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Thermal studies on the six isomers of pyridinedicarboxylic acid

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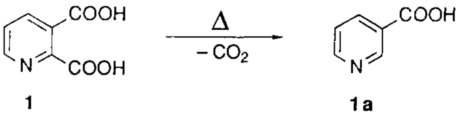
Abstract

The thermoanalytical behaviour of the six isomeric pyridinedicarboxylic acids has been investigated by simultaneous thermal analysis. The measurement of TG and DSC curves allowed us to determine the enthalpies of melting, decarboxylation and decomposition and to estimate the thermal stability of the compounds in relation to the position of the carboxylic groups in the pyridine ring. The stable intermediate products could be identified directly in some cases by TG and DSC analysis.

INTRODUCTION

Because of their donor sites, pyridinedicarboxylic acids have found some interest as ligands for the preparation of metal complexes [1, 2]. Recently we have shown by TG and DSC measurements that the thermal decomposition of pyridine-2,3-dicarboxylic acid **1** occurs in a remarkable manner [3]. The dicarboxylic acid **1** splits off the CO_2 group which is located in the 2-position and pyridine-3-carboxylic acid **1a** forms quantitatively.



The thermal decomposition of **1** and formation of **1a**, the subsequent melting of **1a** and its further thermal behaviour could be seen clearly from the observed TG and DSC signals. Compound **1** is an excellent example

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of the application of thermoanalytical investigation methods in a so-called "one-pot-reaction" for the identification of newly developed organic compounds.

Because there is at present very little information about the thermal behaviour of the other five pyridinedicarboxylic acids, we want to give a comprehensive survey of the thermal stability of all the pyridinedicarboxylic acids. We were also interested to identify stable intermediates occasionally formed in the decomposition reactions.

EXPERIMENTAL

The TG and DSC measurements were carried out on a Netsch STA 409 instrument. All investigations were done in a nitrogen atmosphere with a flow rate of 100 ml min^{-1} of N_2. The heating rate was in most cases 10 K min^{-1}; some exceptions were made in order to increase the resolution of the DSC signals. Each measurement required an amount of 8–11 mg of the compound. The temperature dependent calorimetric sensitivity of the DSC instrument (thermocouple type E, NiCr/CuNi, crucible of aluminium) was calibrated with the standard compounds diphenyl ether, indium, tin, potassium nitrate and potassium perchlorate. All reported temperatures are the so-called extrapolated onset temperatures if not otherwise stated. At the end of the pyrolytic decomposition, all of the investigated compounds left a black residue in the crucible which was not further analyzed. The organic compounds were purchased from Aldrich Chemical Co., W-7924 Steinheim, Germany.

RESULTS AND DISCUSSION

*Pyridine-2,5-dicarboxylic acid **2***

Figure 1 shows the TG and DSC curves for pyridine-2,5-dicarboxylic acid **2**. It can be seen from the curves that the pyrolytic decomposition of the sample starts at 255°C, which is identical with the literature value of the melting point of **2**. When melting, compound **2** simultaneously starts to decompose, and the decomposition is finished at about 270°C. According to the TG measurement the total loss of mass is 82%. A black residue, which was not further investigated, remained in the crucible. The DSC measurement of the total enthalpy for melting and decomposition of **2** is 593 J g^{-1}. The corresponding endothermic peak, with a maximum at 260.5°C, shows a weak shoulder between 265 and 270°C, probably caused by sublimation of pyridine-3-carboxylic acid (nicotinic acid) **1a** as an intermediate (Scheme 1).

All attempts to determine **1a** directly by DSC analysis, for instance by slowing down the heating rate or by interrupting the thermoanalytical

