Thermochimica Acta, 138 (1989) 13–20
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOANALYTICAL INVESTIGATIONS ON HETEROCYCLIC ORGANIC COMPOUNDS. PART V: THERMAL DECOMPOSITION OF SOME SUBSTITUTED *N*-PHENYLPHTHALAMIC ACIDS

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(Received 24 February 1988)

ABSTRACT

N-phenylphthalamic acids are readily obtained from the reaction between phthalic anhydride and substituted aniline. The thermal decomposition reactions of these acids were studied under an inert atmosphere using dynamic thermogravimetry and differential scanning calorimetry. The acids decomposed directly into the corresponding oxazine derivatives. No dehydration reaction could be detected and consequently there was no chance for the formation of imides or isoimides to take place. Practical mechanistic steps are postulated in order to explain the formation of decomposition products during thermal treatment. The effects of various substituents on the mode of decomposition as well as on the thermal stability of the acids were also studied.

INTRODUCTION

N-arylphthalamic acids are used as plant growth regulators, e.g. the number of flowers and of fruit set may be increased significantly by the application of *N*-(*m*-tolyl)phthalamic acid [1,2]. On heating, the amic acids (I, Scheme 1) in general dehydrate into the corresponding imides [3,4] or isoimides (II) which rearrange into the more stable imide (III) upon strong heating [5–7].

In the present paper, the thermal behaviour of several types of amic acids namely, *N*-phenylphthalamic acid, substituted *N*-phenylphthalamic acids, *N*-phenyl(2,3-dicarboxy)pyridylamic acid, *N*-phenyl(3-nitro)phthalamic acid

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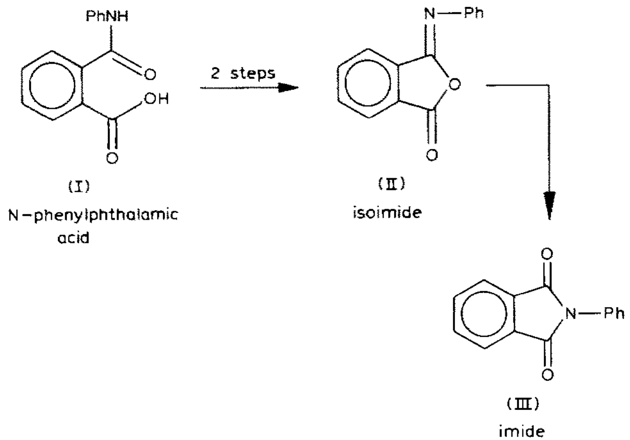


Scheme 1.

is studied with the aid of thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC).

EXPERIMENTAL

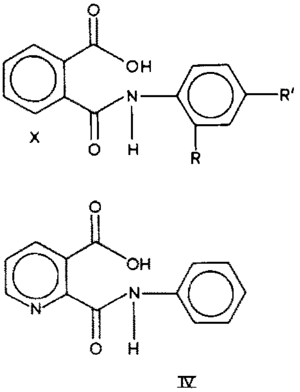
Melting points were determined on a Kopfler hot-bench. Infrared spectra were recorded on a Pye Unicam SP-1100 IR spectrophotometer (Table 1). The elemental analyses were performed by the Central Laboratories of the Iraqi National Oil Company, Baghdad.

The general procedure of the synthesis of *N*-arylphthalamic acids [8,9] was as follows: To a slurry of phthalic anhydride (1 mol) in benzene, a solution of the amine (1 mol) in benzene was added dropwise, with stirring, over 1 h. The reaction mixture was then stirred for two more hours. The precipitate formed was filtered off and air dried. Ethyl acetate or chloroform were employed as solvents in the cases of the nitro derivatives in Scheme 2.

TABLE 1

The IR spectral data of the amic acids

Compound	ν(N–H) (cm^{-1})	ν(C=O) (cm^{-1})
N-Phenylphthalamic acid	3347	1727
N-*o*-Tolylphthalamic acid	3315	1700
N-*o*-Nitrophenylphthalamic acid	3420	1682
N-*p*-Nitrophenylphthalamic acid	3473	1715
N-Phenyl-3-nitrophthalamic acid	3428	1685
N-Phenyl-2,3-dicarboxypyridylamic acid	3352	1718



I, R = R' = H
V, R = R' = H ; X = NO_2
VI, R = H , R' = NO_2
VII, R = CH_3 , R' = H
VIII, R = NO_2 , R' = H

Scheme 2.

