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Review

APPLICATION OF DTA/DSC AND TG FOR STUDYING CHEMICAL REACTIONS OF MONOMERIC ORGANIC COMPOUNDS

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CONTENTS

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1. INTRODUCTION

The application of thermal methods for the investigation of organic compounds is a proven approach [1]. In many cases new compounds which are not otherwise obtainable or which are obtainable only through laborious, many-step preparative methods can be produced in this way. Even very reactive molecules become accessible by using this method if the products can be captured at low temperatures. Thermal methods are also very important for resolving mechanistic problems [2,3] owing to the possibility of trapping unstable intermediates.

Thermoanalytical investigation methods such as TG and especially DTA and DSC have long been successfully utilized in many areas of organic chemistry.

Wendlandt [4] has compiled a list of the most important applications of DTA and DSC techniques for monomeric organic compounds. A portion of Wendlandt's list comprises the areas of "chemical reactions", and as there exists no comprehensive description of the thermoanalytical investigations of organic compounds in this area, it is our intention to fill this gap with the present review.

In this review we have tried to classify the relevant publications published in the last 20 years which deal with DTA, DSC, and TG investigations of the chemical reactions of monomeric organic compounds in any way.

Only those reactions are considered in which changes in the chemical composition or configuration of the educts used are a direct result of thermolytic factors.

While researching the literature it was of particular interest to find exothermic signals in DTA/DSC curves, in that their existence (apart from oxidative decomposition processes) indicates the formation of subsequent thermodynamically more stable products during a thermoanalytical measurement of an organic sample.

Articles were also taken into consideration in which the occurrence of chemical reactions and the subsequent formation of new products was not recognised or not mentioned in detail by the authors, although the thermoanalytical curves point to the formation of stable organic intermediate products.

Since the famous DTA investigations of the "one-pot reaction" of acetone and *p*-nitrophenylhydrazine in the synthesis of *p*-phenylhydrazone by Chiu [5] in 1962, publications which deal with thermoanalytical investigations of reactions of organic compounds have been partially included in the standard works on thermal analysis by Mackenzie [6] and Wendlandt [4].

The present review takes into consideration the most relevant articles concerning the topics mentioned which appeared in journals dealing with thermal analysis, i.e. the *Journal of Thermal Analysis* and *Thermochimica*

Acta, from the time of their first appearance in 1969 or 1970, respectively, up to and including 1988.

In general, thermoanalytical investigations of special areas using monomeric organic compounds such as explosives or pharmaceutical products of high molecular mass, investigations of salts of organic compounds, studies of the behaviour of metal complexes with organic ligands as well as publications in which thermal effects are only briefly mentioned or listed and no DTA/DSC and TG curves are shown, are not considered.

The classification of thermoanalytically demonstrable chemical reactions employed in this review is based on the following.

(i) Thermal reactions of an educt without any mass losses (in general rearrangements).

(ii) Direct reactions of two or more educts with each other.

(iii) Reaction of one educt with cleavage of thermodynamically stable molecules.

(iv) Complex reactions of single educts.

A further subclassification will be made according to the reaction mechanism which underlies the corresponding reaction, as far as this reaction mechanism is visible or can be concluded from information at hand. An attempt was made to differentiate between reactions which proceed in single or multiple stages.

2. EXPERIMENTAL

Some thermoanalytical investigations on organic compounds were made by the authors themselves. The Netzsch instruments DTA 404 P and DSC 404 were used for these DTA and DSC measurements, and simultaneous TG–DTA/DSC analysis was carried out on the Netzsch STA 409 or STA 429, respectively.

The DSC measurements were conducted with the newly developed DSC–TG sample carrier from Netzsch [7].

If not otherwise stated, the compounds investigated were obtained from Aldrich Chemical Co., 7928 Steinheim, F.R.G.

The synthesis of the derivatives of 5-aminomethylidene-2,2-dimethyl-1,3-dioxane-2,6-dione was carried out according to the literature [8]. Ammonium cyanate was obtained from potassium cyanate and ammonium sulphate according to the literature [9].

3. THERMAL ANALYTIC CURVES INDICATING CHEMICAL REACTIONS OF ORGANIC COMPOUNDS

3.1. Rearrangements (intramolecular reactions)

The reactions described in this section are rearrangements which all take place without any mass loss of the initial compound.

We start our study with the historically important synthesis of urea from ammonium cyanate. In this respect this reaction was particularly interesting because Wöhler [10] succeeded in obtaining an organic compound from an inorganic substance for the first time in 1828. Such a transformation was thought to be impossible up to that time because of the belief that a "vital force" was absolutely necessary for the formation of an organic compound.

$$NH_4^+OCN^- \longrightarrow O{=}C(NH_2)_2$$

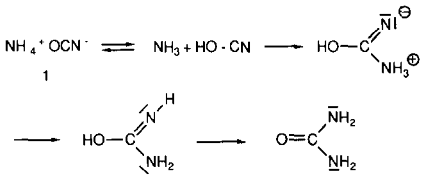
1 2

The DTA curve of ammonium cyanate **1**, obtained using the Netzsch–Schul DTA 404 P (an instrument which was developed by Netzsch especially for educational purposes), shows the exothermic transformation of NH_4OCN into the thermodynamically more stable urea **2** which then has an endothermic melting peak [11].

After cooling down and crystallization, the melting peak of the urea appears again when reheating. The second endothermic peak starting at about 150 °C results from the subsequent formation of biuret (see Fig. 1).

Although even thiourea can be similarly synthesized from ammonium thiocyanate [12] the corresponding isomerization by DTA could not be demonstrated as clearly as in the previous example [13].

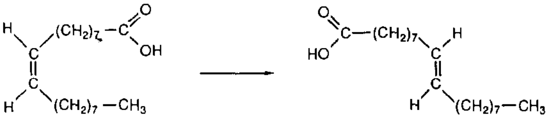
Both reactions are initiated by nucleophilic attack of the basic NH_3 on the CO group or CS group, respectively, followed by two [1,3-*H*]-rearrangements:



2

There are several *cis/trans*-isomerizations which have been investigated by DTA measurements.

Santoro et al. [14] have found exothermic DTA effects both during the rearrangement of oleic acid **3** into elaidic acid **4** and during the *cis/trans*-isomerisation of *cis*-stilbene **5** into *trans*-stilbene **6**, whereas no isomerization of *Z*-1,2-dinitrostilbene **7** into *E*-1,2-dinitrostilbene **8** appeared, as expected [15].



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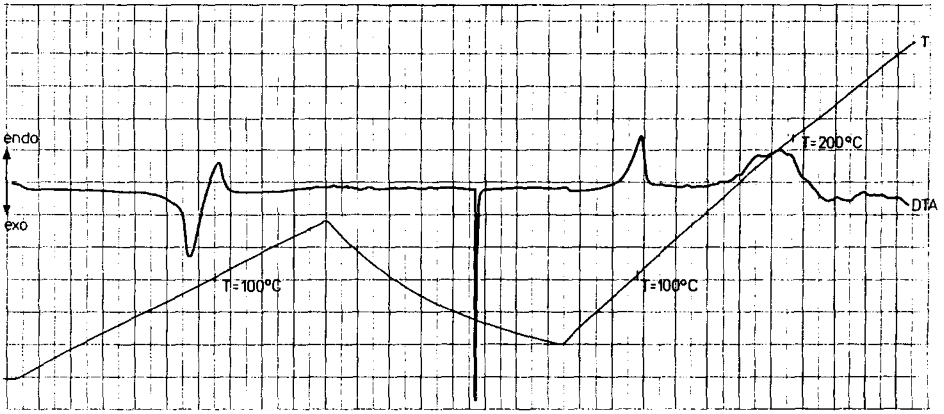
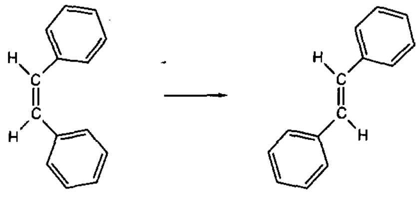


Fig. 1. DTA curves for NH_4OCN and urea.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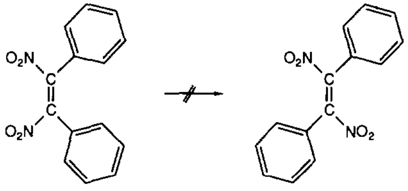
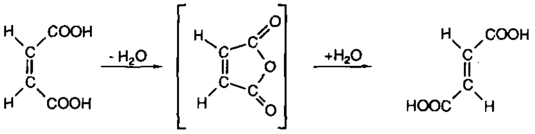

7 8

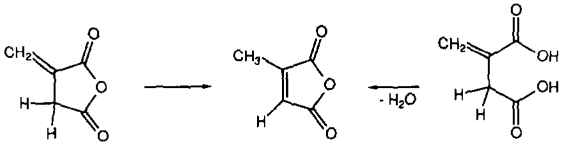
During the second heating the DTA curve of maleic acid **9** showed, apart from the melting and boiling peak of maleic anhydride **10**, a further endothermic peak which could be clearly related to fumaric acid **11** formed by comparing it with a reference sample [13].

The isomerization at least partially took place through maleic acid anhydride **10**, which exists as an intermediate.



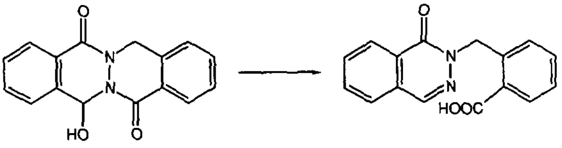
9 10 11

The heating of itaconic anhydride **12** causes a [1,3-*H*]-shift and methyl maleic anhydride **13** emerges. The anhydride **13** was proven by a DTA comparison with a sample produced by heating itaconic acid **14** in a DTA apparatus [13].



12 13 14

Immediately after the endothermic melting begins, 7-hydroxydiftalone **15** rearranges in a more complex reaction exothermically into 2-(1-oxo-1*H*-phthalazino-2-yl)-benzoic acid **16** [16].



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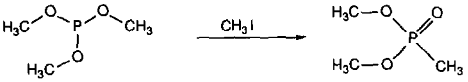
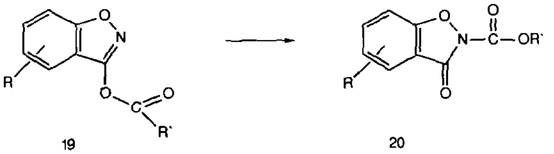
The isomerization of phosphorous acid trimethylester **17** into methylphosphonic acid dimethylester **18** in presence of CH_3I as a catalyst is also an exothermic reaction [17].



17 18

A summary of further DTA investigations on rearrangements, decompositions and reactions with phosphorous compounds has been published by Romanov et al. [18].

