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COMPLEXES OF PYROMELLITIC DIANIL ACID WITH APROTIC SOLVENTS

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Complexing with the participation of polar aprotic solvents plays an important role in all stages of the synthesis of imides and polyimides. The starting compounds, especially dianhydrides, thus form sufficiently stable complexes with dimethylformamide (DMFA) and other solvents of the amide type [1, 2]. The reactivity of these complexes in acylation of aromatic amines is lower than the starting dianhydrides [3]. It was interesting to study the role of complexing in the subsequent stages of the reaction: in the formation and cyclodehydration of the amido acid.

Crystalline complexes of A with DMFA (dimethylformamide) (I), DMAA (dimethylacetamide) (II), MP (N-methyl-2-pyrrolidone) (III), and DMSO (dimethyl sulfoxide) (IV) which are stable in prolonged storage in air were first isolated as a result of precipitation with acetone or benzene from solutions of pyromellitic dianil acid (A) in DMFA, DMAA, MP, and DMSO. Acid A free of solvent was synthesized for comparison and control. The compounds isolated were colorless crystalline powders. Significant differences were observed in the IR spectra* of acid A and product (I) (Fig. 1). In the 20-110°C range where the reaction of cyclization of the amido acid group is excluded, frequency shifts of two absorption bands were observed in the spectrum of (I): 1685 cm^{-1}, assigned to bound DMFA, and 1545 cm^{-1} (amide II), assigned to the amido acid component of the complex. The values of the shifts were equal to 10 cm^{-1} (DMFA, maximum high-frequency shift) and 5 cm^{-1} (amide II, low-frequency shift), and these changes in the spectrum were reversible with respect to the temperature. This indicates the appearance of hydrogen bonds in these compounds, which is evidence of A—DMFA complexing in product (I), probably based on the donor—acceptor reaction of acid A and the organic base (DMFA). The findings of the elemental analysis (Table 1) of compounds (I)-(IV) differ from the calculated data for pure acid A, but are in good agreement with the calculated data for the compounds in which two molecules of the corresponding solvent are required per molecule.

Compounds (I)-(IV) were studied by mass spectrometric thermal (MTA) and thermogravimetric (TGA) analysis (Figs. 2-5).

Three peaks can be distinguished on the (MTA) curves of compounds (I)-(IV) (see Figs. 2a-5a) and correspond to elimination of the solvent, water, and aniline. When the sample was gradually heated (at the rate of 2°/min), the complex decomposed with liberation of the corresponding solvent and subsequent cyclodehydration and partial decomposition of acid A with liberation of aniline. For performing quantitative calculations, the mass spectrometer was calibrated with binary mixtures of water and the solvents used and with a mixture of water and aniline. The results of the calculations (see Table 1) showed that compounds (I)-(IV) had the composition of $[A]_1 \cdot [Sol]_2$, where Sol is a molecule of solvent, regardless of the type of solvent. The presence of complexing with the solvent and the type of solvent significantly affected the process of thermal transformations of A. Although the decomposition of the amido acid of compounds (I) and (II) was almost the same and relatively low (3 and 2%, respectively), it attained 6% for compound (III), 11% for (IV), and 13% of pure amido acid A was decomposed in the same conditions.

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*The IR spectra were made by A. N. Krasovskii.

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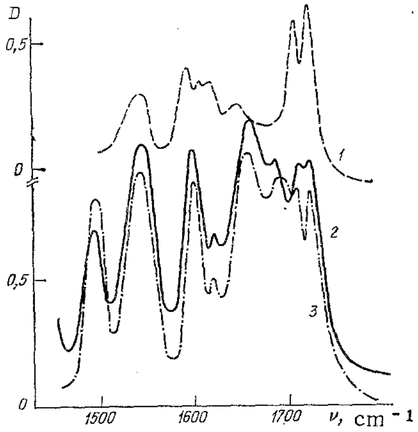


Fig. 1

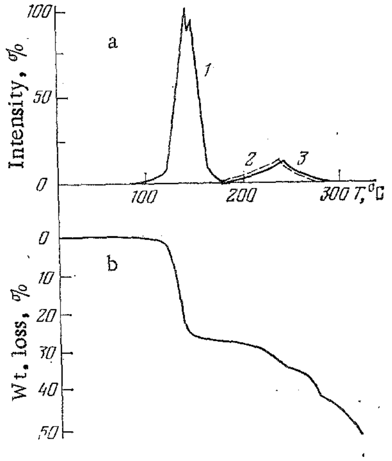


Fig. 2

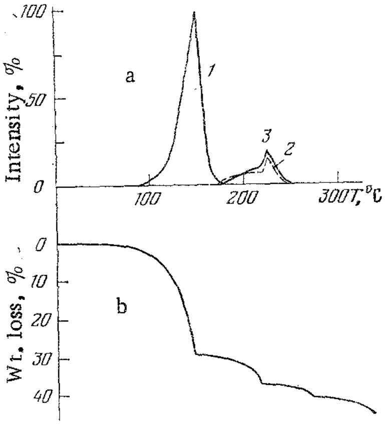


Fig. 3

Fig. 1. IR spectrum of amido acid A (1) and complex (I) (2, 3): 1) in a polyethylene matrix, 21°C, absorption of polyethylene was compensated; 2) 21°C, 3) 90°C.

