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DSC STUDIES OF AROMATIC HYDROCARBON PICRATES

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ABSTRACT

Melting temperatures, enthalpies and entropies of fusion of a number of crystalline, charge-transfer complexes of aromatic hydrocarbons with 2,4,6-trinitrophenol (picric acid) have been measured, together with the corresponding data for some aromatic hydrocarbons themselves and for picric acid. The data suggest that for this, and for other nitroaromatic acceptor molecules, enthalpies of fusion of charge-transfer complexes reflect the complexing ability of the electron acceptor, although the contribution of the charge-transfer interaction to the measured enthalpy is small.

INTRODUCTION

Studies of the thermal stabilities of charge-transfer complexes by means of differential scanning calorimetry have recently been reported for several classes of donors with either nitroaromatic [1,2] or anhydride acceptors [3—6]. This work has established the stabilities of the systems studied at their melting points and has identified crystal transitions, entropies of melting, etc, for the complexes. From the results obtained it is evident that the charge-transfer interaction can be only a minor contributor to the measured enthalpy of melting as no relationships between donor properties and thermochemical data have been found.

In our earlier study of complexes of polynuclear aromatic hydrocarbons with nitroaromatic acceptors [1] we endeavoured to compare the magnitudes of the enthalpy terms for melting and for complexation. We assumed that the enthalpies of formation of liquid complexes from liquid components could be assigned a value of ca. —8 kJ mole^{-1} and that little dissociation of the complex occurred on melting, and hence derived values for the complexation enthalpies for *solid* complexes in the range —4 to —20 kJ mole^{-1}. These values may then be compared with the enthalpies of melting for these complexes, which are in the range +24 to +71 kJ mole^{-1}.

More recently we have studied the stabilities of a number of aromatic hydrocarbon picrates by an electrochemical technique and obtained values for the enthalpies of complex formation from the components in their standard (i.e. solid) states [7]. These data thus provide experimental measurements for comparison with the corresponding enthalpies of melting, and permit the estimation of enthalpies of formation of liquid complexes from liquid components for comparison with our previously assumed value. We have therefore measured the enthalpies of melting for a series of polynuclear aromatic hydrocarbon picrates and report here our results, together with entropies of melting, crystal transitions, enthalpies of melting of some standard compounds (including picric acid) etc.

EXPERIMENTAL

Materials and complexes

Picric acid was a commercial product, recrystallized three times from ethanol and dried at room temperature. The hydrocarbon donors were obtained from Aldrich Chemical Co. and were all purified by recrystallization and/or sublimation to constant melting temperatures in agreement with the literature.

The picrates were generally formed by mixing a hot ethanolic solution of picric acid with a similar volume of solution containing the required amount of donor, and allowing the mixture to cool whereupon the complexes crystallized. They were recrystallized, where necessary, and air-dried to constant melting point in accord with literature values. Picrates of β, β'-binaphthyl, triphenylene, 1,2-benzanthracene, 1,2,3,4-dibenzanthracene, 1,2,5,6-dibenzanthracene and picene were similarly formed in diethyl ether, and anthracene picrate in acetone.

DSC studies

Calorimetric measurements were made as described previously [1,5], using a Perkin-Elmer model 1B instrument calibrated with a standard indium sample ($\geqslant$99.999% purity, $\Delta H_f = -28.42$ J g^{-1} at 429 K).

RESULTS

Values of the temperature of melting, enthalpy and entropy of fusion for a range of aromatic hydrocarbon picrates are shown in Table 1, together with data for any observed crystal transitions in these complexes. The corresponding thermodynamic data for the acceptor and a number of the aromatic hydrocarbons were also used as standards, and these are given in Table 2. Values for the remaining hydrocarbons employed in this study have been published previously [8].