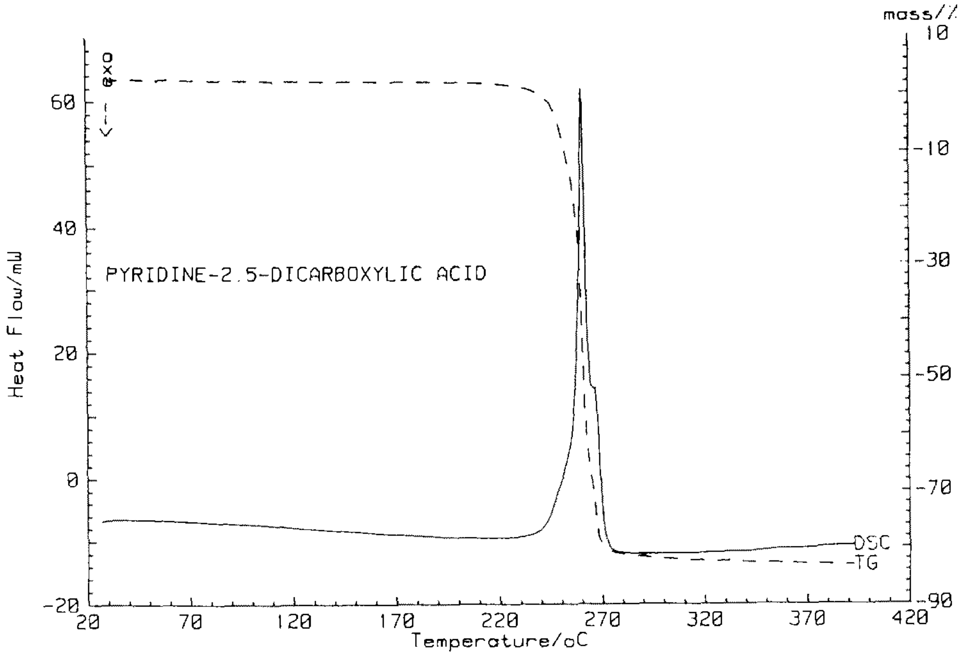
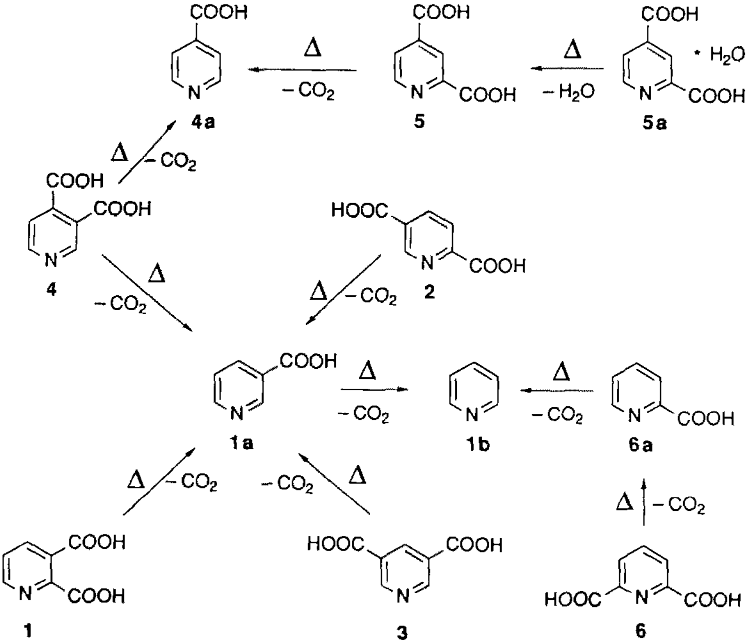


Fig. 1. DSC and TG curves for pyridine-2,5-dicarboxylic acid **2**.



Scheme 1. Reaction pathways for the decarboxylation of the pyridinedicarboxylic acids.

measurement at 260°C and reheating, were unsuccessful, because compound **1a** melts at 240°C and then sublimes immediately from the crucible [3,4].

Pyridine-3,5-dicarboxylic acid 3

The TG and DSC curves of pyridine-3,5-dicarboxylic acid **3** show that this compound is very stable up to 311°C (Fig. 2). Compound **3** decomposes while melting and loses 60% of its mass at 350°C. The enthalpy of melting and decomposition is determined to be 577 J g^{-1}. A possible decarboxylation of **3** to pyridine-3-carboxylic acid **1a** and pyridine **1b** (Scheme 1) cannot be found by TG and DSC measurements because of the high temperature for the decomposition of **3** in comparison with the melting temperatures of **1a** and **1b**.

