THERMAL INVESTIGATION OF ORGANIC CRYSTALLINE COMPLEXES. I. ENTHALPIES AND ENTROPIES OF FUSION

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ABSTRACT

Melting points and enthalpies of a number of crystalline charge-transfer complexes (polynuclear aromatic hydrocarbons and some methyl substituted derivatives with 2,4,6-tri-nitrotoluene and picric acid) were determined by using differential thermal analysis. It was found that the determination of the enthalpy by the thermal analysis method is possible only for thermally stable complexes. For unstable complexes the value of enthalpy are somewhat lower than those expected for stable complexes.

INTRODUCTION

Enthalpies of fusion for various organic compounds can be simply determined by the differential thermal analysis (DTA) method. The sample of a crystalline compound usually gives an endothermic peak on the DTA (or DSC) curve. The area S of the peak between the base line and the DTA curve is assumed to be proportional to the fusion enthalpy. When an inert substance (e.g. aluminium oxide) is used as a standard, the fusion enthalpy $\Delta H = K \cdot S$, where S is the area of the peak and K is the instrument constant, is determined by using compounds of well known enthalpies of phase transition. The accuracy in measurements can be increased by using organic compounds (e.g. naphthalene or benzoic acid) as internal standards. On a thermogram, two peaks corresponding to the phase transitions of the sample and the standard are observed [1,2] and the fusion enthalpy ΔH can be calculated from the known value ΔH_s of the standard by comparison of the areas S and S_s of the peaks for the sample and the standard $\Delta H = \Delta H_s(S/S_s)$. The area of the peaks may be calculated by several methods, mainly planimetric or geometric. For symmetric peaks on DTA curves, like Gaussian curves, the peak area is calculated from the equation [3] $S = hW_{h/2}$, where S, h and $W_{h/2}$ are the area, height and half width of a peak, respectively.

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The thermal properties of simple charge-transfer complexes of aromatic hydrocarbons with some electron acceptors have been investigated by Karpin et al. [4] and the Italian–Canadian group [5–13]. Recently, estimation of the fusion enthalpies of a number of picrates derived from polynuclear hydrocarbons employing the aforementioned method has been reported [7,8,10]. The aim of the present work is to report the determination of melting points and enthalpies of several charge-transfer complexes by differential thermal analysis.

EXPERIMENTAL

Reagents

Trinitrotoluene, acenaphthene, fluorene and fluoranthene were obtained by crystallization from methanol and by zone crystallization from commercial reagents. Anthracene and phenanthrene were purified by crystallization from dimethylsulphoxide, and then recrystallized from methanol and subsequently by zone crystallization. Naphthalene was purified by refining with bentonite (removal of sulphur contamination). Pyrene was purified by the addition of maleic anhydride in hot xylene, crystallized from methanol and from benzene and finally purified by zone crystallization. Picric acid and methylnaphthalenes were prepared as described previously [14].

Preparation of complexes

Equimolar amounts of donor and acceptor were dissolved in hot methanol and then the mixture was allowed to cool to permit the complex to crystallize. If necessary, the complexes were recrystallized from methanol, then collected by filtration and washed with small amounts of methanol and air-dried. The crystallization was repeated to constant and sharp melting point.

Apparatus and procedure

Measurements were made using the Hungarian apparatus Paulik–Paulik–Erdey models 1500 and 1200. The heating rate was $1.2°C$ min^{-1}. Using temperature–time curves, a DTA curve and additionally TG and DTG curves were determined. The TG and DTG curves were used to control the sublimation of a sample.

For every individual measurement the instrument was calibrated by internal standard. Organic internal standards should not undergo any phase transitions in the temperature range considered. These were naphthalene, benzoic acid, anthracene, and *o*- and *m*-dinitrobenzene, of known enthalpies of melting.

Samples weighing about 0.2 g of complexes and internal standards were sealed in platinum pans. They were first heated to complete melting, and then cooled to room temperature and subsequently put in the instrument, as reported by other authors [5,8]. In addition to the above mentioned preliminary melting and cooling outside the apparatus, for each sample two heating–cooling cycles (A and B cycles) were run [5]. A preliminary sample fusing was necessary because the shape of the thermogram is affected by the degree of homogeneity of a sample, which sometimes results in irreproducible thermograms.

The temperatures and areas of the peaks were interpreted as reported in our previous work [15]. In order to calculate fusion enthalpy from the peak area, planimetric and geometric methods were applied. Both of them gave consistent results. The entropy was calculated from the general equation.

RESULTS AND DISCUSSION

The values of melting temperature, fusion enthalpy and fusion entropy for the complexes of picric acid with hydrocarbons, for the two cycles of heating are given in Table 1.

Farrell et al. [8] have reported data for some complexes. Our data are sufficiently consistent with the values reported in the literature. The values for the complexes of 2,4,6-trinitrotoluene (TNT) with hydrocarbons are given in Table 2. These data were not reported in the literature. It may be seen from the tables that the results from two cycles of heating–cooling (A and B) are sometimes different. In our opinion, of the data from the heating cycles, only the higher ones should be taken into consideration. It was found that the differences in the values result from the decomposition of a complex rather than from incorrect measurements.