Alkoxycarboxyloxy-1,2-benzoisoxazole **19** provides an interesting sequence of exothermic and endothermic effects. Compound **19** tautomerizes exothermically into a benzoisoxazolone derivative **20** which consequently isomerizes exothermically again into the benzoxazolone **21** [19]. Apart from the melting peak of **20** the decarboxylation of **21** into 3-alkylbenzoxazol-2-one **22** can be observed in the DTA curve as a further endothermic effect.



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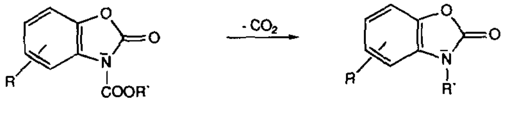
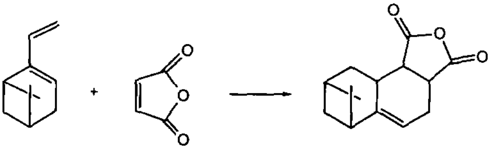


21 22

3.2. Reactions between two or more educts without loss of mass

During the direct reaction of the diene with the dienophile Diels–Alder cycloaddition reactions normally take place without any mass loss of the reacting components.

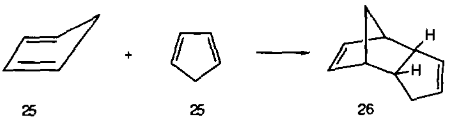
Cycloaddition of 7,7-dimethyl-2-vinyl-bicyclo[3,1,1]hept-2-ene **23**, also called nopadiene, with numerous dienophiles, such as maleic anhydride **10**, citraconic anhydride, benzoquinone, etc., were investigated in detail by DSC by Lange and Sandermann [20].



23 10 24

The formation of addition products such as **24** is exothermic and can be followed easily over the DTA curve.

The influence of catalysts on the Diels–Alder reaction was also investigated, using as an example the exothermic dimerisation of cyclopentadiene **25** into dicyclopentadiene **26** [14].



25 25 26

Even employing the relatively simple Netzsch DTA 404 P one may demonstrate impressively these cycloadditions as so-called "one-pot reactions" [13].

Heating a mixture of 20.8 mg of 1,4-diphenylbutadi-1,3-ene **27** and 10 mg of maleic anhydride **10** (equimolar quantities) up to 160 °C leads at first to two endothermic peaks in the DTA curve at 51 °C and 145 °C which are caused by the melting points of the educts (see Fig. 2). The deviation of the

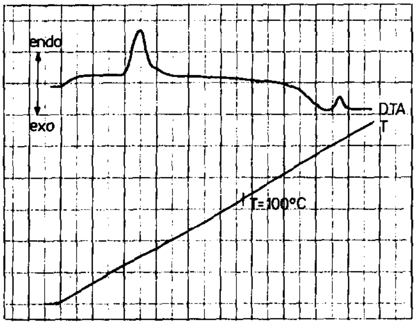
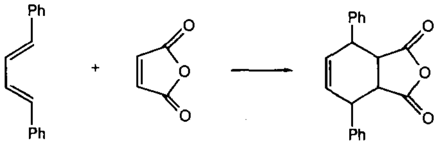


Fig. 2. DTA curve for a mixture of equimolecular quantities of 1,4-diphenylbuta-1,3-diene and maleic anhydride (first heating).

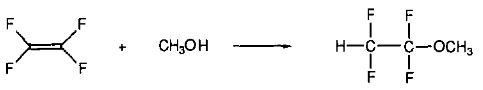
DTA curve in the endothermic direction from about 120 °C indicates the starting of the cycloaddition reaction and the formation of the product **28**.



27 10 28

After cooling the reaction mixture to ambient temperature and reheating to about 220 °C, the aforementioned thermal effects for the melting of the reaction partners are no longer observed (see Fig. 3). However, at 207 °C a further endothermic peak appeared which exactly corresponds to the melting point of the cycloaddition product 3*c*,6*c*-diphenylcyclohex-4-ene-1*r*,2*c*-dicarboxylic anhydride **28** [21].

The reaction of methanol with tetrafluoroethylene **29** to give 1-methoxy-1,1,2,2-tetrafluoroethane **30** comprises a one-step electrophilic addition.



29 30

The exothermic character of this reaction as well as the melting points of the educts and of the product **30** which appeared could be ascertained using the DTA method [22].

Some nucleophilic substitution reactions were thermoanalytically investigated in epoxide systems also.

Nucleophilic reactants, such as amines and their derivatives, for example, cause opening of the epoxide ring. In this way 2-ethyl-4-methylimidazole **31** led in an exothermic reaction with phenylglycidyl ether **32** to the product **33** [23].

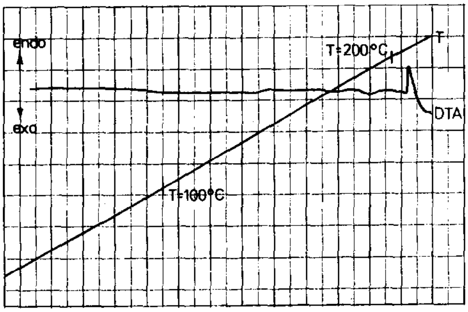
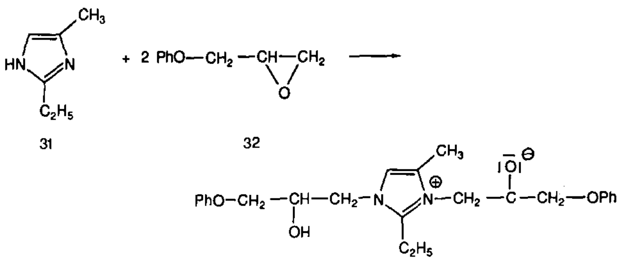
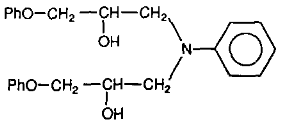


Fig. 3. DTA curve for the cycloaddition product **28**.



31 32 33

In an analogous reaction, the NH_2 group in aniline can be substituted with the oxirane **32** twice to give the *N*,*N*-di(2-hydroxy-3-phenoxy-propyl)-aniline derivative **34** [24].



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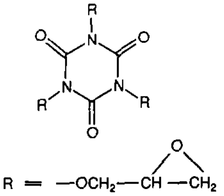
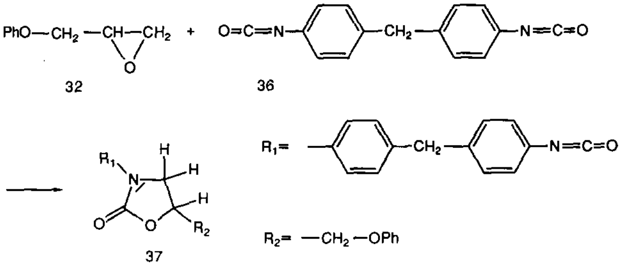
Exothermic effects were seen in the DSC curves for the substitution reaction when transforming some aliphatic and aromatic amines with triglycidylisocyanurate **35** [25].



35

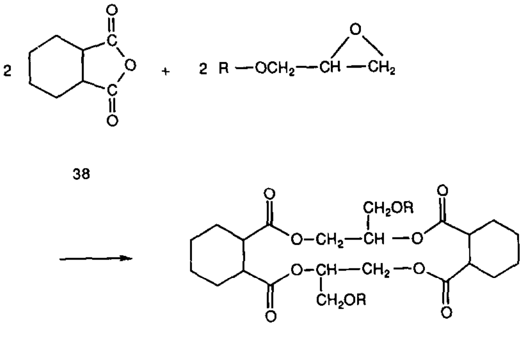
The effect of isocyanates on phenylglycidylether **32** was investigated using DSC on the example of bis(4-isocyanatophenyl)methane **36** [26]. Apart from the oxazolidinone **37**, which was formed in a one step carbonyl reaction, a further exothermic signal appears for the trimerization of the isocyanate **36**.



32 36 37

Additionally, the reactions of epoxides with different anhydrides **38** was examined using DSC instruments [27].

With appropriate catalysts, the formation of the corresponding esters **39** can be accelerated, and the exothermic character of the carbonyl reaction can be shown.



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High-pressure DSC-measurements were conducted in order to examine the influence of catalysts on the synthesis of methanol from carbon monoxide and hydrogen according to

$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$

Apart from the exothermic production of alcohol at 230 °C/40 bar, a further exothermic peak was registered above 350 °C which results from the formation of dimethylether [28].

$$2\,CH_3OH \longrightarrow CH_3\text{-}O\text{-}CH_3 + H_2O$$

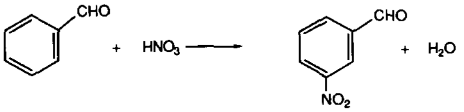
3.3. *Reactions between two or more educts with cleavage of small molecules*

The formation of dimethylether from methanol, described above, occurs concomitantly with the production of water.

During the chemical reactions which are listed below, all products also develop, in principle, at the same time when small molecules such as H_2O, NH_3, CO, CO_2, etc., cleave. Thus, the mass of the organic products decreases in comparison to the sum of the mass of the educts.

The measurement of this mass loss, however, has not always been the goal of the investigation conducted. In many cases, only DTA/DSC measurements are carried out, so that no statements could be made about the thermogravimetric effects from the thermoanalytical curves.

In order to study the chemical reaction process while avoiding side reactions in the synthesis of 3-nitrobenzaldehyde **41**, DSC investigations were made into the nitration of benzaldehyde **40** [29].



40

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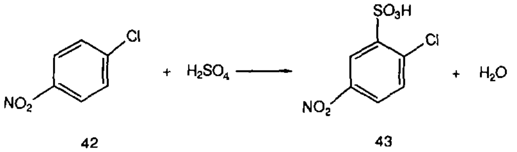
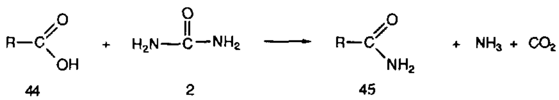
This reaction is mechanistically formulated as a one-step electrophilic aromatic substitution.

The same type of reaction underlies the sulphonation of *p*-nitrochlorobenzene **42**. The released heat of reaction could be thermoanalytically determined during the synthesis of 2-chloro-5-nitrobenzenesulfonic acid **43** [30].

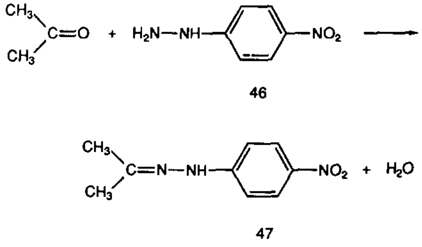


The reactions of different fatty acids **44** with urea **2** was investigated using DTA/DSC and TG [31].