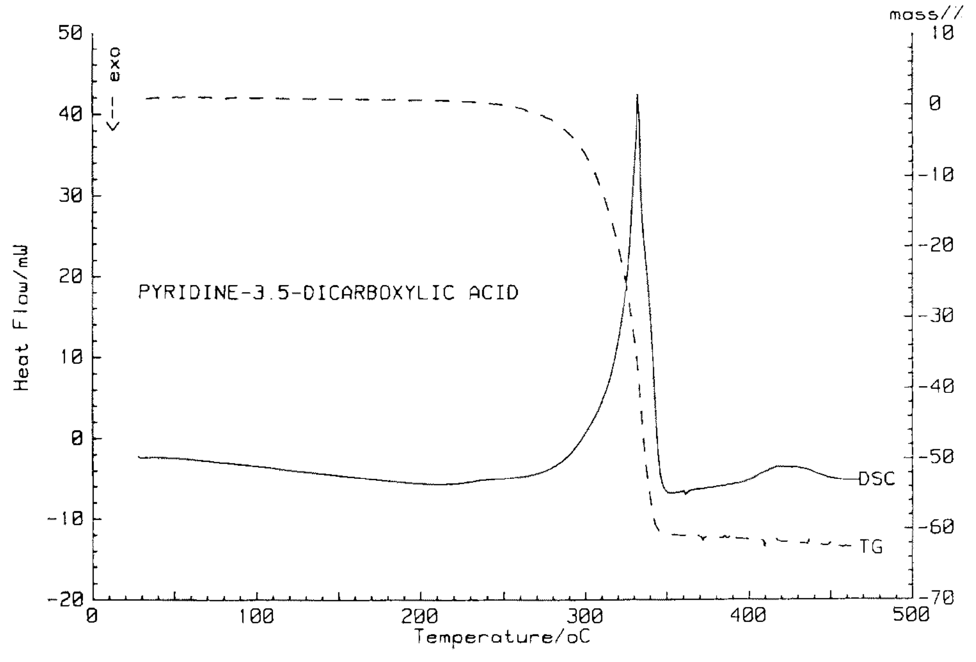


Fig. 2. DSC and TG curves for pyridine-3,5-dicarboxylic acid **3**.

Pyridine-3,4-dicarboxylic acid 4

Compound **4** is thermodynamically stable up to 200°C and then decomposes with a mass loss of 80% at 260°C. The corresponding DSC signal shows the high endothermic enthalpy of decomposition of 1240 J g^{-1} (Fig. 3). Theoretically the decarboxylation of **4** results in a mixture of nicotinic acid **1a** and isonicotinic acid **4a** (Scheme 1). The displayed TG

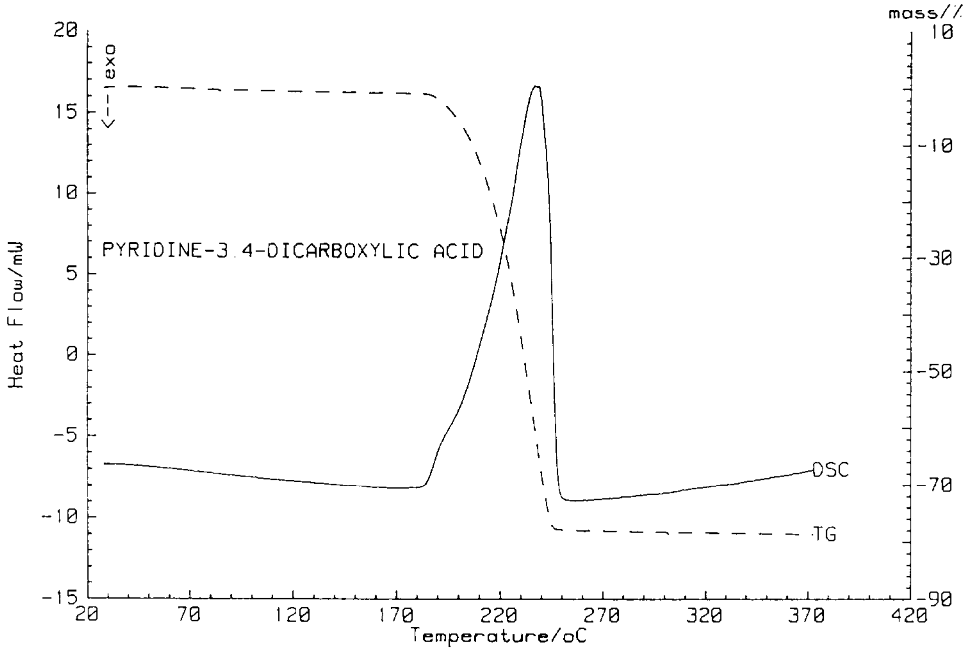


Fig. 3. DSC and TG curves for pyridine-3,4-dicarboxylic acid **4**.

and DSC curves, however, show no significant signals which could be caused by the intermediate acids **1a** and **4a**.

