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THERMOGRAVIMETRIC ANALYSIS OF COMPLEXES OF COMPOUNDS SERVING AS MODELS OF POLYAMIC ACIDS WITH AMIC SOLVENTS

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The thermal transformations of a number of model *o*-amic acids were investigated by thermogravimetric analysis (TG). The TG data pointed to cyclodehydration of the amic acids and accompanying thermal degradation processes. TG in combination with mass-spectrometric thermal analysis provided sufficient information for the description of these processes on both qualitative and quantitative levels.

It has been shown previously [1, 2] that when some aromatic amic acids (modelling fragments of a polyamic acid molecule) interact with amic solvents, stable crystalline complexes are formed. The information obtained by heating these complexes and subjecting them to thermogravimetric analysis (TG) permits conclusions about the compositions of the compounds investigated and their thermal stabilities.

Complexes of pyromellitdianilic acid (PMA) were used as the initial samples for TG. They were obtained from reaction mixtures [2] with the aid of various precipitants such as benzene, acetone, hexane, isopropyl alcohol and water, and are crystalline products in the form of needles or plates, stable on prolonged storage.

TG was carried out by a standard method with a derivatograph in open platinum crucibles at a heating rate of 2–5 degree/min in air.

Figure 1 shows TG-curves for a PMA–DMF complex. Curve 1 was typical when the above organic precipitants were used, while curve 2 characterizes a complex isolated by using water as precipitant.

Complexes which undergo mass loss in accordance with curve 1 on heating at a constant rate of temperature rise were degraded in five stages. These stages can readily be distinguished from one another and are characterized by the following values of temperature and mass loss, respectively: stage 1) 85–125°, 26%; stage 2) 150–210°, 10%; stage 3) 210–265°, 7%; stage 4) 265–370°, 48%; and stage 5) 370–450°, 10%. Under the same conditions, the degradation of the PMA–DMF complex precipitated in water proceeded in four stages: stage 1) 110–190°, 12%; stage 2) 240–285°, 8%; stage 3) 285–415°, 72%; and stage 4) above 450°, 8%.

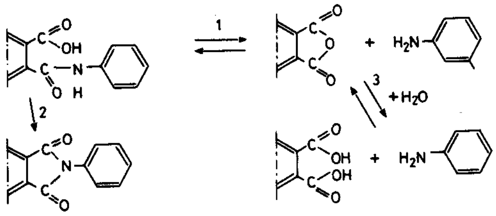
Hence, replacement of an organic precipitant by water for the isolation of the PMA–DMF complex leads to a considerable change in the type of degradation of the complex.

The mass losses observed in stage 1 of the DMA–DMF degradation (curve 1) are in reasonable agreement with the values calculated for the degradation of a PMA complex containing two DMF molecules, whereas the mass losses expressed by curve 2 correspond to the values calculated for the degradation of a complex containing one DMF molecule. The elementary analysis and mass-spectrometric thermal analysis (MTA) data confirm these results.

The activation energy values for the dissociation of the complexes upon heating, calculated from the TG data by the method of Dharwadkar and Kharkanawala [3], vary between 50 and 130 kJ/mole, depending on the nature of the complexing agent.

By analogy with the investigation of polyamic acids, the second stage of degradation of the PMA–DMF complex, beginning after a period of relative stability between 125 and 150°, might be considered to be a process of water elimination as a result of cyclodehydration of PMA. However, the mass loss in this stage greatly exceeded the theoretically possible value. The MTA data helped in elucidating the nature of stage 2. It was shown that in the thermal degradation of PMA–DMF, after DMF is formed aniline and water are also eliminated.

Hence, it may be concluded that the free amic acid formed after degradation of the PMA–DMF complex is a relatively unstable compound which is characterized by competing degradation and cyclodehydration reactions (scheme 1):



(1)

The third stage of mass loss can be clearly distinguished in the TG curve. It ends at a temperature of 260°, whereas the MTA data after the formation of water and aniline is finished do not show the formation of any products up to 300°. Hence, both stages (stages 2 and 3) in the TG curve correspond only to the formation of aniline and water. Proceeding from this conclusion, it is possible to calculate the ratios of these degradation products from the mass of sample remaining after the three degradation stages.