Endothermic energy balances of the carbonyl reactions were conducted throughout the formation of carboxylic acid amides **45**.

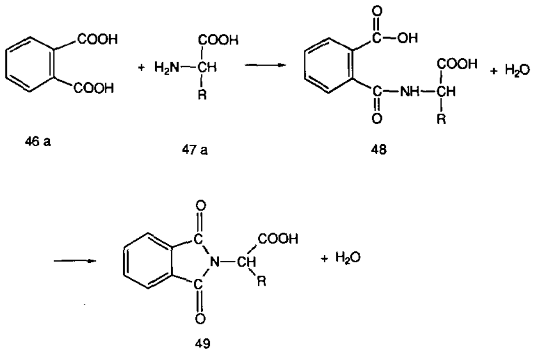
In contrast to most of the reactions between two educts mentioned above, the product was definitely characterised by DTA in the publication of Chiu [5]. In this "one-pot synthesis", Chiu heated acetone and *p*-nitrophenylhydrazine **46** up to 200 °C in a DTA cell. Identification of the hydrazone derivative **47** developed was made during the following second heating above the melting point.



The reaction of triethylamine with picric acid led in an exothermic reaction to the corresponding triethylamine picrate [5].

When resuming the investigation of Chiu, several solid derivatives of alcohols, amines, phenols, aldehydes, ketones and haloalkanes were synthesized in further "one-pot reactions", and were identified using DTA by their melting points [32].

TG, DTG and DTA investigations have appeared concerning α-amino acids **47a** with phthalic acid **46a** [33].



The educts react with each other at temperatures between 120 °C and 140 °C. Endothermic effects in the DTA curves under mass loss which appears at the same time characterized the two-stage reaction to 2-phthalimidocarboxylic acid **49**, although it failed to separate the two reactions and to identify *N*-(carboxymethyl)phthalamide acid **48** which appeared as an intermediate product.

3.4. Reactions of single educts with cleavage of thermodynamically stable molecules

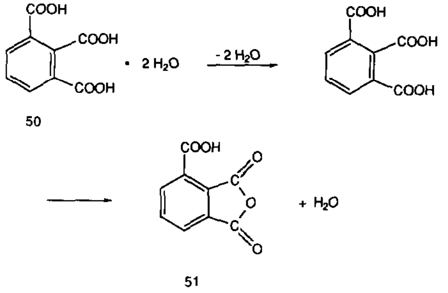
The TG and DTA/DSC investigations on organic substances which are summarized here refer first of all not to chemical reactions between two or more starting compounds, but to the thermoanalytical investigation of a single substance. Of course, the derived products of precursors which were generated by a supply of energy in form of a temperature increase can continue to react and thus in principle should be relegated to the previous section; however, a clear distinction is not possible. It is equally impossible to make an arrangement according to the same fragmentation products, in that one precursor can generate several different but well-defined products. Despite those difficulties, the following subcharacters will attempt to classify reactions according to the different fragmentation products.

In that fragmentation reactions considered in this section normally are related to a decrease in the starting mass, it is necessary to emphasize that particular thermogravimetric measurements in addition to, or even better simultaneous with, DTA/DSC measurements can be useful for thermoanalytical investigations.

3.4.1. Cleavage of water

The carbonyl reaction between α-amino acids and phthalic acid which was already mentioned in the above section could as well be arranged in this section, since a double water cleavage from the reaction of the educts leading to the formation of the final product takes place.

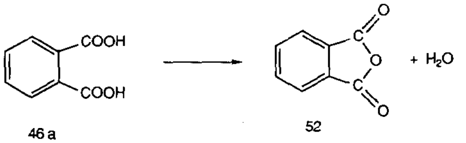
DTA curves as well as TG values for the thermal decomposition of benzene-1,2,3-tricarboxylic acid dihydrate **50** have been recorded. **50** loses its water of hydration at 70 ° C in an endothermic reaction. At 200 ° C, the cleavage of a further molecule of water takes place in developing the benzene-1,2,3-tricarboxylic anhydride **51**, which then melts at 207 ° C [34].



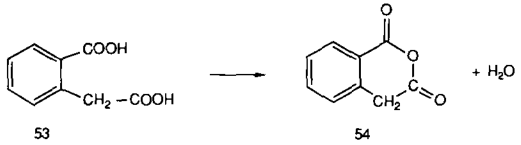
In many cases DTA/DSC proof of a product which developed by fragmentation is again possible in a "one-pot reaction".

The dehydration of phthalic acid **46a** to phthalic anhydride **52** can be conclusively shown by heating **46a** in a DTA-apparatus to 250 ° C, cooling down to about 100 ° C and heating again (see Fig. 4).

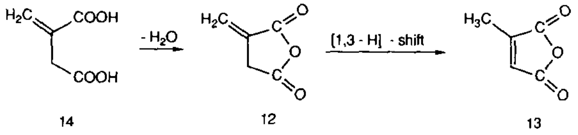
Figure 4 shows an exothermic peak for the crystallization after the endothermic dehydration of **46a** as well as an endothermic effect for the melting of the phthalic anhydride **52**, developed when heating again at 130 ° C [11].



The formation of homophthalic anhydride **54** from homophthalic acid **53** can be also shown in an analogous manner [13].



In the TG, DTA and DSC curves of itaconic acid **14**, a two-stage decomposition can be observed up to 300 ° C [35]. After the melting of **14**, the dehydration is followed by formation of itaconic anhydride **12**, which probably isomerizes partially by a [1,3-*H*]-shift to methylmaleic anhydride **13** (see section 3.1).



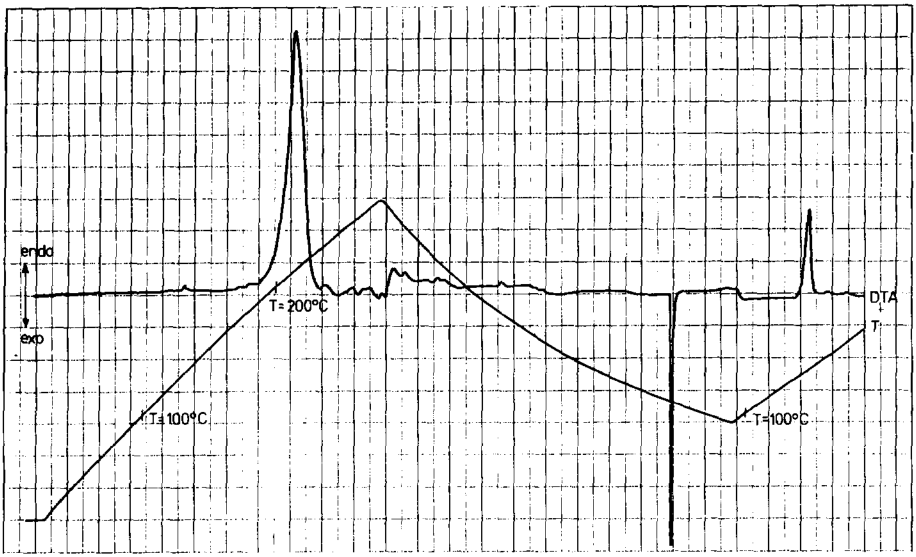
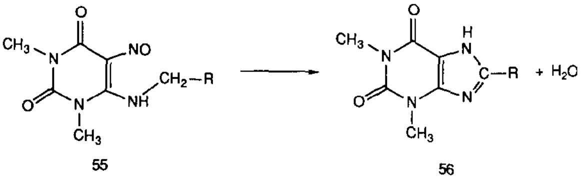


Fig. 4. DTA curve for phthalic acid.

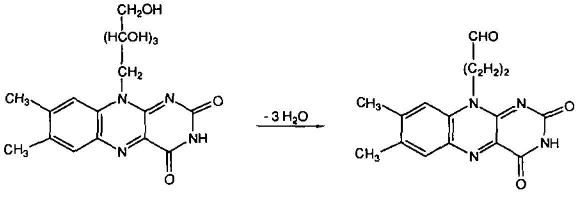
The cleavage of H_2O from 1,3-dimethyl-6-alkylamino-5-nitrosouracil **55** leads in a exothermic cyclocondensation to the corresponding 8-substituted theophyllines **56**, which can be identified by their melting points [36–38].



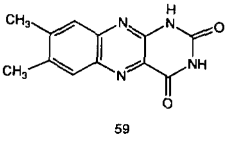
55 56

As the melting points of **56** lie higher than their temperature of formation from **55**, only one DSC run is necessary for the registration of both DSC effects.

Riboflavin **57** (vitamin B2) finally decomposes after several TG stages and a series of mainly endothermic effects to a black residue [39]. The proposed reaction mechanism could be checked for the first step using TG. This step is the cleavage of 3 mol water and leads to the intermediate product **58**; 7,8-dimethylisoalloxazine **59** was proved by CHN analysis and IR spectroscopy to be one of the products.



57 58

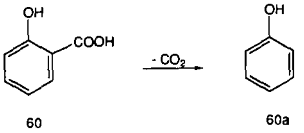


59

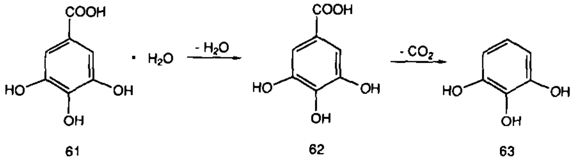
3.4.2. *Cleavage of carbon dioxide*

The cleavage of carbon dioxide certainly has been most often investigated during the thermal decomposition of carboxylic acids. The following section thus mainly deals with this category of substances.

3.4.2.1. Monocarboxylic acids. There are numerous DTA and DSC investigations of benzoic acid which is the most simple aromatic monocarboxylic acid [40–42]. The melting point of benzoic acid is also recommended for the temperature calibration of thermoanalytical measuring instruments [43].The DTA curve of salicylic acid **60** shows two endothermic effects for the melting and sublimation of the substance [44]; to some extent, the formation of phenol **60a** by decarboxylation of **60** was also observed.

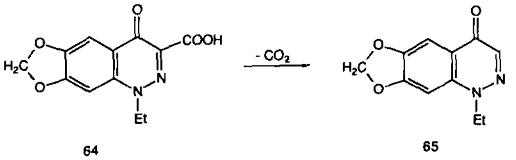


The thermal decomposition of gallic acid monohydrate **61** takes place in a multiple stage process [45].



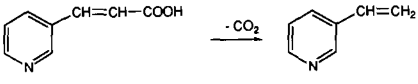
The DTA, TG and DTG curves indicate that the hydrate **61** first loses water, forming gallic acid **62**, which at higher temperatures decomposes at least partially to pyrogallol **63** by cleaving CO_2.

