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THERMAL INVESTIGATION OF ORGANIC CRYSTALLINE COMPLEXES. III. HEAT OF FORMATION OF COMPLEXES

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ABSTRACT

The possibility of the determination of the enthalpy of formation of some crystalline organic complexes by the differential thermal analysis (DTA) method was explored using picric acid and 2,4,6-trinitrotoluene complexes with polynuclear aromatic hydrocarbons and some methyl substitutions.

INTRODUCTION

Enthalpies of formation of organic complexes are usually determined by spectroscopic methods, using their solutions in neutral solvents. They are calculated on the assumption that the enthalpies of mixing for pure components in complexes are zero, i.e. the solutions are ideal. In this case the enthalpy formation of a liquid complex $\Delta H_L^\ominus$ and the enthalpy of its formation in solutions are similar [1]. The hypothetic heat of formation of solid complexes $\Delta H_S^\ominus$ is calculated from the following formula [1,2]

$$\Delta H_{fDA} - \Delta H_{fD} - \Delta H_{fA} = \Delta H_L^\ominus - \Delta H_S^\ominus \qquad (1)$$

In this formula ΔH_{fDA}, ΔH_{fD} and ΔH_{fA} are the values of the enthalpy of melting for the complex, donor and acceptor, respectively. However, the values of the enthalpy of complex formation in solution may not be the same in the liquid phase because of the influence of a solvent in the solution.

During heating, equimolar mixtures of some acceptors and donors displayed an exothermic peak on the DTA curves. This peak was defined as the peak due to complex formation.

The aim of the present paper is to report the results of an investigation of organic complexes by the DTA method and to show the possibility of the direct determination of their enthalpies of formation in the liquid phase without using a solvent.

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EXPERIMENTAL

The materials, apparatus and method of measurements have been described in a previous work [3]. Samples of equimolar mixtures of a donor and an acceptor were used in measurements instead of the prepared complexes. Moreover, as before two cycles of heating (A and B) were applied. For the identification of adequate peaks in the DTA curves, the second cycle of heating (B) was indispensable.

RESULTS AND DISCUSSION

During heating the mixtures of a donor and an acceptor gave exothermic peaks of various magnitudes, which may be easily identified as peaks due to the formation of complexes. In addition, three further endothermic peaks were observed in the DTA curves. The first one corresponded to a lower eutectic melting point, the second to a higher eutectic melting point, and the third to the melting of a complex. The endothermic peaks were identified on the basis of phase diagrams [4,5] and the thermal investigation of the behaviour of complexes during heating, as reported previously [6]. However, these three peaks were not always observed on the thermograms.

An exothermic peak always appeared above the lower eutectic melting point. On the other hand, it never appeared during the heating of a prepared complex, and during its heating in the second cycle of heating. A negligible or very small peak appeared during the heating of mixtures of a donor and an acceptor reacted in the preliminary stage of preparation. Then a colour change was observed. From these facts it may be inferred that this peak is connected with the formation of the complex.

The peak of complex formation appeared at different places on the DTA curves and had various shapes. An exothermic peak often appeared at the higher melting eutectic point. An example of the DTA curve for equimolar acenaphthene and picric acid mixture is shown in Fig. 1. In some cases, for example in 1,5-DMN (Fig. 2) and phenanthrene with picric acid, and 1,4-DMN with TNT, the peak corresponding to the formation of a complex appeared below the higher melting eutectic point. During subsequent heating cycles of these complex mixtures, an endothermic peak appeared in place of the exothermic peak due to the melting of eutectic mixture (Fig. 3), and very often there was no peak at all (Fig. 4).