Fig. 2. MTA (a) and TGA (b) curves of compound (I): 1) m/z 73 (DMFA); 2) m/z 17 (H_2O); 3) m/z 93 (aniline).

Fig. 3. MTA (a) and TGA (b) curves of compound (II): 1) m/z 87 (DMAA), 2) m/z 17 (H_2O); 3) m/z 93 (aniline).

TABLE 1. Results of Determination of the Composition of Crystalline Pyromellitic Dianil Acid—Solvent Complexes

Solvent	MTA			TGA		Elemental analysis, found / calculated,* %		
	Ratio of the areas of the peaks of the solvent and imidization water	Relative H_2O/solvent sensitivity	Ratio of the mole % of solvent and imidization water	Solvent in the $[A]_1\cdot[Sol]_2$ complex, %(calc)	Weight losses in the first step of the TGA curve, %	C	N	H
DMFA	4,9	0,24	1,18	27,5	27	60,97 / 61,09	9,99 / 10,18	5,79 / 5,46
DMAA	6,3	0,15	0,97	30,1	29	62,08 / 62,28	9,42 / 9,69	6,05 / 5,88
DMSO	5,6	0,17	0,95	27,9	33	56,51 / 55,71	5,00 / 5,00	4,98 / 5,00
MP	11,0	0,11	1,20	32,9	36	64,00 / 63,79	9,34 / 9,30	5,44 / 5,65

*Calculation based on the composition of the $[A]_1\cdot[Sol]_2$ complex.

Despite the significant differences in the conditions of conducting the MTA and TGA (in particular, the first analysis was performed at a lower pressure: below 380 mm Hg), the results of both analyses were very similar. The TGA curves of compounds (I)-(IV) (see Figs. 2b-5b) had three characteristic weight loss steps. The first was found in almost the same temperature range as liberation of the solvent in performing MTA, and judging by the value of the weight loss, was due to the liberation of two molecules of solvent per molecule of A, i.e., to decomposition of the complex. The second and third steps should be due to weight losses as a result of cyclodehydration (liberation of water) and intramolecular decomposition of the amido acid (liberation of aniline). A simple calculation permits determining the amount of water liberated and the degree of decomposition of amido acid A, which was 27-30%, based on the sum of the losses in the second and third stages and the amount of substance remaining after the third stage. This difference in the MTA and TGA data could be due to the participation of water in the process of decomposition of amido acid A. Actually, the low pressure in conducting the MTA ensures more complete elimination of the water liberated from the sample during cyclodehydration and hydrolysis of the anhydride groups, and as a consequence, the shift in the equilibrium

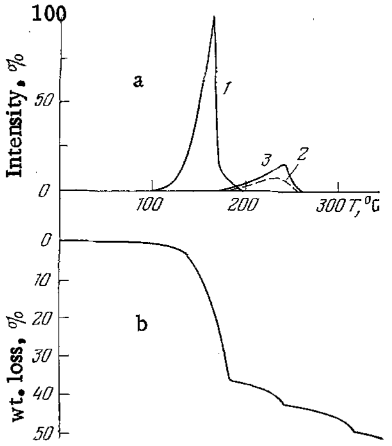


Fig. 4

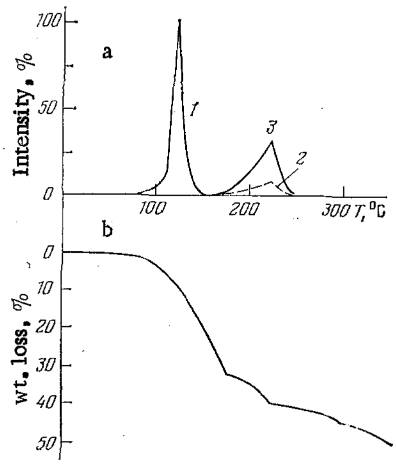
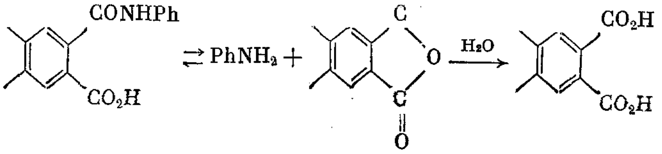


Fig. 5

Fig. 4. MTA (a) and TGA (b) curves of compound (III): 1) m/z 99 (MP), 2) m/z 17 (H_2O), and 3) m/z 93 (aniline).