Let the mass losses in stages 2 and 3 be *a* units. After complete degradation of the PMA molecule into aniline and dianhydride, $2x$ aniline molecules are formed, and x anhydride molecules remain in the sample. Similarly, after complete cyclodehydration of PMA, $2y$ water molecules are eliminated and y pyromellitdianilide (PA) molecules

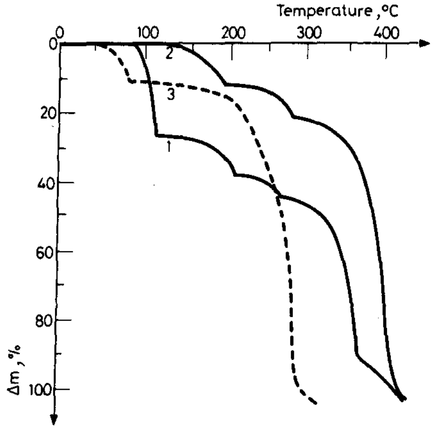


Fig. 1 TG curves: 1) and 2) PMA · DMF complexes (1 – precipitated into benzene, 2 – precipitated into water); 3) crystallohydrate of pyromellitic acid

remain in the sample. If the sample mass is b units after these three stages, then the following system of equations can be written:

$$93 \cdot 2x + 18 \cdot 2y = a, \qquad 218x + 368y = b$$

where 93, 18, 218 and 368 are the molecular masses of aniline, water, pyromellitic dianhydride and PA, respectively. Solving this system for x and y, one obtains the amounts of aniline ($93 \cdot 2x$) and water ($18 \cdot 2y$) formed and the degree of PMA degradation $\left(\frac{x}{x+y} \cdot 100\%\right)$.

For curve 1 (Fig. 1) we have $a = 16\%$ and $b = 57\%$, and the results are as follows: $x = 0.0633$, $y = 0.1174$, $\frac{x}{x+y} \cdot 100\% = 35\%$, the water loss is 4.2% and the aniline loss is 11.8%.*

It is clear that the calculated amounts of aniline and water formed are close to the mass losses in stages 2 and 3, respectively, in the degradation of the PMA complex with DMF. It is noteworthy that the degree of PMA degradation is relatively high (35%). The degradation of PMA free from solvent originally (Fig. 1, curve 3) is still higher, 41%. This high degree of degradation can not be interpreted by the shift of equilibrium 1 (scheme 1) due to the removal of aniline, for under more favourable conditions of low pressure the degradation of pure PMA is 11%.

When the PMA–DMF complex was subjected to degradation under high vacuum (10^{-5} N/m^2), it was observed by MTA that PMA undergoes complete degradation with the formation of aniline before the start of cyclodehydration, thanks to the

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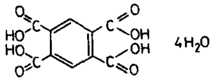
* It can easily be seen that if incomplete degradation and incomplete cyclodehydration of PMA are taken into account, the final result of the calculation will be identical.

facilities for removing the fairly volatile aniline in this case. However, as already mentioned, if TG is carried out at atmospheric pressure, this process will provide only a slight contribution to the total degradation. In this case the water which is the result of cyclodehydration can interact with the anhydride groups and the equilibrium (scheme 1) then shifts towards degradation.

The third stage of degradation may be related to the reverse process: the formation of anhydride groups with water elimination.

This conclusion is confirmed by the results of TG for crystalhydrate of pyromellitic acid with the formula



If this compound is heated under analogous conditions (Fig. 1), two molecules of crystal water are eliminated fairly readily at low temperature. The elimination of two other molecules of crystal water and formation of the anhydride take place in the temperature range 190–250°, which corresponds to the end of stage 2 and the entire stage 3 of mass loss of PMA.

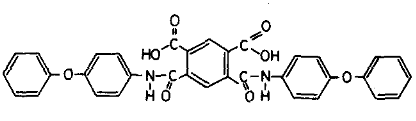
These TG data show that complexing solvents play the part of stabilizers and prevent PMA degradation over a certain temperature range. To confirm this assumption, special experiments were carried out. In one of them, PMA freed from solvent was analyzed by TG. In this case the degradation accompanied by aniline elimination was over 40%. In another experiment PMA was heated under conditions of high vacuum, and it was found that the entire PMA was degraded to initial products before the start of cyclodehydration.

