Journal of Thermal Analysis, Vol. 25 (1982) 441—447

COMPLEXES OF ACID AMIDES WITH POLAR APROTIC SOLVENTS. II. THERMAL ANALYSIS OF THE COMPLEXES OF BIS(N-PHENYL)-PYROMELLITIC ACID AMIDE WITH DIMETHYLFORMAMIDE, DIMETHYLACETAMIDE, N-METHYLPYRROLIDONE AND DIMETHYLSULFOXIDE

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(Received March 1, 1982)

The synthesis of solid complexes of bis(N-phenyl)-pyromellitic acid amide (PMA) with aprotic solvents (dimethylformamide, dimethylacetamide, *N*-methylpyrrolidone and dimethylsulfoxide) and their thermal analysis (evolved gas analysis using mass spectroscopy, and thermogravimetry) is described. In all cases, the composition of the complexes was found to be 1PMA : 2 solvent. The activation energy of the decomposition process of the complexes was determined from TG data. The values found were between 40 and 80 kJ/mol.

We have reported earlier [1] that bis(*N*-phenyl)-pyromellitic acid amide (PMA) forms solid, stable complexes with dimethylformamide (DMFA) having compositions 1PMA : 2DMFA or 1PMA : 1DMFA, depending on the agent used for their precipitation (benzene, acetone and water, resp.).

In this paper the composition of analogous solid complexes obtained from PMA solutions in dimethylacetamide (DMAA), *N*-methylpyrrolidone (N – MP) and dimethylsulfoxide (DMSO) by precipitation with benzene will be described. A comparative study of the thermal decomposition process of the complexes and of the successive cyclodehydration process of PMA was performed by thermal analysis: evolved gas analysis using mass spectrometry, and thermogravimetry.

Experimental

The PMA – solvent complexes were obtained by the reaction of pyromellitic dianhydride with aniline in the corresponding solvent, as described in [1]. The solutions were then poured into a large excess of benzene. The precipitated PMA – solvent crystals were filtered, washed with benzene and dried in vacuum to constant mass. Data of elemental analysis and the corresponding composition of the complexes are listed in Table 1.

Evolved gas analysis by mass spectrometry was performed using the special flow-duct fitted to the cell described in [1].

For TG, a derivatograph (manufacturer: MOM Optical Works, Budapest) was used: the 50 mg samples were heated at a rate of 2.5 degree/min in open ceramic crucibles, in air.

Table 1

PMA— solvent complexes: data of elemental analysis

No.	C calcd. found	N calcd. found	H calcd. found	Composition of complex
I	61.09 60.97	10.18 9.99	5.46 5.79	1PMA: 2DMFA
II	62.28 62.08	9.69 9.42	5.88 6.05	1PMA: 2DMAA
III	55.71 56.51	5.00 5.00	5.00 4.98	1PMA: 2DMSO
IV	63.79 64.00	9.30 9.34	5.65 5.44	1PMA: 2N—MP

Discussion of the results

The composition of the complexes was determined by three independent methods: evolved gas analysis, TG and elemental analysis.

The results of evolved gas analysis are presented in Figs 1a to 4a. In all cases three separate processes can be observed: decomposition of the complex (evolved solvent), cyclodehydration of PMA (evolved water) and partial decomposition of PMA (evolved aniline).

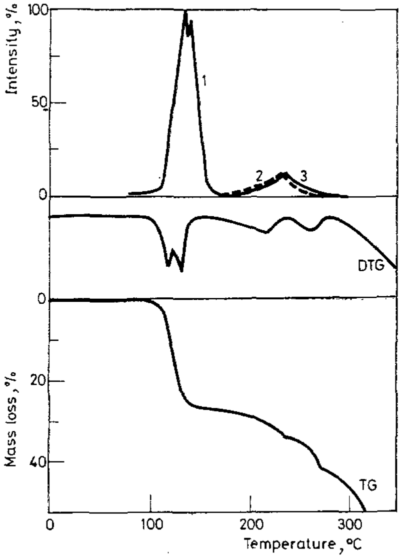


Fig. 1. Evolved gas analysis (a), DTG (b) and TG (c) curves of the comples 1PMA : 2DMFA 1 — m/e 73 (DMFA), 2 — m/e 17 (H_2O), 3 — m/e 93 (aniline)