Roughly half of the investigated complexes were thermally unstable: they dissociate before reaching the melting point in the first, second or both cycles of heating. This inference was based on the nature of the endothermic peak, or peaks corresponding to the melting point of a eutectic mixture. When the complexes were unstable their fusion enthalpies were clearly lower than anticipated.

The main factor responsible for the stability of a complex in the solid state is the crystal lattice energy. The value of the heat of melting of a complex is associated with the destruction of its crystal lattice. Therefore the value of the enthalpy, particulary the entropy, of melting of a complex indicates its stability in the solid state. Such a comparison can be made for complexes having one endothermic peak on the DTA curve due to their melting.

TABLE 1

The values of temperature, fusion enthalpy and entropy for complexes of hydrocarbons with picric acid

Donor	Cycle of heating	Melting of complexes		
		$T(K)$	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K$^-$)
Acenaphthene	A	434	36.9	85.0
	B	434	36.0	82.9
Anthracene [c,d]	A	412	21,3	51.7
	B	412	4.4	10.8
Phenanthrene [c]	A	417	18.5	44.3
	B	418	19.8	47.4
Fluoranthene [c]	A	460	24.6	53.3
	B	460	24.5	53.3
Fluorene [c,d]	A	365	16.8	43.5
	B	364	16.2	44.4
Naphthalene	A	427	33.9	79.5
	B	427	33.6	81.0
Pyrene	A	503	31.1	61.7
	B	496	33.9	68.3
1-Methylnaphtha-lene [b]	A	413	24.0	58.2
	B	412	7.2	17.4
2-Methylnaphtha-lene	A	387	29.5	76.3
	B	387	28.8	74.6
1,3-Dimethylna-phthalene [c]	A	385	17.8	46.4
	B	385	15.2	39.4
1,4-Dimethylna-phthalene [a]	A	413	14.5	35.2
	B	413	17.2	41.6
1,5-Dimethylna-phthalene [c]	A	411	18.5	44.9
	B	409	8.9	21.8
1,6-Dimethylna-phthalene [c]	A	379	10.9	28.7
	B	379	6.5	17.1
1,8-Dimethylna-phthalene	A	425	26.5	62.4
	B	425	25.8	60.7
2,3-Dimethylna-phthalene [b]	A	399	40.7	102.1
	B	399	39.1	97.9
2,6-Dimethylna-phthalene [b]	A	418	44.2	105.8
	B	418	42.8	102.3
9-Methylanthracene	A	387	29.5	76.3
	B	387	28.8	74.6

[a] Decomposes only in the first cycle of heating. [b] Decomposes in the second cycle of heating. [c] Thermally unstable, decomposes in all cycles of heating. [d] Uncertain values because of the formation of a few crystalline forms of complexes.

TABLE 2

The values of temperature, fusion enthalpy and entropy for the complexes of hydrocarbons with 2,4,6-trinitrotoluene (TNT)

Donor	Cycle of heating	Melting of complexes		
		T (K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Acenaphthene	A	387	33.9	87.8
	B	387	33.1	85.5
Anthracene [b]	A	371	12.3	33.2
	B	371	3.9	10.6
Phenanthrene	A	368	31.9	86.6
	B	368	33.7	91.4
Fluoranthene [b]	A	407	20.1	49.4
	B	407	24.3	59.8
Fluorene	A	359	33.3	92.7
	B	359	32.5	90.5
Naphthalene	A	365	23.4	64.1
	B	365	23.1	63.3
Pyrene	A	438	24.4	55.8
	B	436	21.7	49.8
1-Methylnaphtha-lene [b]	A	357	25.4	71.2
	B	357	19.9	55.7
2-Methylnaphtha-lene	A	341	36.2	106.1
	B	342	35.3	103,3
1,3-Dimethylna-phthalene [a]	A	338	10.6	31.4
	B	338	8.6	25.3
1,4-Dimethylna-phthalene	A	357	18.8	50.6
	B	356	17.8	50.2
1,5-Dimethylna-phthalene [b]	A	356	27.1	76.2
	B	355	24.3	68.4
1,6-Dimethylna-phthalene	A	333	33.6	101.1
	B	333	33.6	101.1
1,8-Dimethylna-phthalene	A	387	32.1	82.9
	B	388	32.1	82.7
2,3-Dimethylna-phthalene [a]	A	367	36.0	98.2
	B	367	18.0	49.1
2,6-Dimethylna-phthalene	A	362	26.2	72.3
	B	362	27.1	74.9
9-Methylanthracene	A	380	27.9	73.6
	B	380	30.8	81.8

[a] Decomposes only in the second cycle of heating. [b] Thermally unstable, decomposes in all cycles of heating.

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