TG and DTA curves of 1,4-dihydro-1-ethyl-4-oxo-[1,3]dioxolo[4,5-*g*]cinnoline-3-carboxylic acid **64**, which is also called cinoxacine, have been reported [46].



The DTA curve of **64** shows an exothermic peak directly after the endothermic melting at 260 ° C; at the same time the two-stage mass loss starts at this temperature in the TG curve. This indicates a decarboxylation of the cinoxacine according to an E_i mechanism and the development of **65**.

3-(3-pyridyl)acrylic acid **66** shows a thermal behaviour like that of **64**. After melting, exothermic decomposition starts by simultaneous mass loss [47]. The appearance of two relatively large exothermic peaks probably results from the polymerisation and oxidative decomposition of 3-vinylpyridine **67** which was formed by the decarboxylation of **66** as an intermediate product.

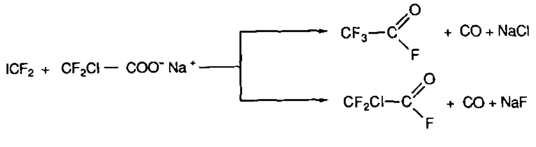


66 67

TG, DTG and DTA investigations of several aminocarboxylic acids exist [48]. The DTA curves of the investigated amino acids show endothermic and exothermic effects. Melting, decarboxylation and dehydration cause endothermic effects, while oxidative decomposition reactions generally lead to exothermic peaks in the DTA curve. The gaseous decomposition products of some amino acids were partially analysed by GC [49].

The alkali salts of difluorochloro- and difluorobromoacetic acids show interesting thermoanalytical effects which indicate the formation of thermodynamically stable intermediate products [50]. For example, an exothermic peak in the DTA curve of **68** develops immediately after its endothermic melting at about 200 °C by losing mass at the same time. The TG curve shows a second stage at about 250 °C also connected with the appearance of an exothermic peak in the DTA curve. The following series of reactions were suggested for the thermal decomposition of **68** by decarboxylation with development of difluorocarbene **69**

$$\underset{68}{CF_2Cl\text{—}COO^-Na^+} \longrightarrow CO_2 + \underset{69}{ICF_2} + NaCl$$



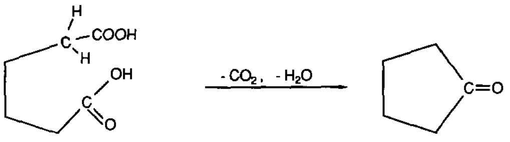
and further reactions

Products were identified by GC and MS.

3.4.2.2. Dicarboxylic acids. The thermal behaviour of aliphatic dicarboxylic acids has been extensively investigated. Erdey et al. [51] published DTA, TG and DTG curves of acids of the general formula $HOOC\text{–}(CH_2)_n\text{–}COOH$ from $n = 0$ (oxalic acid) to $n = 8$ (sebacic acid). Separate investigations for malonic acid ($n = 1$) [52,53] and adipic acid ($n = 4$) [54] have been reported. In summary, it may be said that endothermic effects for melting, boiling, sublimation and decomposition processes were measured in the DTA curves for the carbon acids $n = 0$ up to $n = 5$, while suberic acid ($n = 6$), azelaic acid ($n = 7$) and sebacic acid also show exothermic decomposition reactions.

For the smaller diacids only cleavage of CO_2 is expected, but for the higher homologues the corresponding anhydrides also could be formed by loss of water and cyclisation.

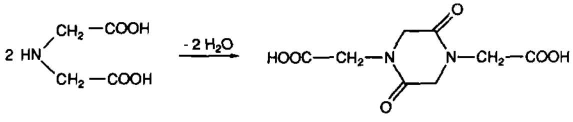
For adipic acid and pimelic acid ($n = 5$) the cleavage of CO_2 and H_2O may be expected because the particularly stable 5- or 6-rings can be formed as products. For example, under appropriate conditions cyclopentanone **71** could arise from adipic acid **70**.



70 71

Because of the low melting and boiling points of **71** and analogous compounds it may be very difficult to prove the presence of such products only by DTA/DSC techniques.

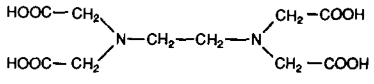
Iminodiacetic acid **72** and some of its derivatives were also thermoanalytically investigated. According to Gonzales-Vilches et al. [55] shortly after **72** melts the cleavage of 1 mol of H_2O per mol of **72** occurs. The DTA curve in an He atmosphere shows an exothermic effect after the endothermic melting of **72**. This is ascribed to a decarboxylation process of the possible intermediate product pyrazin-2,5-dione-*N*,*N*′-diacetic acid **73**. According to the TG curve in this reaction a mass loss occurs which corresponds to a cleavage of 1 mol CO_2.



72 73

GC analysis of the gaseous reaction products proved that in the temperature range around 300 °C mainly H_2O and CO_2 are produced. At higher temperatures, traces of short-chained hydrocarbons were discovered.

N,*N*,*N*′,*N*′-ethylenediaminetetraacetic acid **74** was investigated by the same authors [56] for its thermal behavior.

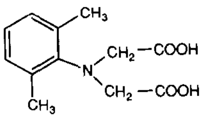


$$(HOOC{-}CH_2)_2N{-}CH_2{-}CH_2{-}N(CH_2{-}COOH)_2$$

74

After the melting of **74** at 260 °C, a mass loss of 60% is detected in the TG curve which corresponds to a cleavage of 4 mol of CO_2. CO_2, CO and H_2O were identified by GC as main products of the decomposition of **74** at 260–300 °C.

Compounds with similar structures, for example, those which are substituted by aromatic rings at the *N*-atom of the iminodiacetic acid, were also thermoanalytically investigated in static and dynamic air atmospheres. The DSC curves of both *N*-(2,6-dimethylphenyl)iminodiacetic acid **75** [57] and *N*-(2,3-dimethylphenyl)iminoacetic acid **76** [58] show first the endothermic melting, then the exothermic effects for pyrolytic decomposition which are related to a two stage mass loss in both cases according to the TG curves.



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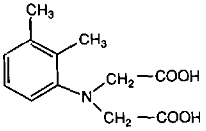
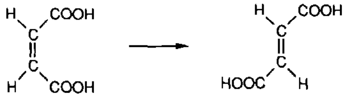


76

However, the decomposition products of **75** and **76** were not analysed, so that no definite statements could be made about the reaction course. The endothermic effects missing in the DSC curves after the melting of the educts was suggested by the authors as a sign that the decarboxylation process did not take place. This need not always be correct because decarboxylations can generate exothermic signals in the DSC curve as other investigations will show in the course of this summary.

Malic acid **9** and fumaric acid **11** are unsaturated dicarboxylic acids. The isomerisation of maleic acid **9** to fumaric acid **11** has already been mentioned in section 3.1 of this review.



9 11

Temesvâri et al. [59] succeeded in quantitatively determining maleic acid **9** and fumaric acid **11** simultaneously in a mixture of both substances by DTA, TG and DTG analysis methods. From the thermoanalytical curves of **9** and **11** the above-mentioned *cis/trans*-isomerization cannot be concluded but an endothermic transition of prismatic fumaric acid to monoclinic fumaric acid at 205° C was reported.

There are also thermoanalytical investigations about the most simple dicarboxylic acid which has a C≡C triple bond. The TG and DSC curves of acetylenedicarboxylic acid **77** show that the pyrolytic decomposition of **77** takes place directly after the melting of the compound [60].

$HOOC{-}C{\equiv}C{-}COOH$

77

The one-stage mass loss of **77** starts at about 190° C linked to an inversion of the endothermic signals of the DSC curve for the melting of **77** in the exothermic direction. The remarkable exothermic peak with a shoulder at about 198°C in the DSC curve of **77** probably results from subsequent reactions (polymerization and oxidative decomposition) of the unstable intermediate products which developed by primary decarboxylation of **77**.

Some heterocyclic nitrogen-containing aromatic dicarboxylic acids show very interesting thermoanalytical curves. Four endothermic and one exothermic signal were measured in the temperature range of 100°C up to 400°C for the DSC curve of pyridine-2,3-dicarboxylic acid **78** which is also called quinolinic acid [61]. The same results were reached when repeating the measurement of **78** in dynamic nitrogen atmosphere (100 ml min^{-1}) at a heating rate of 10 K min^{-1} [13].

The measured TG, DTG and DSC curves clearly speak for the following mechanism for the thermal decomposition of pyridine-2,3-dicarboxylic acid **78**. Immediately after the beginning of the melting process of **78** and after a short induction period (observed as a shoulder in the DTG) the decarboxylation takes place. According to the DSC curve this decarboxylation is at first endothermic, and then the curve rapidly changes to the exothermic direction. Simultaneously with the measurement of this exothermic peak, the first stage of the mass change of the TG curve is finished (see Fig. 5).

The appearance of an exothermic effect and the simultaneous mass loss of 27.4% clearly point to the formation of a thermodynamically more stable consecutive product of **78**. In fact the dicarboxylic acid **78** cleaves the CO_2

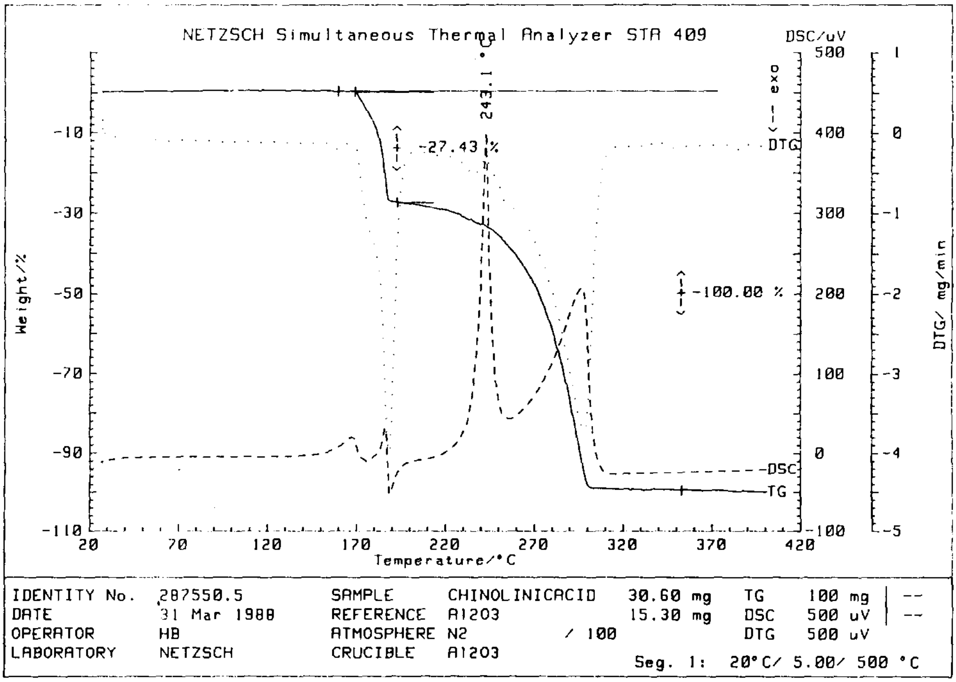
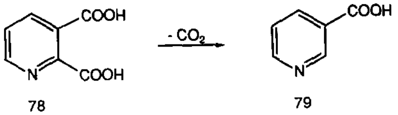


Fig. 5. Simultaneous thermal analysis of pyridine-2,3-dicarboxylic acid.