With the exception of fluorene picrate, all compounds gave melting points at, or above, their reported values as measured by DSC. The value reported here for fluorene picrate was reproducible, both for different samples and on melting—cooling—remelting, although it is somewhat lower (350.3 K)

TABLE 1

Melting temperatures, enthalpies and entropies of fusion of aromatic hydrocarbon picrates

Hydrocarbon	T_m (K)	ΔH (kJ mole^{-1})	ΔS (J K^{-1} mole^{-1})
Acenaphthene	436.3 ± 0.6	36.0 ± 0.4	82.5 ± 1.0
Anthracene [a]	417.6 ± 1.2	24.3 ± 0.8	58.2 ± 2.1
1,2-Benzanthracene	414.3 ± 0.5	32.2 ± 0.8	77.7 ± 2.0
1,2-Benzfluorene	402.7 ± 0.1	45.6 ± 0.4	113.2 ± 1.0
2,3-Benzfluorene	392.8 ± 1.6	33.5 ± 0.8	85.3 ± 2.4
Benzo[*a*]pyrene	475.5 ± 0.4	39.3 ± 0.8	82.7 ± 1.8
$\beta\beta'$-Binaphthyl	464.2 ± 0.6	41.4 ± 0.4	89.2 ± 1.0
1,2,3,4-Dibenzanthracene [b]	485.2 ± 0.5	44.8 ± 0.4	92.3 ± 0.9
1,2,5,6-Dibenzanthracene	493.0 ± 0.5	54.0 ± 0.4	109.6 ± 1.0
Fluoranthene [c]	462.4 ± 0.6	24.7 ± 0.8	53.4 ± 1.8
Fluorene	350.3 ± 0.7	26.8 ± 0.8	76.5 ± 2.4
Indene	366.7 ± 0.9	25.1 ± 1.2	68.5 ± 3.5
Naphthalene	426.2 ± 0.5	34.7 ± 0.4	81.4 ± 1.0
Perylene	495.0 ± 0.7	42.3 ± 0.8	85.5 ± 1.8
Picene [d]	437.9 ± 0.4	21.3 ± 0.4	48.6 ± 1.0
o-Phenylenepyrene	469.6 ± 0.2	39.3 ± 0.4	83.7 ± 0.9
Pyrene [e]	506.6 ± 1.0	32.6 ± 1.2	64.4 ± 2.5
Triphenylene	501.4 ± 0.3	46.9 ± 0.8	93.6 ± 1.7

[a] Transition at 364.0 ± 0.8 K, ΔH = 10.5 ± 0.2 kJ mole^{-1}.

[b] Transition at 446.5 ± 0.1 K, ΔH = 6.7 ± 0.4 kJ mole^{-1}.

[c] Transition at 365.6 ± 0.3 K, ΔH = 13.8 ± 0.4 kJ mole^{-1}.

[d] Transition at 391 ± 0.3 K, ΔH = 3.3 ± 0.2 kJ mole^{-1}.

[e] Transitions at 443.2 ± 0.8 and 456.6 ± 0.6 K, ΔH = 2.9 ± 0.8 and 1.2 ± 0.4 kJ mole^{-1}, respectively.

TABLE 2

Melting temperatures, enthalpies and entropies of fusion of some aromatic hydrocarbons and electron acceptors, used as standards

	T_m (K)	ΔH (kJ mole^{-1})	ΔS (J K^{-1} mole^{-1})
Picric acid	394.1 ± 0.6	17.1 ± 0.2	43.4 ± 0.6
Styphnic acid	454.9 ± 0.4	33.5 ± 0.3	73.6 ± 0.8
1,2-Benzofluorene [a]	462.8 ± 0.1	18.4 ± 0.1	39.7 ± 0.3
2,3-Benzofluorene	489.7 ± 0.4	23.4 ± 0.3	47.8 ± 0.7
$\beta\beta'$-Binaphthyl	461.2 ± 0.6	38.9 ± 0.8	84.4 ± 1.9
Decacyclene [b]	562.0 ± 0.3	45.2 ± 2.0	80.4 ± 3.6
9-Phenylanthracene	427.6 ± 0.8	25.5 ± 0.4	59.7 ± 1.0
o-Phenylenepyrene	437.7 ± 0.6	16.3 ± 1.2	37.2 ± 2.8

[a] Transition at 399.9 ± 0.1 K, ΔH = 3.8 ± 0.3 kJ mole^{-1}.

[b] Very small endotherm at 533 ± 5 K; decomposes on melting.

than previously reported value (357 K). The picrate of 1,2-benzanthracene appears to be stable at its melting point, in contrast to literature reports.