A PMA–DMF complex precipitated in water after appropriate reaction is a specific case. According to TG, in this case a 12–13% mass loss occurs in stage 1 of the degradation. Calculations indicate that this corresponds to the content of about one DMF molecule in the complex. However, the rate of mass loss and the temperature range in the first stage differ greatly from those for the PMA · 2DMF complex. The MTA confirms the fact that in the first stage DMF is present in a slightly greater amount than that corresponding to the PMA:DMF ratio of 1:1. From the MTA data it was established that in this case only trace amounts of aniline are formed. Stage 2 of the mass loss is due to the elimination of water as a result of cyclodehydration.

The interpretation of the above data yields a mechanism in which the water used to precipitate the PMA · DMF complex competes with DMF and forms part of the complex.

This competition is observed by means of MTA for the PMA complex precipitated in water. This complex compound probably has no distinct stages of elimination of complexing agents, unlike PMA. 2DMF, and upon heating the complexed water can be eliminated in stages 1 and 2.

It should be noted that the PMA complexes are convenient for the observation of the degradation processes accompanying cyclodehydration, because the isolation and identification of aniline make it possible to follow clearly the course of degradation of the amic acid. This is due to the high volatility of aniline, which is rapidly removed from the reaction vessel during the heating of PMA, particularly under reduced pressure conditions. If other aromatic amines are used which form corresponding amic acids in the interaction with pyromellitic dianhydride, it is difficult to record the process of thermal degradation by TG because of the low volatility of these amines. We can take as an example the TG data for an amic acid with the following structure



free from solvent (as confirmed by MTA data). Figure 2 shows the TG curve for this compound, from which it can be seen that the degradation of the amic acid can be divided into several stages only tentatively. The stages of mass up to 220° and above this temperature are fairly well defined. Above 380°, sublimation and thermal degradation of the resultant imide take place, and this stage is therefore not of interest in a consideration of the degradation of the amic acid. As concerns the mass losses observed in the TG curve over the temperature range 70–220°, this range can be divided into two stages: up to 125°, and between 125 and 220°. The first stage (about 4% mass loss) may be accounted for by the evaporation of sorption water, and the second stage should include the stage of water elimination due to cyclodehydration (about 6% mass loss). The difference between the actual mass loss and the water loss (about 13%) is due to amine formation according to the MTA data. However, it is difficult to establish the temperature of its formation from the shape of the TG curve.

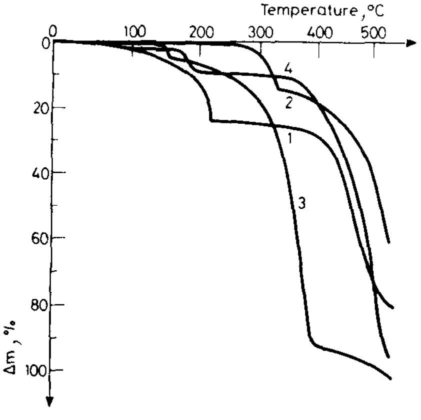
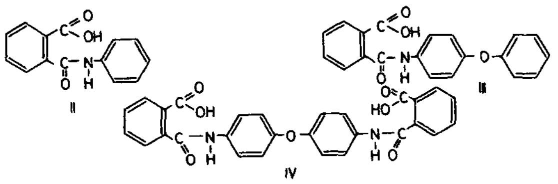


Fig. 2 TG curves of compounds I, II, III and IV (curves 1, 2, 3 and 4, respectively)

If TG is used to study model compounds based on phthalic anhydride and the same aromatic amines having the following formulae



II

III

IV

the shape of the TG curves is simpler than that for the model compounds based on pyromellitic dianhydride. Even if phthalanilic acid was heated (Fig. 2, curve 2), no separation of the stages of degradation and cyclodehydration was observed, although, according to the calculation of the mass loss for the first stage (220–330°), apart from cyclodehydration the decomposition of 7–10% of the phthalanilic acid should take place. When amic acids III and IV were heated, no degradation was observed. The first stage of mass loss is related to cyclodehydration, and further mass loss corresponds to the decomposition of the imide formed.