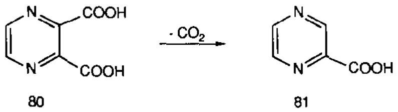
group which is located in the 2-position and pyridine-3-carboxylic acid **79**, also known as nicotinic acid, develops.



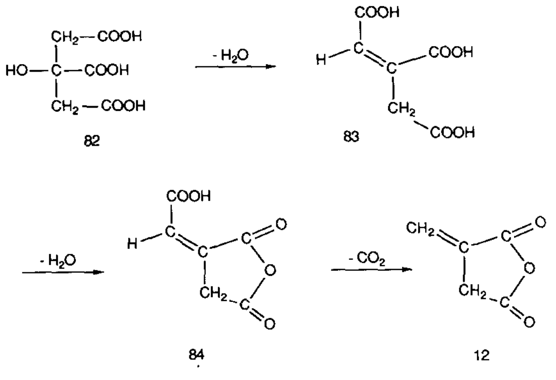
The endothermic signal in the DSC curve at about 240 °C definitely characterizes the melting point of nicotinic acid **79** which was formed from **78**. The TG curve shows a further mass loss already during melting of **79**, and particularly in the temperature range of 250 °C up to 300 °C which at 300 °C is exactly 100% of the weight of the initial substance. At the same time a broad endothermic effect occurs in the DSC curve. From this it follows that the nicotinic acid **79**, after its pyrolytic synthesis, gradually sublimes from the crucible, if possible by further decarboxylation and formation of pyridine which would evaporate at once at this relatively high temperature (b.p. of pyridine, 115 °C).

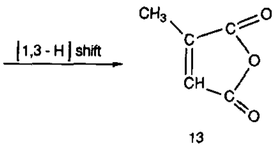
Thus, quinolinic acid **78** is again an excellent example of the application of thermoanalytical investigation methods in a so-called "one-pot reaction" for the identification of newly developed organic compounds.

Similar thermoanalytical curves and data like those for compound **78** were published for pyrazine-2,3-dicarboxylic acid **80** [62]. In this case careful consideration of the published results leads to the conclusion that first of all pyrazinecarboxylic acid **81** is formed from **80** by exothermic decarboxylation. The endothermic signal at 230 °C in the DSC curve of **80** represents exactly the melting point for the newly developed compound **81**.



3.4.2.3. Tricarboxylic acids. TG, DTG and DSC investigations of citric acid **82** or its monohydrate [63,64] have been published. The following reaction mechanism was given for the pyrolytic decomposition of **82** [63].

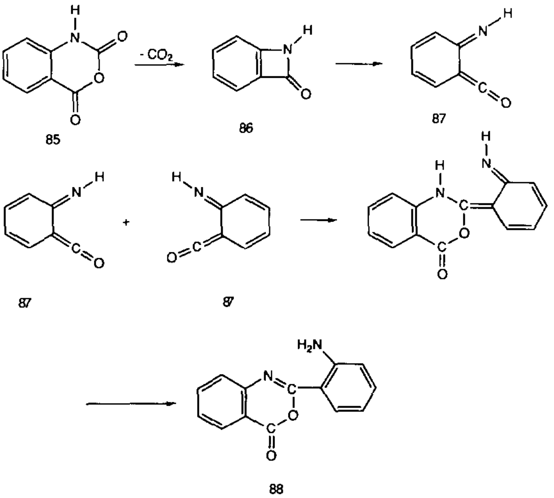




Elimination of water from **82** gives *trans*-aconitic acid **83**, which is dehydrated to compound **84**. Decarboxylation of **84** gives itaconic anhydride **12**, which as previously described undergoes [1,3-*H*]-shift to give methylmaleic anhydride **13**.

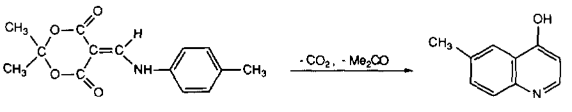
In contrast to the dicarboxylic acids **78** and **80**, the individual intermediate products of the thermal decomposition of citric acid **82** cannot be easily determined using DTA/DSC and TG.

3.4.2.4. CO_2-cleavage from other compounds. In TG, DTG, DTA and DSC investigations 2-*H*-1,3-benzoxazine-2,4-dione **85** and its derivatives showed complex transformations [65]. **85** cleaves at first CO_2 in an endothermic reaction according to the DSC curve. At 238 °C the DSC curve suddenly changes its direction by forming an exothermic signal which points to the formation of the benzoxazine-4-one **88** which can develop from the unstable primary product benzazetidinone **86** or its isomeric ketenimine **87** by dimerization.



3,4-Dihydroxycyclobut-3-en-1,2-dione **89**, also called squaric acid, decomposes in a nitrogen atmosphere above 300 °C in an exothermic reaction. The DSC curve of **89** (heating rate 20 K min^{-1}) shows a distinct peak with a maximum at about 350 °C [66]. Apart from a black residue, CO_2, CO and H_2O were found by evolved gas analysis as products of the pyrolytic decomposition of **89**.

Meldrum's acid derivatives also cleave CO_2. Moreover, it is known that compound **90** loses acetone as well as CO_2 during pyrolysis, generating 4-hydroxyquinoline **91** [8].



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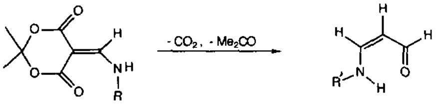
91

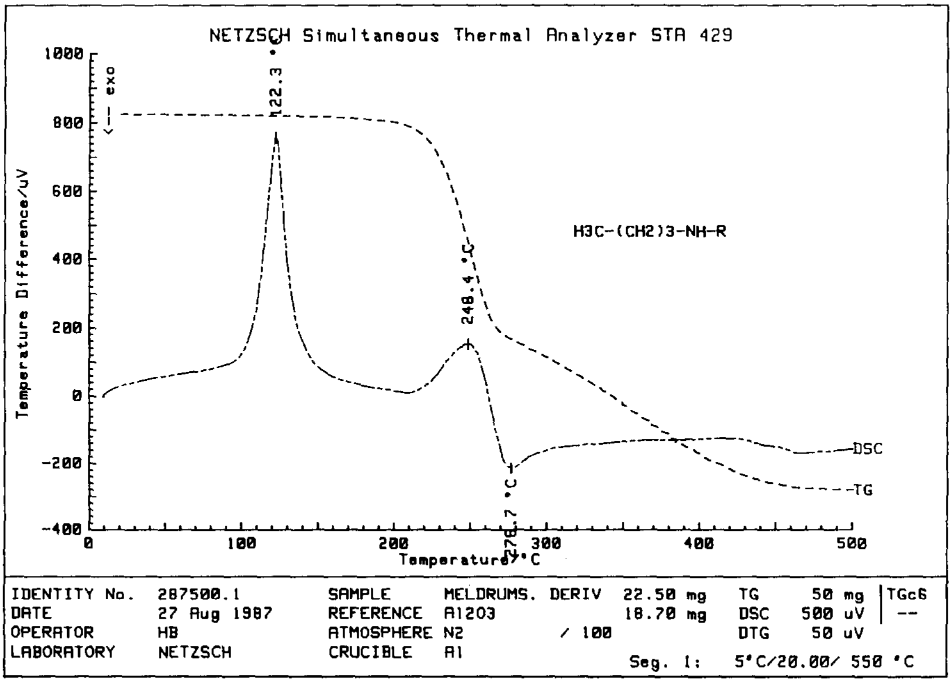
The pyrolytic decomposition of related alkyl- or cycloalkylaminosubstituted derivatives **92** also leads by fragmentation of CO_2 and acetone over a number of well-investigated [1,3-*H*]- and [1,5-*H*]-migrations to the enaminoacroleins **93** in high yields [8].



92

93

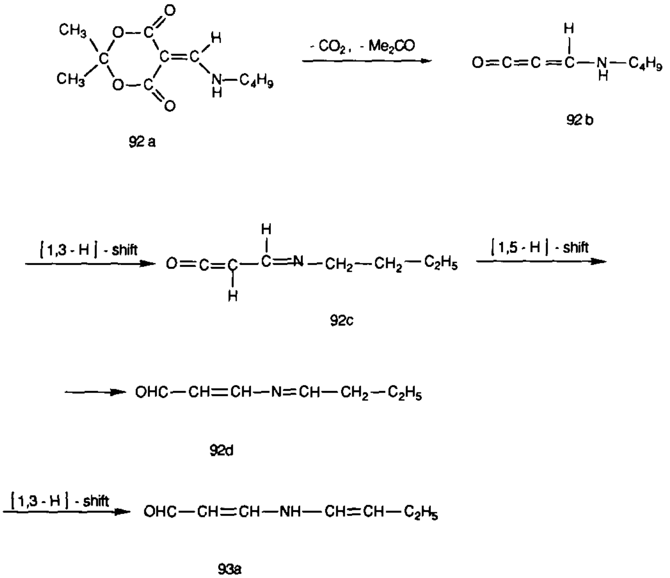
The influence of different substituents at the *N*-atom of **92** on the formation of the enaminoacroleins **93** can also be investigated using TG and DSC analysis [13].



IDENTITY No.	287500.1	SAMPLE	MELDRUMS. DERIV	22.50 mg	TG	50 mg	TGc6
DATE	27 Aug 1987	REFERENCE	A1203	18.70 mg	DSC	500 uV	--
OPERATOR	HB	ATMOSPHERE	N2 / 100		DTG	50 uV	
LABORATORY	NETZSCH	CRUCIBLE	A1	Seg. 1:	5°C/20.00/ 550 °C		

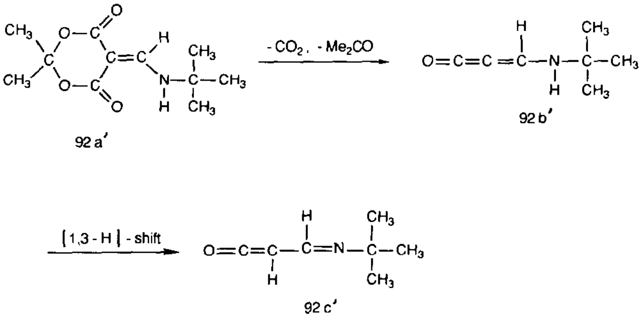
Fig. 6. DSC and TG curves for 2,2-dimethyl-5-[(*n*-butylamino)methylidene]-1,3-dioxan-4,6-dione **92a**.

