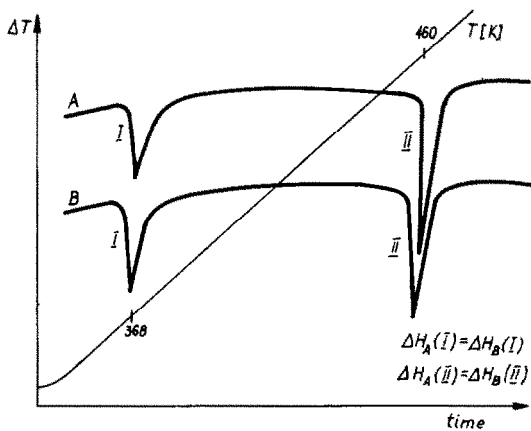


Fig. 5. Thermogram of picric acid complex with fluoranthene.

TABLE 1

Phase transitions of complexes

Complex	Cycle of heating	Crystal transitions in solid state					
		T (K)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
Anthracene-TNT	A	357.5	7.6	21.2			
	B	358.0	0.9	2.5			
Pyrene-picric acid	A	438.5	2.4	5.5	454.0	0.8	1.8
	B	438.5	1.5	3.4	454.0	0.6	1.3
Pyrene-TNT	A	332.0	12.7	38.3			
	B	332.0	8.5	25.6			

TABLE 2

Thermodynamic data for the melting of eutectic mixtures

Donor	Cycle of melting	Melting of first eutectic mixtures			Melting of second eutectic mixtures		
		T (K)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	T (K)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
<i>Picric acid</i>							
Anthracene	A	381	5.3	13.9			
	B	382	12.4	32.4			
Phenanthrene	A				374	14.9	40.0
	B				374	13.9	51.8
Fluoranthene	A				368	17.2	46.6
	B				368	16.4	44.7
Fluorene	A	351	14.8	42.2			
	B	350	13.4	38.3			
1-Methylnaphthalene	A						
	B				379	7.0	18.6
1,3-Dimethylnaphthalene	A	353	12.8	36.3			
	B	353	12.4	35.2	371	1.6	4.4
1,4-Dimethylnaphthalene	A	381	1.0	2.7	405	3.5	8.7
	B						
1,5-Dimethylnaphthalene	A				384	2.6	9.4
	B				384	7.6	19.8
1,6-Dimethylnaphthalene	A	354	5.8	16.5	367	0.5	1.4
	B	355	6.2	17.5	367	4.4	11.9
2,3-Dimethylnaphthalene	A						
	B				378	3.6	9.5
2,6-Dimethylnaphthalene	A						
	B	374	0.5	1.3			
<i>2,4,6-Trinitrotoluene (TNT)</i>							
Anthracene	A	348	9.2	26.4			
	B	348	15.1	43.4			
Fluoranthene	A	344	17.3	50.4			
	B	344	15.5	45.0			
1-Methylnaphthalene	A	339	0.5	1.6			
	B	338	2.5	7.4			
1,3-Dimethylnaphthalene	A						
	B	329	0.9	2.9			
1,5-Dimethylnaphthalene	A				341	2.2	6.5
	B				341	4.8	17.3
2,3-Dimethylnaphthalene	A						
	B	342	10.9	32.1			

Single peaks always correspond to the melting points of complexes and are connected with the enthalpy of melting. A comparison of the peak temperatures with the previously determined phase diagrams indicates that, below the melting point of the complexes, additional peaks are connected with phase transitions in the solid phase or with the melting of a eutectic mixture. Phase transitions take place only for complexes of pyrene with picric acid or TNT, and anthracene with picric acid (Table 1). The temperatures, enthalpies and entropies of melting of the eutectic mixtures are listed in Table 2.

DISCUSSION

From the above mentioned results it follows that complexes which belong to the first group are thermally the most stable ones. During melting not as many donors as electron acceptors appear, which leads to the absence of the peak corresponding with the melting point of a eutectic mixture.

The complexes of the second group are relatively stable. These complexes exhibit a small endothermic peak in the B cycle because of their small dissociation in the A cycle.

The third group comprises thermally unstable complexes which dissociate during heating. Here the increase or decrease in the melting enthalpy of a eutectic mixture is caused by the gradual decomposition of the complex or the decrease of its dissociation in the subsequent cycle of heating. However, if there are no changes in a peak in the subsequent cycles of heating, an equilibrium state is reached due to equal rates of dissociation and formation of complex.

The correct and precise method for the evaluation of the stability of complexes is the determination of their equilibrium constant. The equilibrium constant may be determined from spectroscopic data of the complexes in solutions. However the values of constants determined from spectroscopic measurement in solvents cannot be compared with those of liquid or solid complexes (without solvents). In order to evaluate the stability of solid complexes however, we must know the values of lattice energy and donor-acceptor interaction energy.

In conclusion it must be emphasized that without previously determined phase diagrams of a complex, preferably by DTA and on the same apparatus, identification and interpretation of all peaks is not always possible.

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