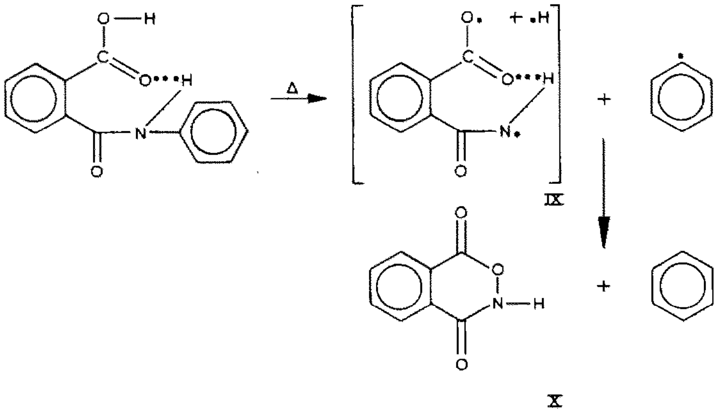
Thermal analysis

The TG and DTG curves were recorded on a Stanton Redcroft Model TG 760 thermobalance equipped with a three-pen strip chart recorder for the simultaneous recording of TG, DTG and temperature signals. The measurements were carried out on samples weighing 3–5 mg under a stream of nitrogen (30 ml min^{-1}). The DSC measurements were carried out on a DuPont (Model 1090) thermal analyser system under a N_2 atmosphere, at a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION:

The TG and DTG curves of compounds IV, V, and VI (Scheme 2) are shown in Fig. 1. The corresponding DSC curves are given in Fig. 2. *N*-phthalamic acid lost ~ 2.5% of its weight in the range 100–140 °C. The main decomposition reaction commenced at 142 °C and a DTG peak maximum was noticed at 169 °C. The reaction was endothermic and the DSC peak maximum occurred at 148 °C. This step can be referred to the cleavage of the amidic C–N bond, i.e. one benzene molecule is lost per molecule of the amic acid. Good agreement was found between the experimental and the predicted weight losses. The mechanism proposed for this reaction is shown in Scheme 3.

However, the DTG peak corresponding to this step was not symmetric, which may be explained as follows. The decomposition of the material is aided by melting, whereupon the evolved benzene must pass through the molten acid. As the surface material is decomposed, the thickness of the solid product is increased gradually at the uppermost part of the sample. The benzene formed thereafter must penetrate this hard layer of oxazinedione derivative X. Similar explanations were postulated for the decomposi-



Scheme 3.

tion pattern of the alkali pyrosulphate [10] and the discontinuity in the decomposition of barium perchlorate [11].

The previous reports showed that the pyrolysis of amic acids yields the corresponding imides through a dehydration reaction [4]. This is in contrast with the present results obtained from the TG and DSC experiments. Mechanistically, the loss of a water molecule from the acid requires the cleavage of the carboxy C–OH and amidic N–H bonds, whilst the formation of a benzene radical involves the cleavage of the amidic C–N bond only. Energetically, the dehydration will be less favourable than the cleavage to form the benzene radical. Besides, the intra-hydrogen bonding within the

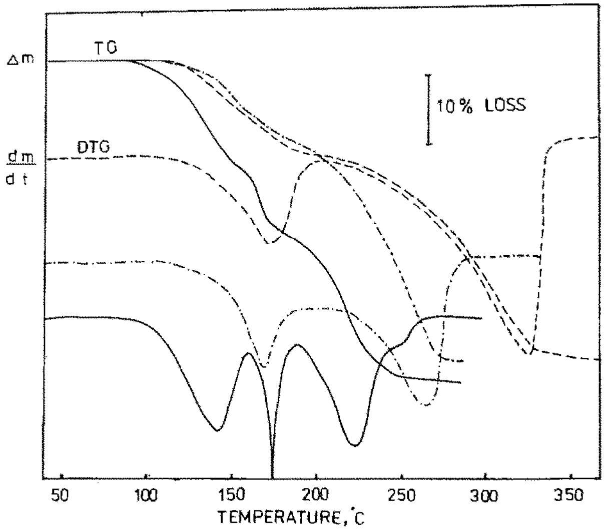


Fig. 1. TG, and DTG curves of Compounds I (–·–·–), IV (———) and V (— — —).

