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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF CHARGE-TRANSFER COMPLEXES OF POLYNUCLEAR AROMATIC HYDROCARBONS WITH THE ASYMMETRIC ACCEPTORS 3- AND 4-NITROPHTHALIC ANHYDRIDE

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ABSTRACT

Charge-transfer, crystalline complexes of 3- and 4-nitrophthalic anhydrides with a number of unsubstituted polynuclear aromatic hydrocarbons were studied by differential scanning calorimetry. The 3- and 4-nitrophthalic anhydrides are complexing agents more selective than *s*.trinitrobenzene and pyromellitic dianhydride, and only form complexes with a few of the twelve hydrocarbons investigated.

Under the adopted conditions 3-NPA forms complexes with: pyrene, 3,4-benzopyrene, and 1,2,5,6-dibenzoanthracene; 4-NPA forms complexes with these hydrocarbons and with anthracene, phenanthrene, 1,2-benzoanthracene, benzoperylene, and coronene. Though having an electron affinity close to that of *s*.trinitrobenzene, 4-NPA forms less stable complexes with the polynuclear aromatic hydrocarbons, due to the asymmetry and non-planarity of its molecule.

INTRODUCTION

Charge-transfer (donor–acceptor) complexes of polynuclear aromatic hydrocarbons (PAH) with aromatic anhydrides or nitro derivatives generally have a rather high thermal stability[1-3]. Most complexes of this kind can be melted and repeatedly crystallized from the melt without separation of the components. We, therefore, thought it interesting to ascertain whether acceptors containing one nitro and one anhydride group also form with the PAHs crystalline complexes with a thermal stability comparable to that of the previously studied complexes.

With this aim, we prepared and studied by differential scanning calorimetry (DSC) the charge-transfer complexes of PAHs with 3- and 4-nitrophthalic anhydride (NPA). These acceptors, besides being the simplest nitro-aromatic anhydrides, have asymmetric molecules and therefore are selective complexing agents[4]. We determined the temperature, enthalpy and entropy of fusion of the above-mentioned complexes. In addition, coupled with X-ray powder diffraction, the thermal study allowed to characterize the crystal transitions taking place in the temperature range considered.

EXPERIMENTAL

Reagents and apparatus

All the PAHs (Fluka, Buchs, CH) were used as received. The nitrophthalic anhydrides (3-NPA Aldrich Chemical Co., and 4-NPA Eastman Kodak Co., Rochester, N.Y.) were contaminated with the corresponding acid. For purification, heating in an oven was applied, at 215–218°C for 3-NPA and at 165–168°C for 4-NPA, during three hours; the anhydrides were re-crystallized from acetyl chloride[5, 6].

Measurements and analyses were carried out with a differential scanning calorimeter Perkin-Elmer DSC 1B; IR and UV-vis spectrophotometers Perkin-Elmer Model 21 and EPS-3T, respectively; X-ray diffraction unit Philips Model PW 1050/25.

Preparation and analysis of the complexes

The complexes were prepared as previously described[4].

The stoichiometry resulted 1 : 1, except for 1,2-benzoanthracene/4-NPA, 1,2,5,6-dibenzoanthracene/4-NPA, and 1,2,5,6-dibenzoanthracene/3-NPA. These complexes have a donor/acceptor molar ratio 1 : 2.

Calorimetry

From 2 to 5 mg of sample were heated at 16°C min^{-1} in a nitrogen flow, in sealed pans to collect volatile materials, from about 30°C to complete melting. The melt was cooled, kept at room temperature during about 30 min and re-heated. Each sample was melted at least three times. The instrument was calibrated by an indium standard (99.999%), m.p., 156°C; ΔH_f, — 6.79 kcal g^{-1}. Transition and melting temperatures and the area of the related peaks were calculated as previously described[1]. X-Ray diffraction patterns were recorded whenever the complexes showed curves with peaks before the melting.

RESULTS

Table 1 gives the thermodynamic data (T_f, ΔH_f, ΔS_f) of the acceptors heated and re-crystallized. The values for 4-NPA refer to the first melting, as this compound crystallizes with extreme difficulty; also leaving the sample at room temperature for an extended period, the fusion peak areas after the first run were always slightly smaller. The corresponding data for the PAHs are given elsewhere[7].

TABLE 1

THERMODYNAMIC DATA OF 3- AND 4-NITROPHTHALIC ANHYDRIDES

	T_f (°C)	ΔH_f (kcal mol^{-1})	ΔS_f (cal mol^{-1} K^{-1})
3-NPA	163.4	4.4 ± 0.2	10.1 ± 0.4
4-NPA	115	4.1 ± 0.2	10.3 ± 0.4