Pyridine-2,4-dicarboxylic acid 5

Pyridine-2,4-dicarboxylic acid was purchased as the monohydrate **5a** from Aldrich Chemical Co. Thermoanalytical investigations (Fig. 4), however, show only a small TG step, corresponding to a mass loss of 2.3% at 100°C instead of the theoretically expected value of 9.7%. For the cleavage of water and vaporization the measured enthalpy is 57.6 J g^{-1} (peak temperature 95°C). Together with the literature value for the enthalpy of vaporization of water (40.66 kJ mol^{-1} [5]), one can calculate the content of water in **5a** as 2.5%, which is in good agreement with the value obtained thermogravimetrically. This indicates that the water is not bound stoichiometrically, but is contained only as moisture.

Two poorly separated peaks with maxima at 257 and 270°C appear in the further course of the DSC curve of compound **5a**. A mass loss of about 80% of the original amount is indicated at 300°C. The beginning of the first signal of the DSC curve of **5a** at 252°C corresponds to the melting point of **5**. The broader second endothermic effect is attributed to the decomposition of isonicotinic acid **4a** (Scheme 1), formed by decarboxylation of **5** (cleavage of the carboxylic group in position 2). This second

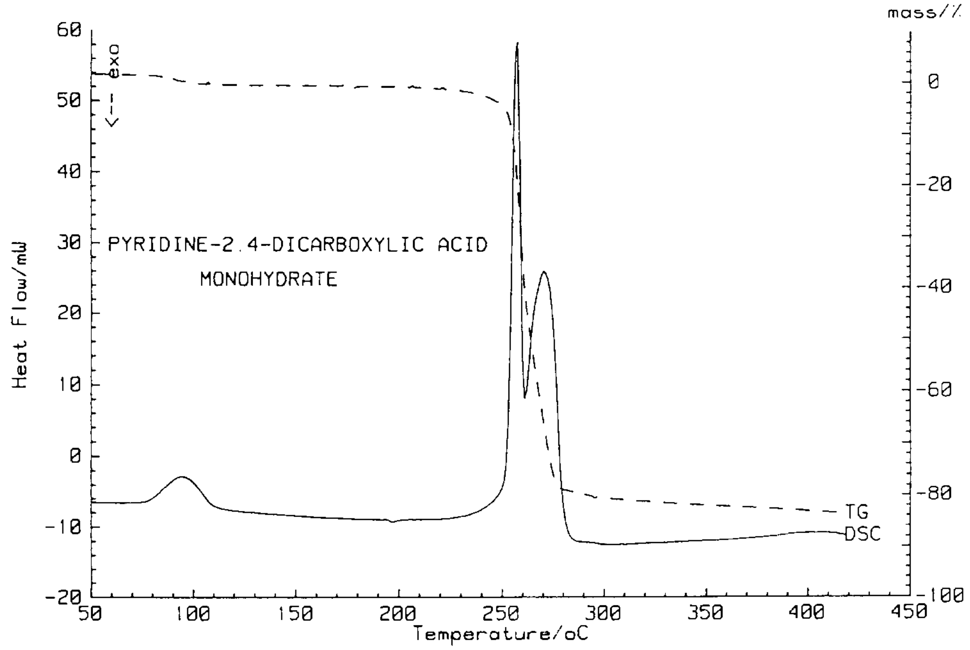


Fig. 4. DSC and TG curves for pyridine-2,4-dicarboxylic acid monohydrate **5**.

DSC signal due to the intermediate **4a** is in agreement with separate DSC measurements on isonicotinic acid **4a** [4]. The total enthalpy for both endothermic effects is determined to be 587 J g^{-1}.