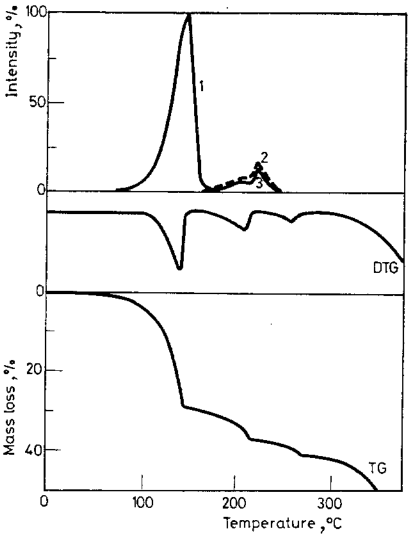


Fig. 2. Evolved gas analysis (a), DTG (b) and TG (c) curves of the complex 1PMA : 2DMAA
1 — *m/e* 87 (DMAA), 2 — *m/e* 17 (H_2O), 3 — *m/e* 93 (aniline)

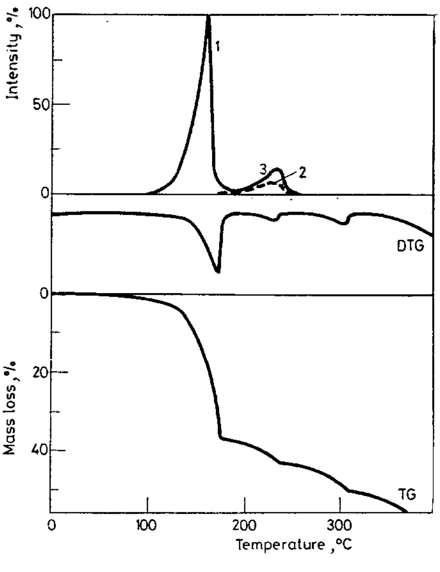


Fig. 3. Evolved gas analysis (a), DTG (b) and TG (c) curves of the complex 1PMA : 2N—MP
1 — *m/e* 99 (N—MP), 2 — *m/e* 17 (H_2O), 3 — *m/e* 93 (aniline)

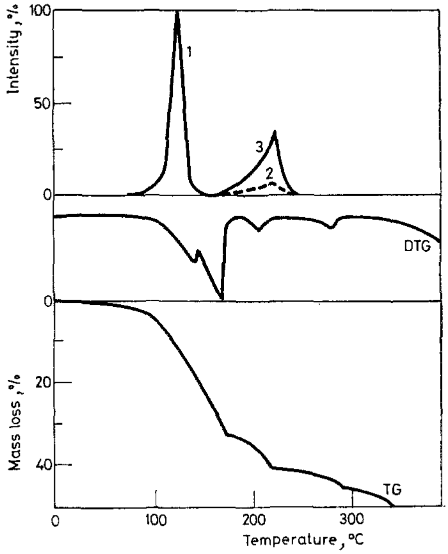


Fig. 4. Evolved gas analysis (a), DTG (b) and TG (c) curves of the complex 1PMA : 2DMSO 1 — *m/e* 78 (DMSO), 2 — *m/e* 17 (H_2O), 3 — *m/e* 93 (aniline)

Notwithstanding the difference in experimental conditions (evolved gases determined by mass spectroscopy being carried out at reduced pressures, TG at atmospheric pressure), similar features are observed with both methods. In fact, the peak corresponding to solvent evolution is at about the same temperature and is followed by two further processes, that of cyclodehydration and PMA decomposition (Figs 1b to 4b). To evaluate the amount of solvent evolved in the decomposition of the complex by means of mass spectroscopy we calculated the relative sensitivities H_2O (*m/e* 17) to DMFA (*m/e* 73) DMAA (*m/e* 87) DMSO (*m/e* 78) and N–MP