Figure 6 shows the DSC and TG curves of 2,2-dimethyl-5-[(*n*-butylamino)methylidene]-1,3-dioxan-4,6-dione **92a**. After the melting of **92a** at about 110 ° C (peak maximum of the DSC curve at 122 ° C) pyrolytic decomposition starts above 210 ° C. The first TG stage and the endothermic effect in the DSC curve with its maximum at 248 ° C show the cleavage of CO_2 and acetone. The primarily formed methylene ketene **92b** rearranges by way of the unstable intermediate products imidoylketene **92c** and aldehyde **92d** to the stable 3-(but-1-en-1-ylamino)acrolein **93a**.



The formation of the thermodynamically stable product **93a** is demonstrated in the DSC curve of **92a** by the appearance of the exothermic signal at 227 ° C. Finally the complete thermal decomposition of **93a** takes place up to 500 ° C with a further mass loss.

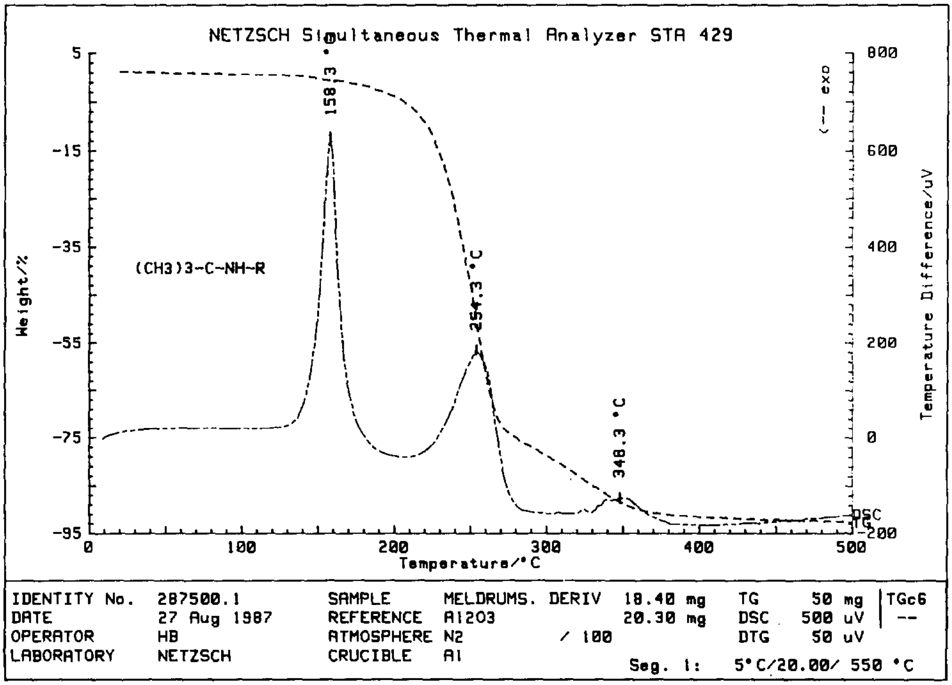
The pyrolysis of 2,2-dimethyl-5-[(*t*-butylamino)methylidene]-1,3-dioxan-4,6-dione **92a′**, however, does not lead to the formation of the corresponding enaminoacrolein because the unstable methylketene **92b′** rearranges to imidoylketene **92c′** in which a further [1,5-*H*]-shifts and thus the formation of an enaminoacrolein **93** is not possible.



The DSC curve of the precursor **92a′** shows two distinct endothermic effects for the melting and fragmentation of **92a′**, as well as a small endothermic signal at about 350 °C (Fig. 7). The missing exothermic peak directly after the cleavage of CO_2 and acetone at 280 °C can be attributed to the lack of further reactions which would form the corresponding enaminoacrolein. However, during the pyrolytic preparation of 4-hydroxyquinoline **91** from aryl-substituted acid **90** exothermic reactions are again seen. An exothermic signal in the DSC curve at 268 °C can be observed after the fragmentation of the phenyl derivative, while the *p*-tolyl derivative **90** causes an exothermic signal at 254 °C [13].

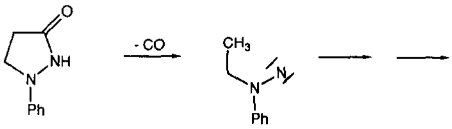
3.4.3. Cleavage of carbon monoxide

The cleavage of CO alone from simple organic compounds by thermal analysis has been rarely observed or documented. Endothermic as well as exothermic signals appear during the pyrolytic decomposition of 1-phenylpyrazolin-3-one **94** [67,68]. Probably, ring opening of **94** takes place with cleavage of CO and the formation of nitrene **95**, which can react further to give stable final products by subsequent reactions. Corresponding results from the study of similar reactions have been published [69].



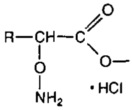
IDENTITY No.	287500.1	SAMPLE	MELDRUMS. DERIV	18.40 mg	TG	50 mg	TGc6
DATE	27 Aug 1987	REFERENCE	A1203	20.30 mg	DSC	500 uV	--
OPERATOR	HB	ATMOSPHERE	N2 / 100		DTG	50 uV	
LABORATORY	NETZSCH	CRUCIBLE	Al		Seg. 1:	5°C/20.00/ 550 °C	

Fig. 7. DSC and TG curves for 2,2-dimethyl-5-[(*t*-butylamino)methylidene]-1,3-dioxan-4,6-dione **92a′**.



94 95

A two-step decomposition (DTG curve) was detected during the thermal analysis of the hydrochlorides of some 2-aminooxyacids and their esters **96** [70]. For the second step an exothermic signal in the thermal DSC curve was observed and the formation of CO was concluded from consideration of the reaction products.

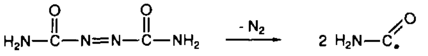


96

3.4.4. Cleavage of nitrogen

Generally, it can be said that the pyrolytic decomposition of organic compounds takes place exothermically with formation of N_2 molecules through radical reactions.

3.4.4.1. Aliphatic compounds. Azodicarboxylic diamide **97** was investigated using TG, DTA [71,72] and DSC [73] methods. Exothermic cleavage of nitrogen gives radical **98**, which forms in subsequent reactions cyanuric acid **99** and cyamelide **100** as well as 3,5-dihydroxy-1,2,4-triazole (urazole) **101** or its tautomer 2*H*,4*H*-1,2,4-triazole-3,5-dione **102**. These compounds were identified by IR spectroscopy [71].



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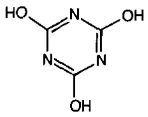

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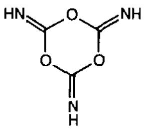

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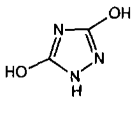

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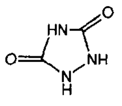
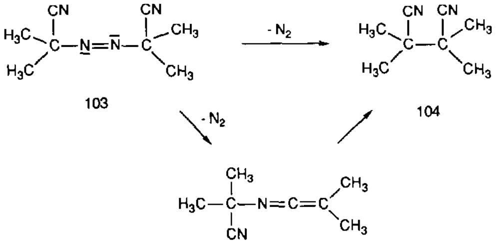
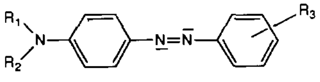


102

The DSC curve of azobisisobutyronitrile (AIBN) **103** shows two exothermic effects directly after the melting of the compound. It is discussed whether these exothermic effects result from the cleavage of N_2 from **103** and the formation of tetramethylsuccinonitrile **104** or from the development of radical coupling product **105** and its further rearrangement to **104** [74].



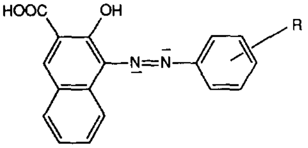
3.4.4.2. Aromatic compounds. DTA, DSC, TG and DTG curves were measured from some amide derivatives of *N*,*N*-dialkylaminobenzene of the general structural formula **106** [75]. After endothermic melting the compounds decompose by homolytically and exothermically cleaving N_2.



106

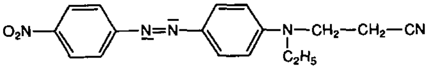
No statements were made about the identification of the pyrolysis products of **106**.

Substituted 4-phenylazo-3-hydroxy-2-naphthoic acids **107** react analogously [76].

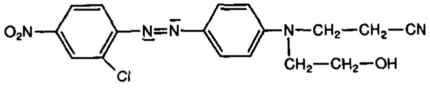


107

Similar thermoanalytical curves also exist for the two disperse dyestuffs **108** and **109** [77].



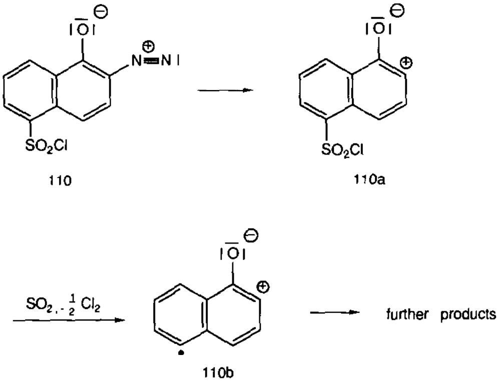
108



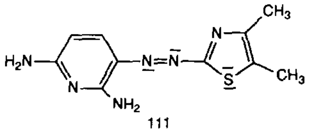
109

In an exothermic reaction 2-diazo-5-chlorosulfonyl-1-naphtholate **110** cleaves nitrogen at about 120 ° C while the SO_2Cl group is lost depending on the reaction conditions between 200 ° C and 400 ° C, as can be seen in the

DTA and TG curves [78]. Liberated sulphur dioxide and chlorine could be traced using thermo-gas-titrimetry.



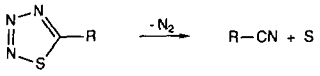
3.4.4.3. *Heterocyclic compounds.* In contrast to the diazocompounds mentioned above the DSC curve for the denitrogenation reaction of 3-(4,5-dimethyl-2-thiazoylazo)-2,6-diaminopyridine **111** shows a broad endothermic signal [79].



111

Gaseous products of the pyrolytic decomposition of **111**, for example nitrogen, could be identified by gas chromatography.