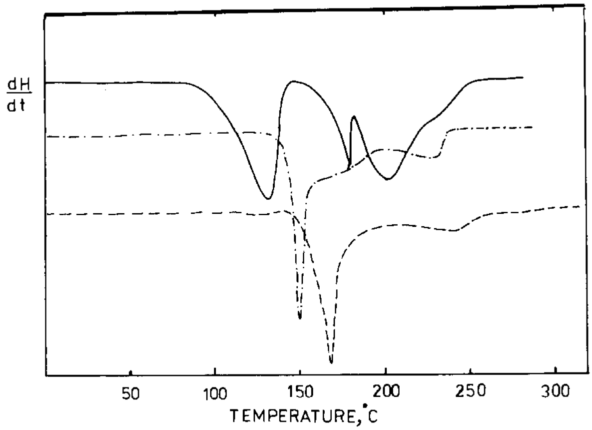
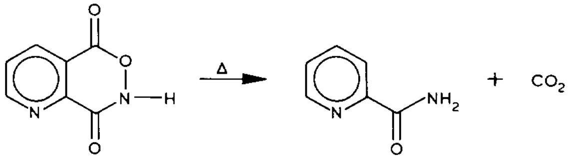


Fig. 2. DSC curves of compounds I (–·–·–), IV (———) and V (— — —).

amic acid molecule (Scheme 1) inhibits the dehydration and makes the formation of the oxazinedione radical easier.

A comparison of Figs. 1 and 2 indicates that the decomposition temperatures of *N*-phenylphthalamic acid (I), *N*-phenyl (2,3-dicarboxy)pyridylamic acid (IV) and the 3-nitro(*N* – phenyl) phthalamic acid (V) are in the order IV < I < V. This sequence may be attributed to electronic and surface area factors. The presence of the nitro group increases the surface area of the whole compound with respect to the unsubstituted acid. Consequently, the melting point of V will be higher than that of the other two and will cause decomposition to occur at higher temperature. Electronically, the nitro group withdraws electrons and thus destabilizes the intermediate IX (Scheme 3). The low decomposition temperature of IV is due to the relatively high stabilization of the intermediate radical IX by the pyridine ring. A similar pattern was reported for the decomposition of isatoic anhydride derivatives [12], where the pyridine ring caused a reduction of the decomposition temperature of ~ 40 °C.

At the end of the first step in the decompositions, the resulting oxazinediones, which were formed from the intermediate radical IX, gave different thermal behaviours. The oxazinedione formed from IV decomposed rapidly and lost 18.1% of its weight between 158 and 183 °C. The most probable reaction at this stage seems to be the decarboxylation of the oxazinedione derivative giving the 2-amidopyridine



Scheme 4.

The reaction was strongly endothermic, as indicated from the DSC curve of the acid (Fig. 2). The occurrence of the first step at a relatively low temperature range allows the oxazine to undergo decarboxylation reaction [13] giving the corresponding amide (XII). However, the decarboxylation step was not clear for the amic acids I and V, because the thermal environment in which the corresponding oxazinediones were formed is sufficient to cause their overall decomposition.

Substituted N*-phenylphthalamic acids*

In an attempt to study the effect of electronic withdrawal and donation from and to the amidic ring on the nature of decomposition, the following acids were analysed: *N*-(*p*-nitrophenyl)phthalamic acid (VI) *N*-(*o*-tolyl)phthalamic acid (VII) and *N*-(*o*-nitrophenyl)phthalamic acid (VIII). The TG, DTG and DSC curves of compound VI are shown in Fig. 3. The material lost 43.7% of weight in the temperature range 150–234 ° C and gave a symmetric DTG peak with a maximum at 200 ° C. Such a weight loss (42.65%) would be expected if each molecule of the compound were to lose a molecule of nitrobenzene. The nitro group at the *para* position lowers the basicity of the amic nitrogen atom by withdrawing the lone pair through conjugation, i.e. the dehydration reaction is inhibited and amidic C–N bond cleavage is favoured leading to the oxazinedione formation.

On the other hand, the amic acid VIII decomposed in a significantly different manner. The acid decomposed as a whole with no obvious intermediate formation (Fig. 4). This might be attributed to the existence of intra-hydrogen bonding between the $-NO_2$ group and the amidic N–H.

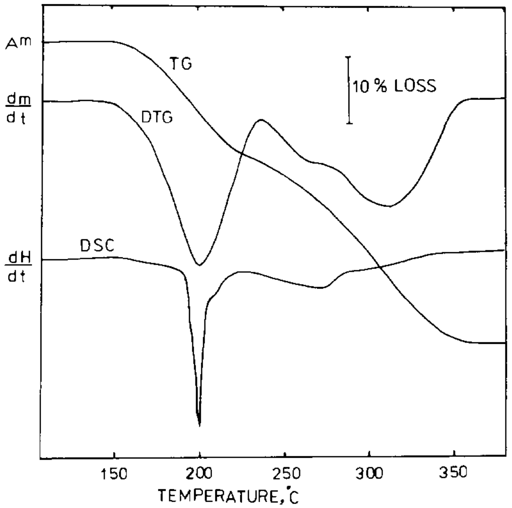


Fig. 3. TG, DTG and DSC curves of compound VI.