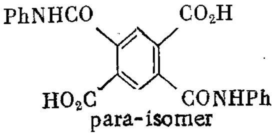
Fig. 5. MTA (a) and TGA (b) curves of compound (IV): 1) m/z 78 (DMSO), 2) m/z 17 (H_2O), and 3) m/z 93 (aniline).



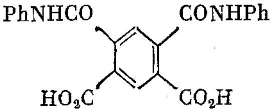
(1)

toward decomposition of the amido acid according to Eq. (1) takes place to a lesser degree than in the case of TGA performed at atmospheric pressure. It should be noted that the TGA data also indicated greater decomposition of pure amido acid A (42%) in comparison to decomposition of amido acid A in a solvent complex.

In conclusion, it is necessary to note that the method of synthesis used assumes the possibility of the formation of two isomeric forms of amido acid A



para-isomer



meta-isomer

However, the crystalline complexes isolated contained only the p-isomer of amido acid A, with the exception of complex (I) precipitated with benzene; it was an equimolar mixture of the p- and m-isomers. The problems related to the separation of these isomers in the pure form and the study of the isomeric composition of solutions of amido acid A were described in detail previously [4].

EXPERIMENTAL

Complexes (I)-(IV) were prepared by the reaction of pyromellitic acid dianhydride with aniline in the corresponding solvent. The reaction was conducted for 1 h at 50°C in a current of dry Ar. The reaction mixture was poured into a tenfold excess of benzene or acetone. The white crystalline residue precipitated was filtered and dried in a vacuum at 50°C to a constant weight. The amido acid, free of solvent, was prepared by the reaction of pyromellitic acid dianhydride with aniline in acetone at 50°C in an atmosphere of Ar. The precipitated residue was filtered and dried in a vacuum to a constant weight.

The IR spectra were made on a Specord 75-IR spectrophotometer. The mass spectrometric thermal analysis (MTA) was conducted on an MX-1320 mass spectrometer. The sample (2.5 mg) was placed in a stainless steel container with a leak. The container was placed in a glass ampul connected to the direct input system of the mass spectrometer. The ampul was heated at the rate of 2°/min. The mass spectrum was recorded after 1-3 min. The dependence of the intensity of the characteristic ions of the products separated on the temperature of the reaction was plotted based on the mass spectra obtained. The values of the relative sensitivity of the instrument to water and the solvents and also to the aniline used for the quantitative calculations were: water/DMFA = 0.24, water/DMAA = 0.15, water/DMSO = 0.17, water/N-methyl-2-pyrrolidone = 0.11, and water/aniline = 0.037. Ions with m/z = 17, 73, 87, 83, 99, and 93, respectively, were selected as the characteristic ions of water, DMFA, DMAA, DMSO, N-methyl-2-pyrrolidone, and aniline. The amount of gaseous products liberated was calculated with the ratio of the areas under the curves of the separation of the products in consideration of the relative sensitivity.

The thermogravimetric analysis (TGA) was conducted on a MOM thermal analyzer in an atmosphere of air with a temperature elevation rate of 2.5°/min in an open ceramic crucible. The weighed portion was 50 mg. The weight losses as a result of elimination of water and aniline were calculated with the system of equations

$$
\begin{gathered}
18 \cdot 2x + 93 \cdot 2y = a \\
368x + 218y = b
\end{gathered}
$$

where x and y are the number of moles of pyromellitic dianilide and pyromellitic acid dianhydride remaining in the crucible after the third stage of the weight loss; *a* is the sum of the weight losses in the second and third stages; b is the weight of the sample in the crucible after the third stage; 18, 93, 368, and 218 are the molecular weights of water, aniline, pyromellitic dianilide, and pyromellitic acid dianhydride, respectively. In solving the system for x and y, we obtain the amount of water (36x) and aniline (186y) separated, and the degree of decomposition of the amido acid $(y/(x + y)) \cdot 100\%$.

CONCLUSIONS

1. Crystalline complexes of pyromellitic dianil acid with DMFA, DMAA, DMSO, and N-methyl-2-pyrrolidone were isolated.

2. Three independent methods (mass spectrometry, thermogravimetric analysis, and elemental analysis) showed that the complexes contained one molecule of amido acid and two molecules of solvent.

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