DISCUSSION

In the previous thermodynamic study of the complexes of aromatic hydrocarbons with *s*-trinitrobenzene, etc., we suggested that the heats of formation of solid and liquid complexes, ΔH_s^0 and ΔH_l^0 respectively, should be related to the experimental heats of fusion of the donor, acceptor and complex by

$$\Delta H_{f,DA} - \Delta H_{f,D} - \Delta H_{f,A} = \Delta H_l^0 - \Delta H_s^0$$

where $\Delta H_{f,X}$ is the heat of fusion of component X. Values of ($\Delta H_{f,DA} - \Delta H_{f,D} - \Delta H_{f,A}$) for a number of hydrocarbon picrates are shown in Table 3, together with their corresponding ΔH_s^0 values and the derived ΔH_l^0 values.

Inspection of these data shows that our previous assumption of a value of ca. −8 kJ mole^{-1} for ΔH_l^0 is not in accord with the derived values for aromatic hydrocarbon picrates. Further, the values of ΔH_l^0 are greater than ΔH_s^0 for those systems with positive ΔH_s^0 values, in general, and similarly more negative for those systems with negative ΔH_s^0 values. Values of $\Delta H_{f,D}$ lie mainly in the range 16—25 kJ mole^{-1} and thus ($\Delta H_{f,D} + \Delta H_{f,A}$) is constant, to within ±4 kJ mole^{-1}, for most donors [8]. The ΔH_l^0 data thus suggest that there is some approximate correspondence between the enthalpies of fusion for the complexes and the ΔH_s^0 values for complexation for this series. The larger $\Delta H_{f,DA}$ values are found for those complexes having positive ΔH_s^0 values and the smaller $\Delta H_{f,DA}$ values for those with negative ΔH_s^0 values. The observation of a positive ΔH_s^0 value implies that the extent of complexing increases with temperature, as opposed to the more usual situa-

TABLE 3

Values of ($\Delta H_{f,DA} - \Delta H_{f,D} - \Delta H_{f,A}$) and ΔH_s^0, together with derived values of ΔH_l^0, for some aromatic hydrocarbon picrates

Donor	($\Delta H_{f,DA} -$ $\Delta H_{f,D} - \Delta H_{f,A}$) (kJ mole^{-1})	ΔH_s^0 [a] (kJ mole^{-1})	ΔH_l^0 (kJ mole^{-1})
Acenaphthene	−2.9	−3.63	−6.53
Benzo[*a*]pyrene	5.6	17.63	23.23
β,β'-Binaphthyl	−14.6	24.18	9.58
1,2,3,4-Dibenzanthracene	1.9	12.57	14.47
1,2,5,6-Dibenzanthracene	5.7	7.25	12.95
Fluoranthene	−11.3	−7.02	−18.32
Naphthalene	−1.5	−8.03	−9.53
Perylene	−6.6	22.58	15.98
Pyrene	−1.6	−10.39	−11.99
Triphenylene	4.7	−6.77	−2.07

[a] Data from ref. 7.

tion in solution where negative values are found for enthalpies of complex formation. Assuming the general stacking pattern for charge-transfer complexes [9], an increase in ΔH_s^0 thus leads to greater interaction between the molecules in the solid state, both within and between stacks. This in turn implies that greater energy will be required to separate constituent complexes in the crystal lattice, and hence an increased $\Delta H_{f,DA}$, in accord with our observations.

Some further support for the suggestion that, for these complexes, the enthalpies of fusion do reflect the charge-transfer interaction, even though its magnitude is relatively small, is obtained from comparisons of data for aromatic hydrocarbon complexes with various nitroaromatic acceptors. In Table 4 a comparison of the available data for complexes of a given hydrocarbon with *s*-trinitrobenzene [1] (TNB) and picric acid (PA), and with 2,4,7-trinitrofluorenone (TNF) and 2,4,5,7-tetranitrofluorenone [1] (TENF), is shown.

Although many compounds form isolable complexes with picric acid, the same donors frequently form complexes with *s*-trinitrobenzene only in solution. However, the ability to isolate a solid complex is not dependent only on the charge-transfer interaction. This is shown in part by the greater free energies and enthalpies of complex formation for *s*-trinitrobenzene complexes [10] than for picrates [11] of various aromatic hydrocarbons in carbon tetrachloride.