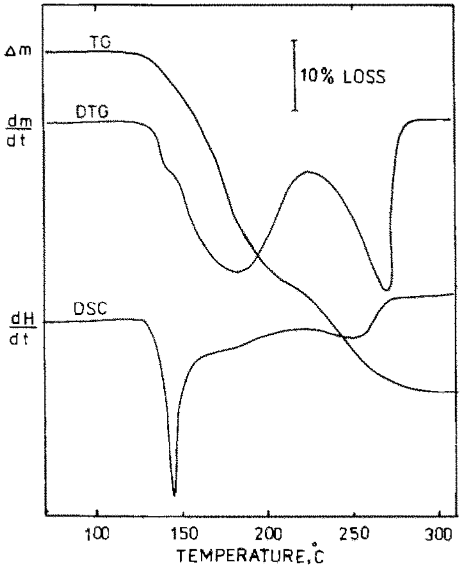


Fig. 4. TG, DTG and DSC curves of compound VIII.

Thus, the disproportionation of the molecule is inhibited in comparison with the overall degradation.

The mode of the decomposition of the amic acid VII was identical to that of the unsubstituted acid I and a toluene molecule was produced in the first step (Fig. 5). The absence of hydrogen bonding between the methyl group and amidic N–H confirms the explanation of the decomposition of the amic acid VIII given above.

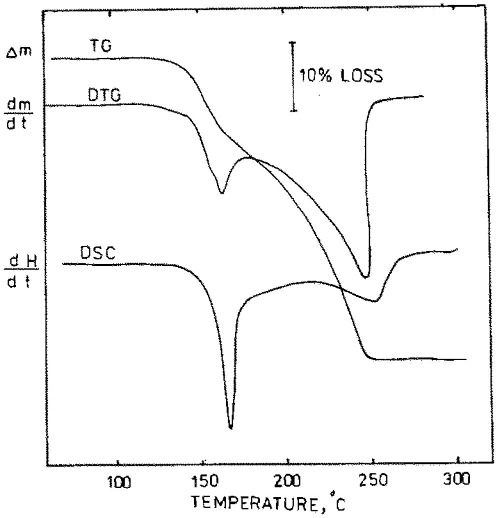


Fig. 5. TG, DTG and DSC curves of compound VII.

The last stages of the TG and DSC curves of compounds IV–VIII were identical to those of the unsubstituted acid I, which is indicative of the validity of the proposed decomposition mechanism.

REFERENCES

1 J.R. Lane, Food Additives, 5 (1967) 405.
2 A. Binchy, Sci. Proc. R. Dublin Soc., Ser. B, 2 (1968) 141.
3 J. Brown, S.C.K. Su and J.A. Schafer, J. Am. Chem. Soc. 88 (1966) 4405.
4 B. Lando, Am. Chem. Soc., Div. Polymer Chem., Prep., 5 (1964) 1579.
5 R. Cotter, J. Org. Chem., 26 (1961) 10.
6 E. Testa and L. Fontanella, Annalen, 660 (1962) 118; Br. Pat. Appl. 829,663 (May 6, 1957); Chem. Abstr., 56 (1962) 1429f.
7 M.L. Bender, Y.L. Chen and F. Chloupek, J. Am. Chem. Soc., 80 (1958) 5380.
8 H. Martin, J. Rufener and G. Pissiotas, Ger. Offen., 1 813 727 (Cl. C 07_c, A 01_n), 21 Aug. 1969; Swiss Appl. 19 Dec. 1967, 23 pp.; Chem. Abstr., 71 (1969) 123975.
9 J. Cahn, C. Wermuth and E. Rottenberg, Ger. Offen., 2 040 578 (1971).
10 M.M. Barbooti and F. Jasim, Thermochim. Acta, 16 (1976) 402.
11 F. Jasim, M.M. Barbooti and K.I. Hussain, Thermochim. Acta, 58 (1982) 289.
12 M.M. Barbooti, H.T.Al-Badri and A.F. Roomaya, Thermochim. Acta, 70 (1983) 347.
13 H.E. Crabree, R.K. Smalley and H. Suschitzky, J. Chem. Soc., C (1968) 2730.