Pyridine-2,6-dicarboxylic acid 6

The DSC curve of pyridine-2,6-dicarboxylic acid **6** shows an endothermic signal with a small shoulder (Fig. 5). In the same range 234–268°C a simultaneous mass loss of about 85% can be observed. The enthalpy of decomposition of **6** amounts to 521 J g^{-1}. The primary product of decomposition is expected to be pyridine-2-carboxylic acid **6a**, but because of its low melting point (140°C) and ease of sublimation, **6a** cannot be analysed by DSC measurements directly in this case. Pyridine **1b** (b.p. 115°C), the second product (Scheme 1), would vaporize at once and is also not detected by DSC.

CONCLUSIONS

As expected, the six isomers of the pyridinedicarboxylic acids decompose at different temperatures with different decarboxylation and decomposition enthalpies. It turned out that the derivatives **1**, **2**, **5** and **6**, with carboxylic substituents in position 2, are not very stable at high tempera-

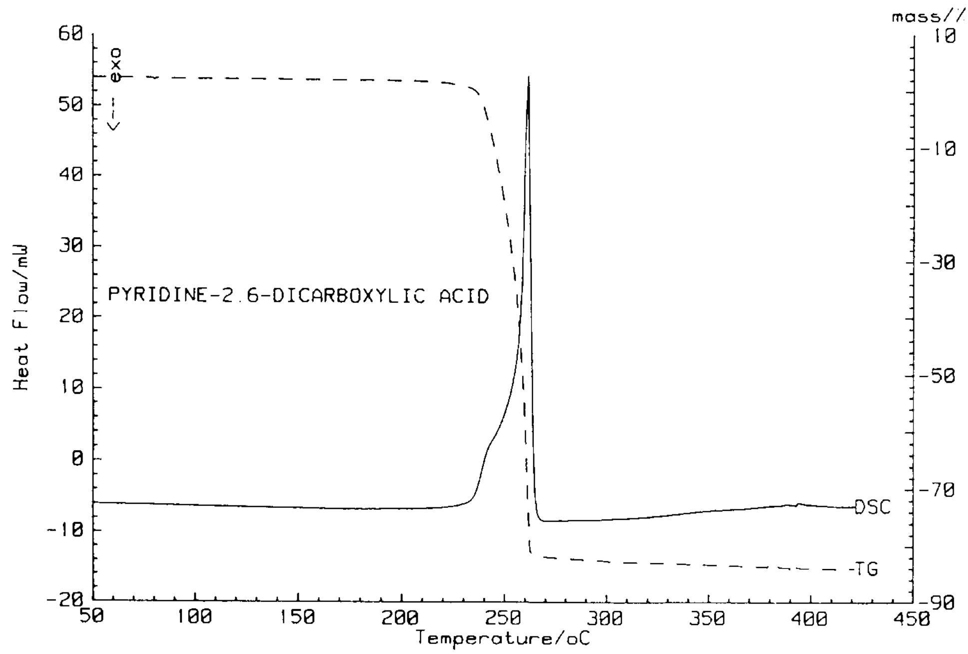
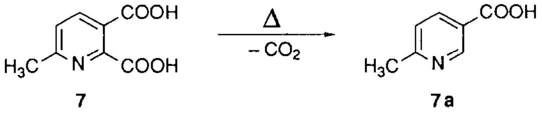


Fig. 5. DSC and TG curves for pyridine-2,6-dicarboxylic acid **6**.

tures and they therefore show low enthalpies of decomposition. Compound **1**, with the two carboxylic groups in positions 2 and 3, decarboxylates at the lowest temperature (165°C). This low temperature enables the detection of nicotinic acid **1a** formed by decarboxylation of compound **1** within a single DSC run [3]. This cannot be done with the other pyridinedicarboxylic acids because of the much higher temperatures required for the decomposition of these compounds.

We investigated one further compound, 6-methylpyridine-2,3-dicarboxylic acid **7**, which shows similar thermal effects to **1**. After an endothermic peak at 165°C (enthalpy + 89.7 J g^{-1}) the DSC curve immediately changes to the exothermic direction (enthalpy −89.9 J g^{-1}). The mass loss observed simultaneously was 24.0% (Fig. 6). This mass loss agrees well with the theoretical value of 24.3% for cleaving CO_2 from **7** stoichiometrically and, as expected, the product 6-methylpyridine-3-carboxylic acid **7a** is formed.