The above examples concerned the behaviour of amic acids obtained in DMF solution which, as a result of its polarity and the presence of mobile hydrogen, is a strong complexing agent. It has been shown that other amide solvents also complex to PMA. The TG study of the behaviour of these complexes upon heating showed that these transformations also proceed in several stages and the results are very similar to those obtained for the PMA • 2DMF complex.

Figure 3 presents TG curves for PMA complexes with DMAA, N–MP and DMSO; these snow very distinctly the stages of complex degradation, with the elimination of two molecules of solvent (temperature range between 80–110° and 135–180°, depending on the boiling temperature of the solvent); two stages characterize the partial degradation and cyclodehydration of PMA, and the final stages relate to the sublimation and degradation of the imide formed and of the product of PMA degradation. From calculations based on the TG curve, the degree of thermal degradation of PMA with the elimination of aniline is independent of the nature of the complexing agent and varies between 20 and 25%. However, the degradation of PMA is directly dependent on the conditions determining the possibility of aniline evaporation from the sample. A clear example of the effect of the TG conditions on the transformation of the complexes upon heating is given in Fig. 4, which shows the TG curves obtained for the PMA • 2DMF complex in a crucible without a lid, in a crucible with a lid and in a labyrinth crucible. It is clear that when the removal of volatile products from the reaction vessel becomes more difficult, the ratio of the mass losses in the different stages of transformation of PMA • 2DMF changes drastically. In the first stage the mass losses are virtually the same in all three cases, whereas upon further

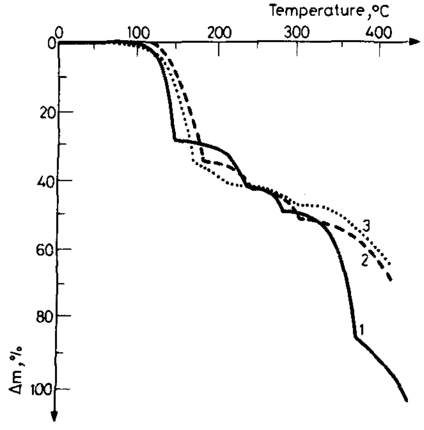


Fig. 3 TG curves of the complexes 1) PMA • DMAA, 2) PMA • N–MP, 3) PMA • DMSO

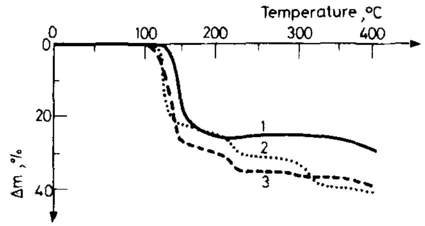


Fig. 4 TG curves of the PMA • DMF complex: 1. placed in a platinum crucible, without a lid, 2. placed in a platinum crucible with a lid, 3. placed in a labyrinth crucible

heating under the conditions when the possibility of the evaporation of volatile products is reduced to a minimum, mass losses due to PMA degradation are virtually absent.

Hence, for the individual organic substances investigated the TG method enabled us to determine with sufficient precision the processes of multistage transformations of aromatic amic acids into cyclic imides, whereas the calculation of mass loss from the TG curves and the comparison of the results with MTA data permitted determination of the dependence of the structure of these complexes and the ratio of the reactions of thermal degradation and cyclodehydration of the polyamic acid on many factors.

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Zusammenfassung — Die thermischen Umwandlungen einer Reihe von Modellverbindungen der *o*-Amicsäuren wurden thermogravimetrisch untersucht. Die TG-Daten weisen auf eine Cyclodehydratisierung der Amicsäuren und parallel verlaufende thermische Zersetzungsprozesse hin. Die Thermogravimetrie liefert zusammen mit der massenspektrometrischen thermischen Analyse genügend Informationen zur Beschreibung dieser Prozesse sowohl auf qualitativer wie auch auf quantitativer Ebene.

Резюме — Методом термогравиметрии (ТГА) исследованы термические превращения ряда модельных орто-амидокислот. По данным ТГА изучены циклодегидратация амидокислот и сопутствующие ей процессы термодеструкции. Показано, что ТГА в сочетании с масс-спектрометрическим термическим анализом дает достаточную информацию для описания этих процессов как на качественном, так и на количественном уровне.