Table 2

PMA— solvent complexes: evolved gas analysis by mass spectroscopy

No.	Solvent	Peak area ratio solvent/ H_2O	Rel. sensitivity H_2O/solvent	Mol-% solv. mol-% H_2O	Decomposition of PMA, mol-%	Composition of complex
I	DMFA	4.9	0.24	1.18	3	1PMA: 2DMFA
II	DMAA	6.3	0.15	0.97	2	1PMA: 2DMAA
III	DMSO	5.6	0.17	0.95	11	1PMA: 2DMSO
IV	N—MP	11.0	0.11	1.20	6	1PMA: 2N—MP

Table 3

PMA–solvent complexes: thermogravimetric analysis

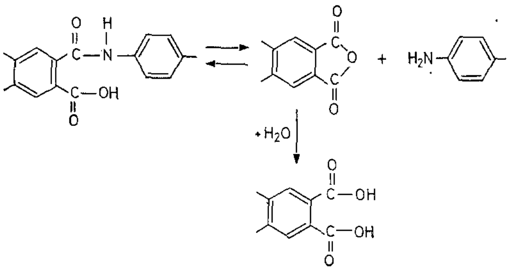
No.	Solv.	Mass loss on account of solv., %		Mass loss on account of H_2O, %	Mass loss on account of aniline, %	Decompos. of PMA, mol-%	E_a, KJ/mol	Composition of complex
		found	calcd. as 1PMA : 2solv.					
I	DMFA	27	27.5	4.6	10.4	30.2	72±8	1PMA: 2DMFA
II	DMAA	29	30.1	4.0	8.0	27.7	59±8	1PMA: 2DMAA
III	DMSO	33	27.9	4.2	8.3	27.3	46±8	1PMA: 2DMSO
IV	N–MP	36	32.9	3.8	8.7	30.7	63±8	1PMA: 2N–MP

(*m/e* 99), and also to aniline (*m/e* 93) for the purpose of determining the extent of decomposition of PMA. The data are listed in Table 2. In the thermogravimetric experiments we determined the amount of solvent evolved by assuming that the first step on the TG curve corresponds to mass loss due to the decomposition of the complex. TG data are presented in Table 3. Both thermoanalytical methods (Tables 2 and 3) and elemental analysis (Table 1) demonstrate that the composition of all four complexes studied is identical: 1PMA : 2 solvent.

As noted earlier [1], the thermal decomposition of the PMA–DMFA complex proceeds in two stages. In contrast, the decomposition of the other three complexes proceeds in one single stage, as confirmed by both thermoanalytical methods applied for their study. Evolved gas analysis demonstrates that the maximum temperature of solvent evolution from the complex successively rises in the order DMFA, DMAA and N–MP, in agreement with the order of the boiling points of these solvents. The only exception is the complex PMA–DMSO showing the lowest temperature maximum (125^{c}) of solvent evolution. This might be explained by the thermal instability of this complex.

It would be unjustified to make any conclusion regarding the structure of these complexes, relying on our findings. One may state that the activation energy of the decomposition process of the complex formed with DMFA is higher than the corresponding values for the other complexes. From TG data, the values for the complexes of PMA with DMFA, DMAA, DMSO and N–MP are 71, 59, 46 and 63 kJ/mol, resp.

Aniline formed in the decomposition of PMA is recorded simultaneously on the mass spectrometer with the water formed in the cyclodehydration process. Considering that the flow rate of water through the flow-duct is 2.3 times as high as that of aniline, one would assume that aniline is formed previously than water. The situation becomes, however, more complex by taking into account that the evolved water may promote the decomposition of PMA by interfering with the equilibrium established [2]:



shifting it towards pyromellitic acid and aniline formation. Since in this reaction one part of the water evolved in cyclodehydratation will be used up for the hydrolysis of the anhydride group, the strict sequence of these two processes could only be found in a detailed study of the reactions occurring in the system. As shown in Table 2, the extent of the decomposition of PMA at the conditions of evolved gas analysis with the mass spectrometer is 2 . . . 6% for the complexes formed with DMFA, DMAA, N – MP and as high as 11% for the complex with DMSO.