The endothermic peak at 210°C corresponds exactly to the melting point of compound **7a** (lit. 209–210°C [6]). The TG curve indicates a further loss of mass during the melting of compound **7a**, especially in the

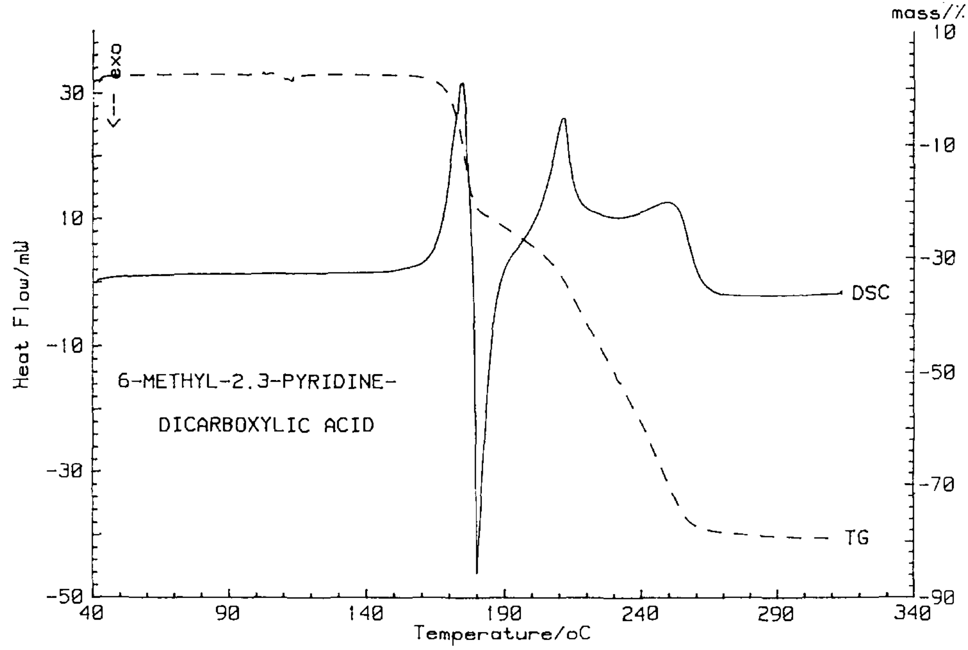
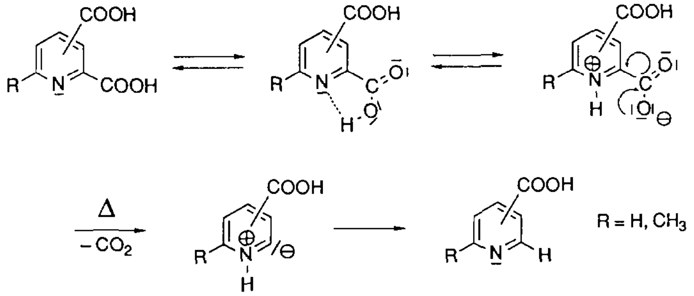


Fig. 6. DSC and TG curves for 6-methylpyridine-2,3-dicarboxylic acid **7**.

range 220–250°C. At 260°C the initial weight of the compound is reduced to 20%. The broad endothermic effect simultaneously appearing in the DSC measurement at 220–260°C characterizes the sublimation of **7a**. 20% of compound **7** remained as a black residue in the crucible.

This experiment with a derivative of a pyridine-2,3-dicarboxylic acid is another example demonstrating the use of thermoanalytical methods in the so-called "one-pot-reaction" for the identification of newly formed compounds. On the other hand, decarboxylation reactions of the pyridinedicarboxylic acids with carboxylic groups in the 3,4- and 3,5-positions are very hindered. This fact is due to the high decarboxylation enthalpy of **4**.



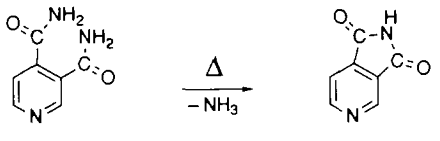
Scheme 2. Mechanism for the decarboxylation of pyridinedicarboxylic acids with carboxylic groups in *o*-position.

The most stable isomer is pyridine-3,5-dicarboxylic acid **3**, which decomposes above 311°C.

The results of these TG and DSC investigations indicate that the nitrogen atom of the heterocyclic ring is involved in the cleavage of CO_2. The reaction mechanism therefore is assumed to be as follows (Scheme 2).