In some cases for example in the systems, fluorene, anthracene, 1,3-DMN and 2,6-DMN with picric acid, and also in anthracene, 2-MN (Fig. 5), 1,5-DMN and 1,6-DMN with TNT, an exothermic peak did not appear in the first heating cycle. Many of these mixtures, e.g. anthracene (after 1 h), 1,3-DMN and 2,6-DMN with picric acid and 2-MN and 1,6-DMN with

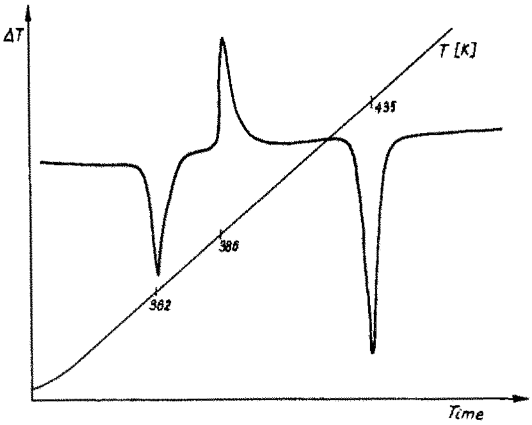

Fig. 1. Thermogram of an equimolar mixture of acenaphthene and picric acid.

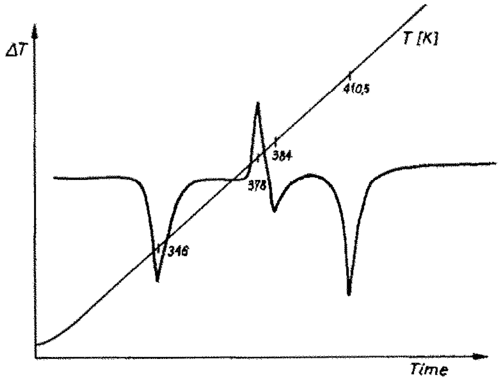

Fig. 2. Thermogram of an equimolar mixture of 1,5-dimethylnaphthalene and picric acid.

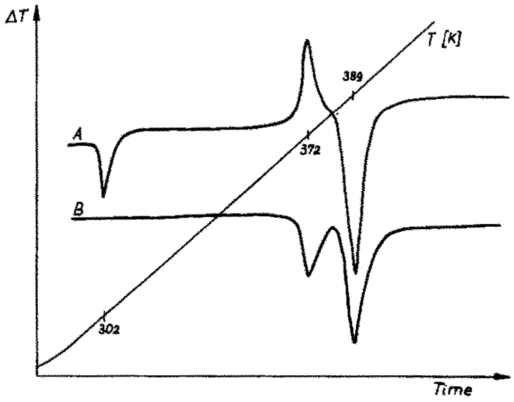

Fig. 3. Thermogram of an equimolar mixture of 2-methylnaphthalene and picric acid.

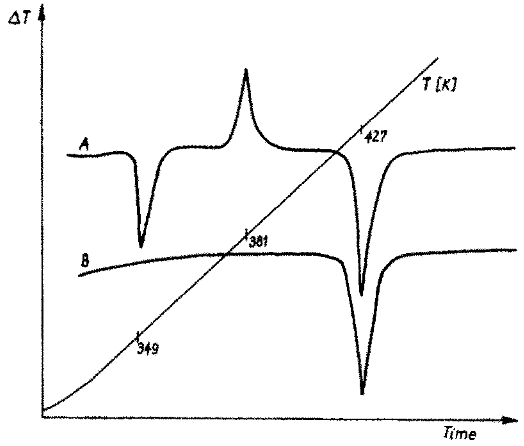

Fig. 4. Thermogram of an equimolar mixture of naphthalene and picric acid.

TNT, exhibited colour changes during their mixing. This means that the complexes are formed spontaneously at room temperature.

The observations demonstrate that complexes are formed more easily in the liquid phase when the eutectic mixture and one or both components are in the liquid phase. In these cases, the exothermic peak was also absent on the thermograms during the heating of the samples. Sometimes the components reacted only partially during their mixing, which gave a small peak during the heating of the samples.

We believe that an exothermic peak is always connected with complex formation not only in the liquid phase, but also during the mixing of the solid donor and solid acceptor components. However, a noticeable peak is not observed because of the slow diffusion of the components in the solid

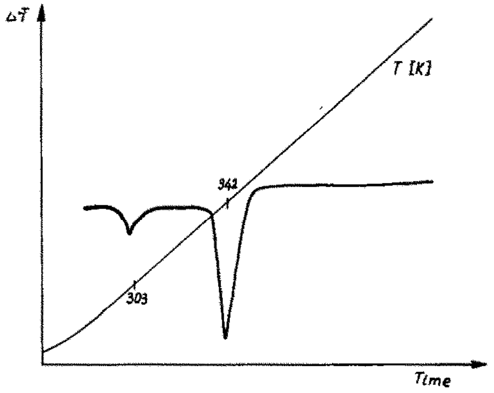

Fig. 5. Thermogram of an equimolar mixture of 2-methylnaphthalene and 2,4,6-trinitrotoluene.