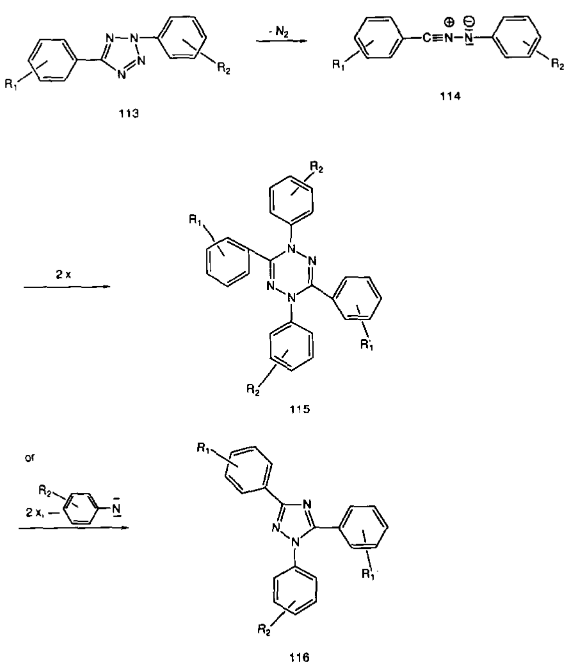
5-(substituted)-amino-1,2,3,4-thiatriazoles **112** decompose after melting in an exothermic reaction [80]. The primary formation of nitriles and sulphur probably takes place by cleavage of nitrogen.



112

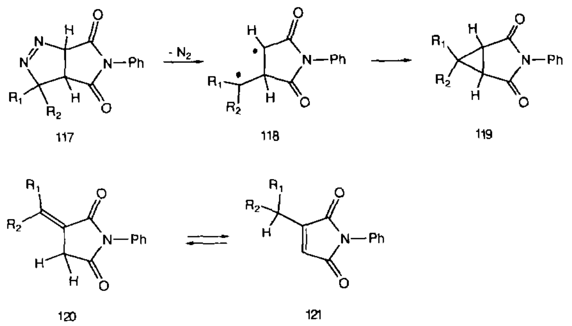
In the case of R ≡ phenyl, nitrogen or sulphur, benzonitrile and even phenylisothiocyanate could be identified by mass spectrometry [81].

TG, DTG and DTA curves were measured for some 2,5-diarylsubstituted 2*H*-tetrazoles **113**, [82,83]. The elimination of nitrogen takes place after the melting of the tetrazoles **113** in an exothermic reaction, with the appearance of a TG step at the same time. This first TG step stoichiometrically corresponds to the cleavage of exactly 1 mol N_2 per mol tetrazole **113**, forming diarylnitrileimines **114**.

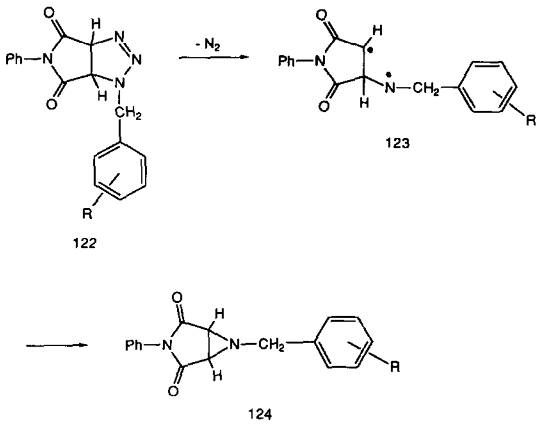


The primarily generated diarylnitrileimines **114** react further and result in the corresponding substituted 1,2,4,5-tetrazines **115** and 1,2,4-triazoles **116** as main products, which are identified by UV, HPLC and MS.

Derivatives of the diazo-compounds **117** also cleave nitrogen, giving rise to exothermic signals in the DTA curves [84]. The resulting intermediate biradicals **118** can form either cyclopropane derivatives **119** or the corresponding olefins **120** and **121**.



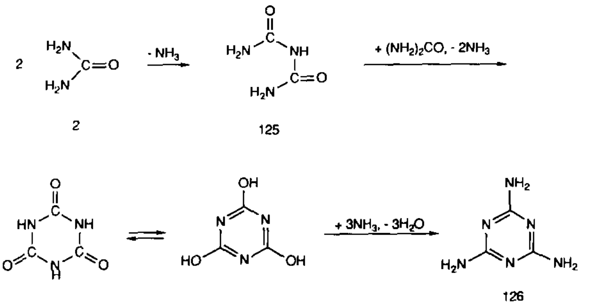
The pyrolytic decomposition of the substituted triazoles **122** runs analogously to that of **117**. According to the DSC and TG curves the exothermic cleavage of nitrogen takes place directly after the melting of **122** [85]. The biradicals **123** form the corresponding aziridine derivatives **124** as primary products which on heating undergo further decomposition to polymeric products.



122 123 124

3.4.5. *Cleavage of ammonia*

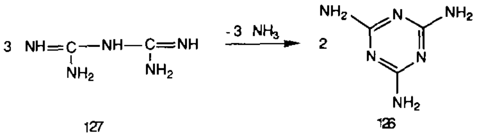
When describing the urea synthesis out of ammonium cyanate (see section 3.1), it was already mentioned that the urea formed decomposes at temperatures of about above 150 °C forming biuret. Several endothermic as well as exothermic DTA effects could be measured during the complete decompositions of urea **2** in a nitrogen atmosphere [86]. The following reaction course seems plausible in light of the TG and DTG curves



2 125 126

By cleaving NH_3 from urea **2**, biuret **125** develops at first, which cyclizes after reacting with urea and by further cleaving NH_3 to give cyanuric acid. This forms the cyanuric acid amide (Melamine) **126** by addition of ammonia and loss of water.

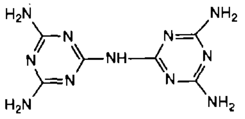
Melamine **126** also arises from biguanidine **127** after the latter's melting in an exothermic reaction which, according to the TG curve, involves cleaving one mol NH_3 per mol **127**.



127 126

Melamine **126** was identified by comparison of its NMR and IR spectra with those of reference samples [87].

Some thermoanalytical investigations deal with melamine itself [88–90]. After melting of the melamine ammonia is eliminated and in further complex multistep reactions the sparingly soluble condensation products melem **128**, melam **129** and melon **130** appear, as determined by IR spectroscopy.



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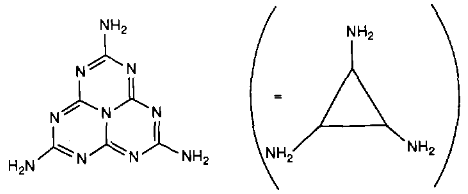
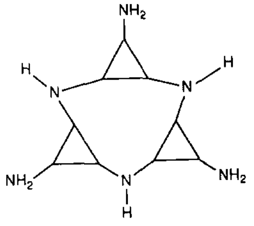
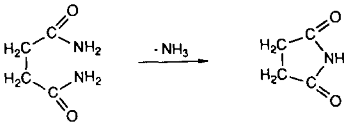


129



130

Liquid succinamide **131** decomposes in air above 250 °C in a two-step strongly endothermic reaction (see Fig. 8). At first, cleavage of NH_3 probably takes place with the formation of succinimide **132** which vaporizes from the sample carrier directly after its formation because of its relatively low melting and decomposition points [13]. Such pyrolytic reactions are known [1].



131 132

3.4.6. Fragmentation of sulphur compounds

A great number of different sulphanilic acid amides **133** were thermoanalytically investigated by Khattab et al. [91–93]. Endothermic and exothermic signals were registered in the DTA curves for the decomposition reactions of the sulphanilic acid amides. The cleavage of SO_2 from **134** could be proved by mass spectrometry [94]. Also, *p*-toluenesulphonamide **134a** shows after melting two exothermic effects in the DTA curve, which are both connected

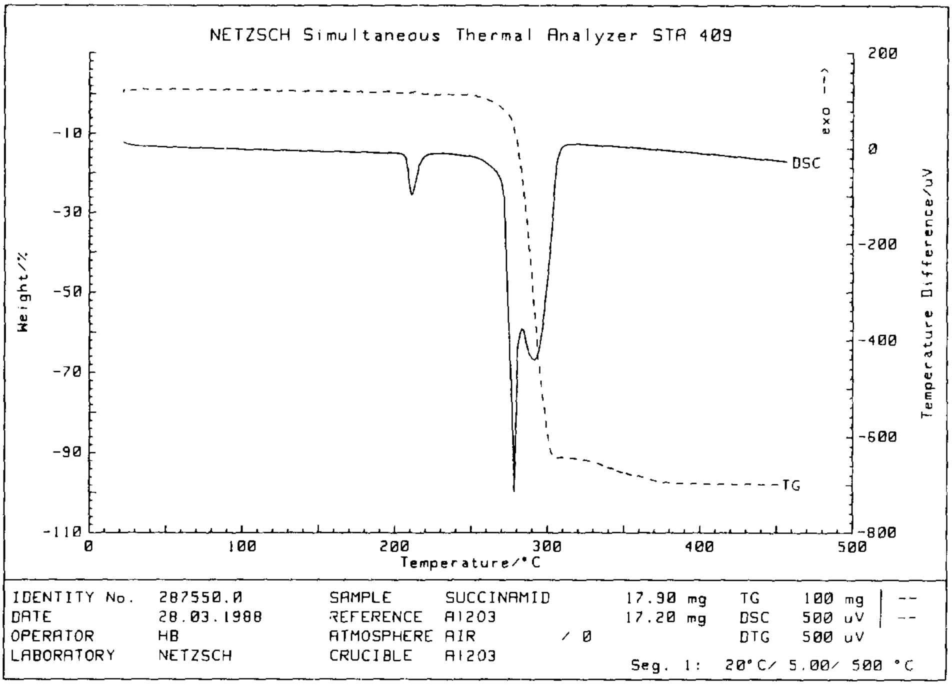
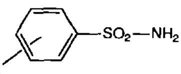


Fig. 8. DSC and TG curves for succinamide **131**.

with a mass loss at the same time [95]. However, the authors did not state anything about the identification of the decomposition products of **134a**.

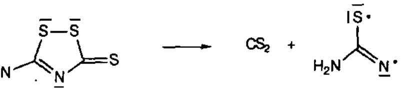


133

134 R = H

134a R = 4 - Methyl

5-Amino-1,2,4-dithiazole-3-thione **135** decomposes in a two-step reaction where the first endothermic step is caused by the cleaving of CS_2 [96]

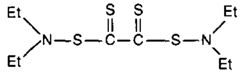


135

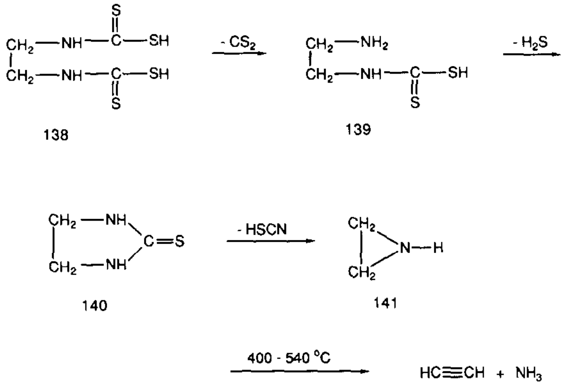
136

The primarily formed biradical **136** further reacts to insoluble condensation products which were not investigated in detail. CS_2 was determined both qualitatively and quantitatively.