The introduction of an hydroxyl group into *s*-trinitrobenzene should decrease its acceptor ability because of the possibility of resonance delocalization of the oxygen lone pair electrons into the ring, and also the increased probability of non-planarity of the nitro groups. The adverse steric effect resulting from twisting of the nitro groups is unlikely to be of significance either in complex formation, or in the enthalpies of fusion of picrates. Aromatic hydrocarbons are normally planar, or almost so, and have interplanar spacings in the range 3.3—3.5 Å. Complexes with picric acid or *s*-trinitrobenzene normally have slightly smaller interplanar spacings than that but the nitro groups are often significantly non-planar, e.g. a twist of 14° for one nitro group in the skatole—*s*-trinitrobenzene complex [12]. The complete miscibility of various substituted naphthalene picrates also suggests that steric factors do not seriously affect complex formation [9], as does the formation of derivatives of sterically hindered hydrocarbons, e.g., 1- and 2-*t*-butylnaphthalene picrates [13]. The major contribution to the weaker complexing ability of picric acid, relative to *s*-trinitrobenzene, is therefore most likely to be electronic. The lower $\Delta H_{f,DA}$ values for picrates, shown in Table 4, are thus in accord with the lower complexing ability of this acceptor.

Comparison of $\Delta H_{f,DA}$ values for complexes with trinitrofluorenone and tetranitrofluorenone again shows that those with the stronger acceptor have, in general, the higher values. The extra nitro group in the tetranitro-compound will increase its electron-accepting ability, but there will be some, potentially unfavourable, steric interaction introduced between the 4- and 5-nitro groups. That this is again less important than the electronic factor is shown by the results obtained (Table 4).

The results presented here are thus in accord with a small contribution

TABLE 4

Comparisons of the heats of fusion of aromatic hydrocarbon complexes with various nitroaromatic acceptors

Donor	Acceptor			
	TNB [a] $\Delta H_{f,DA}$ (kJ mole^{-1})	PA $\Delta H_{f,DA}$ (kJ mole^{-1})	TNF [a] $\Delta H_{f,DA}$ (kJ mole^{-1})	TENF [a] $\Delta H_{f,DA}$ (kJ mole^{-1})
Anthracene	39.7	24.3	45.2	69.9
1,2-Benzanthracene	37.2	32.2	50.6	43.9
1,2,5,6-Dibenzanthracene	60.7	54.0	52.7	59.0
Perylene	56.5	42.3	66.5	59.4
Pyrene	38.5	32.6	43.9	44.4
Triphenylene	50.6	46.9	53.1	67.8

[a] Data from ref. 1.

from the charge-transfer interaction to the overall enthalpy of fusion of the complexes studied, but the data do reflect the presence of such interactions, hitherto unobserved for other charge-transfer complexes.

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REFERENCES

1 F. Casellato, C. Vecchi, A. Girelli and P.G. Farrell, Thermochim. Acta, 13 (1975) 37.
2 F. Casellato, C. Vecchi, and A. Girelli, Chim. Ind. (Milan), in press.
3 P.G. Farrell, F. Shahidi, J.V. Westwood, F. Casellato, C. Vecchi and A. Girelli, unpublished data.
4 F. Casellato, C. Vecchi and A. Girelli, Thermochim. Acta, 21 (1977) 195; Chem. Ind. (London), (1977) 83.
5 F. Pelizza, F. Casellato and A. Girelli, Thermochim. Acta, 4 (1972) 135.
6 F. Casellato, C. Vecchi and A. Girelli, Gazz. Chim. Ital., 108 (1978) 21.
7 F. Shahidi and P.G. Farrell, J. Chem. Soc., Perkin Trans. 2, submitted for publication.
8 F. Casellato, C. Vecchi, A. Girelli and B. Casu, Thermochim. Acta, 6 (1973) 361.
9 See F. Herbstein, J.D. Dunitz and J.A. Ibers (Eds.), Perspectives in Structural Chemistry, Vol. 4, Wiley, New York, 1971, p. 166.
10 G. Briegleb and J. Czekalla, Z. Elektrochem., 59 (1955) 184.
11 G. Briegleb, J. Czekalla and A. Hauser, Z. Phys. Chem., 21 (1959) 99.
12 A.W. Hanson, Acta Crystallogr., 17 (1964) 559.
13 N.G. Bromby, A.T. Peters and F.M. Rowe, J. Chem. Soc., (1943) 144; E. Illingworth and A.T. Peters, J. Chem. Soc., (1951) 1602.