Intermolecular hydrogen bonds between the nitrogen atom and the carboxylic groups in meta or para position are not possible, so that the 3,4- and 3,5-dicarboxylic acids show the stability mentioned previously.

The pyridine dicarboxyamides, another group of pyridine derivatives, also show interesting thermoanalytical effects. The cleavage of NH_3 from pyridine-3,4-dicarboxylic acid diamide **8** and the formation of the corresponding imide **8a** can be detected in a single DSC run in the same way.



8 **8a**

The DSC curve of the diamide **8** shows an endothermic effect at 180°C (enthalpy 365 J g^{-1}) and a simultaneous mass loss of 10.5% for the cleavage of NH_3 according to the TG curve (Fig. 7).

The imide **8a** formed melts at 230°C (lit. 229–230°C [7]) with a melting enthalpy of 126 J g^{-1}. On increasing the temperature the product sub-

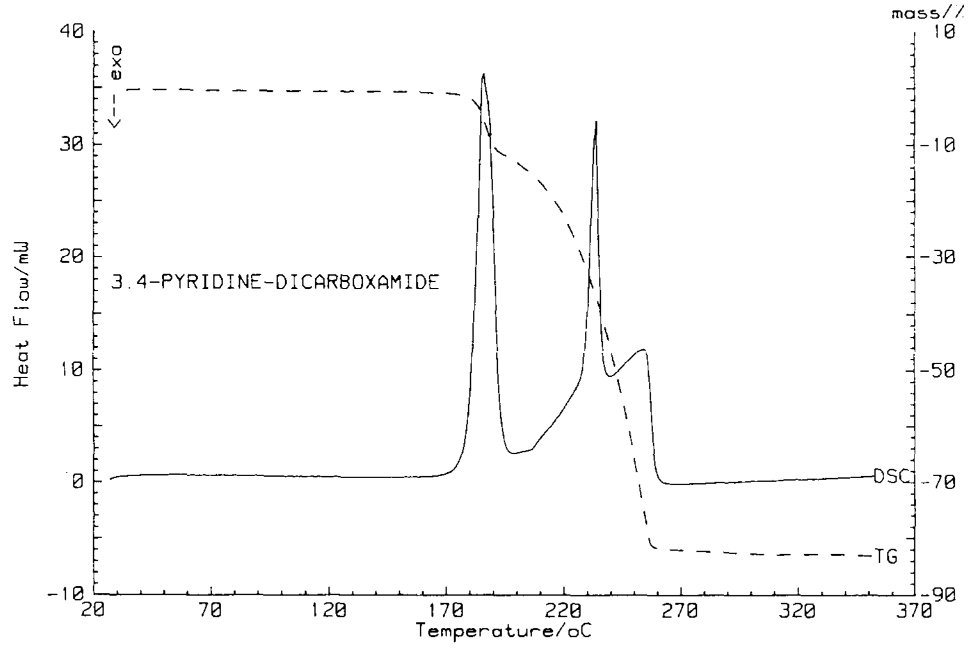


Fig. 7. DSC and TG curves for pyridine-3,4-dicarboxamide **8**.

limes. The thermochemical decomposition is finished at about 260°C and 15% of the starting material remains, again as a black residue.

Further investigations of nitrogen-containing heterocyclic compounds with the goal of finding intermediates directly by TG and DSC measurements are in progress at present.

ACKNOWLEDGEMENT

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REFERENCES

1 J.R. Allan, M. Barron and A.R. Werninck, Thermochim. Acta, 116 (1987) 275.
2 J.R. Allan, A. Renton, W.E. Smith, D.L. Gerrard and J. Birnie, Thermochim. Acta, 161 (1990) 111.
3 H. Briehl and J. Butenuth, Thermochim. Acta, 167 (1990) 249.
4 J.R. Allan, W.C. Geddes, C.S. Hindle and A.E. Orr, Thermochim. Acta, 153 (1989) 249.
5 J. d'Ans and E. Lax, Taschenbuch für Chemiker und Physiker, Springer-Verlag, Berlin, Volume 1, 1992, p. 594.
6 E.C. Kooyman and J.P. Wibaut, Recl. Trav. Chim. Pays-Bas, 65 (1946) 10.
7 E. Klingsberg, Pyridine and its Derivatives, Part III, Wiley, New York, 1962, p. 267.