TABLE 1

Experimental and calculated values of the enthalpies of complex formation in the liquid and solid phases

Donor	Picric acid			2,4,6-TNT		
	T (K)	$\Delta H_L^{\ominus}$ (kJ mol^{-1})	$\Delta H_S^{\ominus}$ (kJ mol^{-1})	T (K)	$\Delta H_L^{\ominus}$ (kJ mol^{-1})	$\Delta H_S^{\ominus}$ (kJ mol^{-1})
Acenaphthene	386.0	−11.7	−10.7	358.0	−6.6	−0.5
Phenanthrene	373.0	−7.0	11.1	352.0	−13.6	−6.3
Fluoranthene	388.0	−6.8	6.8	368.5	−6.2	10.8
Fluorene				355.0	−5.2	3.7
Naphthalene	386.0	−12.3	−7.9	348.0	−4.1	13.9
Pyrene	416.0	−8.1	−5.1	398.0	−14.0	3.1
1-MN	381.0	(−1.9)	14.4	339.5	−12.5	5.5
2-MN	372.0	−12.5	17.1			
1,3-DMN				329.0	(−1.6)	21.6
1,4-DMN	379.0	(−2.0)	−6.5	335.0	(−3.4)	11.6
1,5-DMN	378.0	−9.5	11.9			
1,6-DMN	367,0	−2.4				
1,8-DMN	385.0	−7.2	−0.5	348.0	−13.5	−9.3
2,3-DMN	382.0	−19.9	−16.7	353.5	−6.4	4.6

Values in parentheses are lower than expected (see text).

state. Complex formation in the "solid state" occurs in the presence of the liquid phase, which is formed by the fusion of crystals in places of contact. The appearance of the liquid phase is facilitated by an exothermic reaction. A solution of eutectic mixtures always has a lower melting point than that of the complex and thus allows further complex formation in the liquid phase.

The enthalpies of formation of complexes in the liquid phase $\Delta H_L^{\ominus}$ calculated from the area under exothermic peaks are given in Table 1. Some values are lower because of the above mentioned reasons. These cases are in parentheses in the table.

From the enthalpies of formation of complex in the liquid phase, enthalpies of formation in the solid phase $\Delta H_S^{\ominus}$, were calculated using eqn. (1). These values are also included in Table 1. From the table it follows that the enthalpies of formation in the solid phase may have positive as well as negative values. In our opinion, if the enthalpy for complex formation in the solid phase $\Delta H_S^{\ominus}$ has positive values then the lattice energy exceeds the energy of formation of a complex and the complex exists in the crystalline state. However, if the enthalpy for complex formation has negative values, then it participates in the lattice energy of the crystal. Our values of ΔH are consistent with the literature values. This indicates that the crystal lattice energy is much higher than the energy of interaction between a donor and an acceptor. However, the enthalpies for complex formation are not always higher in the solid phase than those in the liquid phase, as reported by Casellato et al. [1].

It should be mentioned that the values of the enthalpies for complex formation in the liquid phase calculated from spectroscopic investigation in solutions do not agree with the values obtained by the DTA method. This means that the enthalpies for complex formation obtained even in neutral solvents by spectroscopic method should not be compared with those for liquid complexes.

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REFERENCES

1 F. Casellato, C. Vecchi, A. Girelli and P.G. Farrell, Thermochim. Acta, 13 (1975) 37.
2 P.G. Farrell, F. Shahidi, F. Casellato, C. Vecchi and A. Girelli, Thermochim. Acta, 33 (1979) 275.
3 I. Kotuła and A. Rabczuk, Thermochim. Acta, 126 (1988) 61.
4 I. Kotuła and A. Rabczuk, J. Therm. Anal., 19 (1980) 143.
5 I. Kotuła and A. Rabczuk, J. Therm. Anal., 30 (1985) 195.
6 I. Kotuła and A. Rabczuk, Thermochim. Acta, 126 (1988) 67.