At the conditions of TG the extent of PMA decomposition is substantially higher (Table 3). As mentioned, the first step of mass loss recorded on the TG curves (cf. Figs 1 – 4) corresponds to the decomposition of the complex and evolution of solvent, while the second two correspond to cyclodehydration and PMA decomposition. Up to 300°, the mass losses consist of evolved water and aniline (confirmed by mass spectrometric data). Let us assume that after the third step of mass loss the material in the crucible is a mixture of X mol pyromellitdianilide and Y mol pyromellitic dianhydride (PMDA). In this case $2X$ mol water were evolved in step 2 and $2Y$ mol aniline in step 3. Let us use the symbol a for the sum of mass losses in steps 2 and 3, and the symbol b for the mass of the residue in the crucible after step 3. Then

$$18 \cdot 2X + 93 \cdot 2Y = a, \text{ and}$$

$$368\,X + 218\,Y = b$$

where 18, 93, 368 and 218 are the molecular masses of water, aniline, pyromellitdianilide and pyromellitic dianhydride, resp. By solving this system of equations for X Y, and one obtains the amount of evolved water ($36\,X$), the amount of evolved aniline ($186\,Y$) and the degree of decomposition of PMA $\left(\frac{Y}{X+Y} \cdot 100, \%\right)$.

The data on PMA decomposition in TG are listed in Table 3. The degree of decomposition is fairly similar in all cases: 27 . . . 30%. One may assume that the difference against the values obtained in evolved gas analysis is related to the participation of the water evolved in the cyclodehydration process in PMA decomposition. Actually at the conditions used for mass spectrometry (reduced pressure) water will be evolved more rapidly from the sample, and the hydrolysis of the anhydride groups – and hence the shift of the equilibrium towards the decomposition of PMA – will occur in a lesser degree than in the case of TG performed at atmospheric pressure.

Let us finally note that in the thermal analysis of solid PMA complexes with solvents by evolved gas analysis and thermogravimetry the temperatures for the decomposition of the complex and for cyclodehydratation of PMA are usually sharply separated. This is, however, only the case if the solvents used are satisfactorily dry and pure. In our practice, cases occurred where solvent, water and aniline were recorded in one and the same temperature interval. To explain this anomaly further studies will be needed.

References

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2. L. W. Frost and J. Kesse, J. Appl. Polymer Sci., 8 (1964) 1039.

Zusammenfassung – Es wird die Synthese der festen Komplexe von Bis(N-phenyl)-pyromellithsäureamid (PMA) mit aprotischen Lösungsmitteln (Dimethylformamid, Dimethylacetamid, N-Methylpyrrolidon und Dimethylsulfoxid) und deren thermische Analyse (massenspektrometrische Analyse der gebildeten Gase und Thermogravimetrie) beschreiben. In allen untersuchten Komplexen betrug das Zahlenverhältnis von PMA- zu Lösungsmittelmolekülen 2 : 1. Die für die Zersetzung der Komplexe aufzubringenden Aktivierungsenergien wurden aus TG-Daten bestimmt. Die ermittelten Werte lagen zwischen 40 und 80 kJ · mol^{-1}.

Резюме — Описаны синтез и исследование методами масс-спектрометрического термического анализа (МТА) и термогравиметрического анализа (ТГ) твердых комплексов бис-(N-фенил)-пиромеллит-амидокислоты (ПМК) с апротонными растворителями (диметилформамид, диметилацетамид, N-метилпирролидон, диметилсульфоксид). Показано, что во всех исследованных случаях комплексы имеют состав $[\text{ПМК}]_1$: $[\text{Sol}]_2$. По данным ТГ определены энергии активации распада комплексов, которые лежат в пределах 40—80 кж/моль.