TABLE 2

THERMODYNAMIC DATA OF CRYSTALLINE COMPLEXES OF POLYNUCLEAR AROMATIC HYDROCARBONS WITH 3- AND 4-NITROPHTHALIC ANHYDRIDES

	T_f (°C)	ΔH_f (kcal mol^{-1})	ΔS_f (cal mol^{-1} K^{-1})
3-NPA complexes			
Pyrene	175	14.5 ± 0.1	32.4 ± 0.1
3,4-Benzopyrene	136	8.3 ± 0.05	20.2 ± 0.2
1,2,5,6-Dibenzoanthracene	191	17.1 ± 0.08	36.9 ± 0.2
4-NPA complexes			
Anthracene	118	5.5 ± 0.04	14 ± 0.1
Phenanthrene	96	7 ± 0.09	19.2 ± 0.2
Pyrene	179.5	5.8 ± 0.1	12.8 ± 0.2
1,2-Benzoanthracene	123.5	15 ± 0.2	37.9 ± 0.4
3,4-Benzopyrene	151	8.1 ± 0.2	19.2 ± 0.4
1,2,5,6-Dibenzoanthracene	195.8	17.3 ± 0.07	36.9 ± 0.2
1,12-Benzoperylene	237.5	7.7 ± 0.1	15.1 ± 0.3
Coronene	280	5.8 ± 0.05	10.4 ± 0.1

Table 2 gives the thermodynamic data of the PAH-anhydride complexes. The data reported refer to the second melting of each sample, except for the cases discussed later on.

3-NPA forms crystalline complexes with the following PAHs only: pyrene, 3,4-benzopyrene, 1,2,5,6-dibenzoanthracene. In the temperature range considered, the above complexes do not undergo crystal transitions.

The pyrene/3-NPA complex shows — during the first heating — only the fusion peak. Re-crystallization from the melt is very slow and not always quantitative. During the second heating two new small peaks (area not reproducible) occasionally appear, due to the melting of the two components of the complex. The ΔH values of the second and further meltings remain constant and equal to that of first melting: the complex, partially dissociated, is completely re-formed at the melting temperature of pyrene and of 3-NPA.

The 3-NPA/1,2,5,6-DBA (2:1) complex has a peculiar behaviour. The first DSC run shows only the melting peak reported in Table 2. In successive runs this peak has a smaller area. In addition, a new peak shows up at 160°C. X-Ray powder diagrams and phase studies suggest that the peak at 160°C does not arise from a crystalline transition, but most probably from the formation of a eutectic mixture involving components of the partially dissociated complex.

4-NPA forms crystalline complexes with eight of the PAHs investigated. Only with pyrene and with 1,12-benzoperylene the complex shows crystal transitions. Thermodynamic data (T_{tr}, ΔH_{tr} and ΔS_{tr}) are in Table 3. The data given in Table 2 related to anthracene/4-NPA and to coronene/4-NPA refer to first melting. These complexes, after melting, are only partially re-formed and the DSC curves of samples which were previously melted are not superimposable.

TABLE 3

CRYSTAL TRANSITIONS OF PAH/4-NPA COMPLEXES

Complex of	T_{tr} *(°C)*	ΔH_{tr} *(kcal mol^{-1})*	ΔS_{tr} *(cal mol^{-1} K^{-1})*
Pyrene	122	4.2 ± 0.07	10.6 ± 0.2
	105	2.6 ± 0.05	7 ± 0.1
1,12-Benzoperylene	124	0.8 ± 0.02	2.1 ± 0.1

Of the pyrene/4-NPA complex three crystal forms were observed, indicated here as I, II, and III. Form I is obtained by crystallization from a solvent, form II by cooling from the melt, and form III is formed by both procedures at high temperature.

Form I transforms into III at 122°C; after melting and recrystallization of I, form II is obtained; at 105°C the II → III transition takes place. X-Ray diffraction patterns at different temperatures confirmed these transitions.

The 1,2,5,6-dibenzoanthracene/4-NPA complex crystallizes in two forms: yellow and red. We failed to separate the red form even by mechanically sorting the crystals. The results in Table 2 refer to the yellow form, the most stable at room temperature. On heating mixtures of the two forms in the differential scanning calorimeter, a curve with two peaks was recorded: one of the yellow form at about 195°C and the other of the red form at about 210°C.

The mixture resulting from crystallization of the melt has a composition different from the original one. The area of the first peak increases, while that of the second decreases. On repeated melting-cooling of the mixture, the red form is completely converted into the yellow. The same takes place on heating the complex in a sealed vial.

DISCUSSION

Most of the complexes studied are stable enough to withstand repeated melting–cooling cycles. Temperatures and enthalpies of fusion, however, are lower than those of the corresponding hydrocarbon complexes with acceptors containing only nitro- or anhydride groups. Electron affinity of 4-NPA is very close to that of the symmetric acceptor 1, 3, 5-trinitrobenzene[4], but the asymmetry of the nitrophthalic anhydride molecule can account for the lower thermal stability of the complex.

Since the complexes between PAHs and 3- and 4-NPA have physico-chemical characteristics similar to those of the corresponding complexes of TNB, the same considerations reported in ref. 2 concerning strength of the D : A interaction apply. Consequently, the D : A interaction is correspondingly weakened in the order DAPM > TNB > 4-NPA.

Actually, comparison of thermal stability among complexes of the nitro-anhydrides here investigated is not sufficiently significant, due to the small number of data related to 3-NPA. It might be noticed, however, that although this acceptor melts at higher temperature than its isomer, the few crystalline complexes of 3-NPA melt at temperatures lower than the corresponding 4-NPA complexes.

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