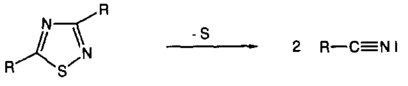
CS_2 develops along with N_2, CO_2 and H_2O as a product of the oxidative pyrolytic decomposition of bis-*S*,*S*′-diethylaminotetrathiooxalic acid **137** as shown by gas chromatography. The homolytic reaction which starts at about 200 °C takes place endothermically in one step with simultaneous mass loss [97].


137

The reaction mechanism of the decomposition of 1,2-bis(dithiocarboxyamino)ethane **138** is concluded from four endothermic reactions and the corresponding TG steps [98]. At first, cleavage of CS_2 from **138** gives 1-amino-2-dithiocarboxaminoethane **139**, which then eliminates H_2S to produce imidazolidin-2-thione **140**. At temperatures above 180 °C **140** loses HSCN to form aziridine **141**, which decomposes to NH_3 and ethyne in the temperature range 400–540 °C. The authors, however, do not report identification of the individual products.



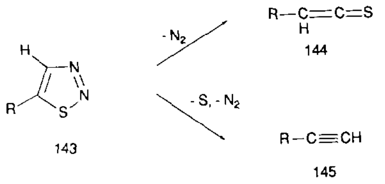
Both exothermic and endothermic decomposition reactions were observed after melting of 3,5-disubstituted-1,2,4-thiadiazoles **142** [99]. Beside sulphur the corresponding nitriles were mentioned as reaction products.



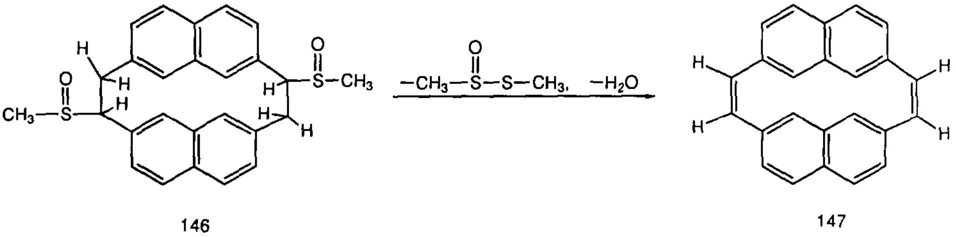
142

5-Substituted-1,2,3-thiadiazoles **143** cause strongly exothermic signals in the DSC curves after their melting, accompanied by explosive decomposition [100]. No statements were made about the nature of the products formed.

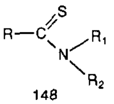
Presumably the corresponding thioketenes **144** develop thermally from **143** by loss of nitrogen or by cleaving sulphur and nitrogen to give the analogous ethynes **145**. Such reactions of 1,2,3-thiadiazoles are known [101].



TG and DTG curves were measured for some cyclophane-bis-sulphoxides [102]. Discussed here is the exemplary compound **146**. The cyclophane **146** at first cleaves the unstable methanesulphenic acid (CH_3SOH) which at once disproportionates to methylthiosulphinic-*S*-acid methylester (CH_3–SO–SCH_3) and H_2O. The two-step mass loss as well as the mass spectrometric investigations speak for a stepwise cleavage of the methyl sulphoxide groups with formation of the cyclophane dienes **147**.

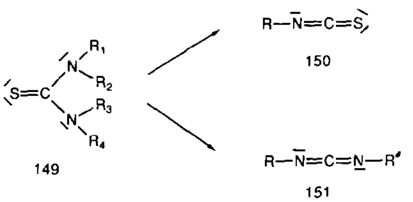


The DTA, TG and DTG curves obtained during the pyrolytic decomposition of numerous substituted thioamides **148** showed, after melting, a two-step decomposition in further endothermic reactions [103,104]. Exclusively gaseous substances were obtained as products; these were not investigated further.



148

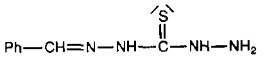
Similarly, thioureas **149** bearing alkyl residues thermally decomposed to indeterminate gaseous products. The IR spectra of the vapour condensate material in the intermediate stages suggested the formation of isothiocyanates **150** or carbodiimides **151** [105]. The DTA curves of the substituted thioureas **149** show both endothermic and exothermic effects.



The DSC measurement of unsubstituted thiourea results in an endothermic signal for the melting process and a further endothermic effect for the decomposition and vaporization process [106].

In their thermoanalytical curves, the monothiocarbonohydrazones **152** show exothermic signals immediately after the melting process where the initial mass decreases at the same time [107]. Among other products, H_2S, NH_3, N_2, benzonitriles and other complex condensation products containing

C=N linkages were found as the main products of the decomposition of **152**, which proceeds by radical mechanisms.



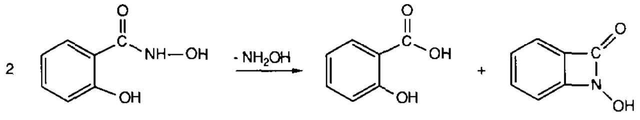
$Ph-CH=N-NH-\overset{S}{\overset{\|}{C}}-NH-NH_2$

152

3.4.7. *Miscellaneous fragmentations*

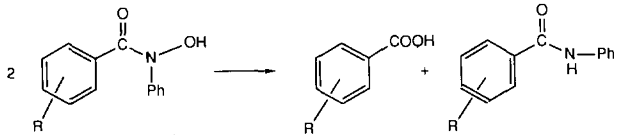
The thermoanalytical investigations of monomeric organic substances summarized in this section can no longer be arranged according to the cleavage of the same volatile decomposition products. Thus, the following are divided only roughly into aromatic as well as aliphatic hydrocarbons, and heterocyclic systems.

3.4.7.1. Aromatic and aliphatic compounds. DTA, TG and DTG curves exist for salicylhydroxamic acid **153** [108]. By cleaving hydroxylamine in the temperature range 165–180 °C salicylic acid **60** as well as the *N*-hydroxyl-actam **154** appear after the melting of **153** in an exothermic reaction. Both reaction products could be identified by IR spectroscopy.



153 60 154

Likewise, the thermal decomposition of *N*-phenylbenzohydroxamic acid **155a** is exothermic and, according to DTA and TG curves, occurs in two stages [109]. The main products benzoic acid **156** and benzanilide **157** were identified by UV, IR and X-ray analysis.



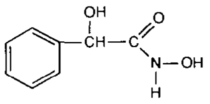
155a R = H
155b R = 2 - Chloro
155c R = 3 - Chloro

156

157

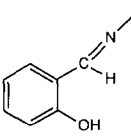
Similarly, *N*-*o*-chloro- and *N*-*m*-chlorophenylbenzohydroxamic acids **155b** and **155c** show two exothermic effects in their DTA curves [110]. Fatty acids, carboxylic acids and anilides were spectroscopically identified as the main products.

The TG and DTG curves of mandelic acid hydroxamide **158** also hint at its two-step decomposition [111].



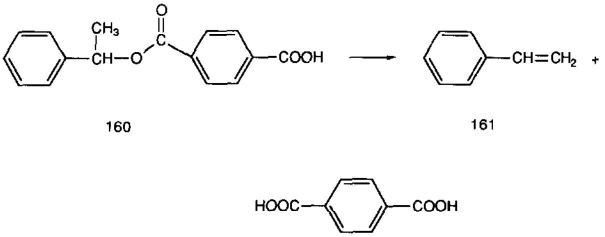
158

According to the published TG curve the decomposition of salicylaldoxime **159** in a static air atmosphere starts by suddenly losing mass at about 85 °C [112]. Several products which were formed by a series of elimination reactions were identified by mass spectrometry as well as by GC.



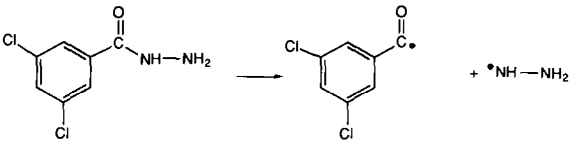
159

Terephthalic acid esters can decompose by thermal *cis*-elimination. Thus the pyrolysis of terephthalic acid-(1-phenyl)-ethylester **160** results in styrene **161** and terephthalic acid **162**. The formation of styrene was proved by TG and DTG analysis by the corresponding mass loss of the first TG step, whereas the remaining residue after this TG step was analysed and found to be nearly pure **162** [113].



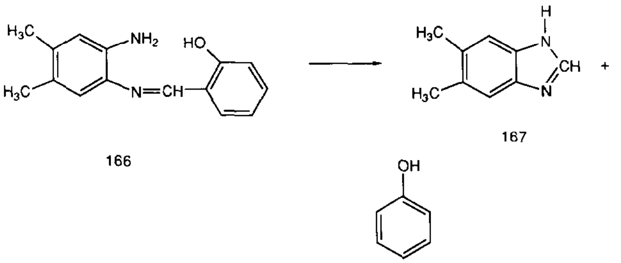
160 161 162

The primary formation of the radicals **164** and **165** can be concluded from the percentages of the TG steps of the decomposition of some dichlorobenzoylhydrazines such as **163**, although the reaction products were not analysed [114].



163 164 165

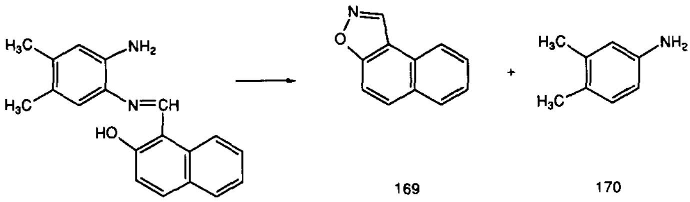
TG and DTG curves were published from the thermoanalytical investigations of some aromatic imine derivatives [115]. For example, the pyrolytic decomposition of *N*-(2-amino-4,5-dimethylphenyl)-salicylaldimine **166** takes place thermogravimetrically in a two-step reaction. Cleavage of phenol leads to 5,6-dimethylbenzimidazole **167**, which was identified by MS, IR, UV and elemental analysis.



166

167

Similarly, as a product of the pyrolysis of the imine derivative **168** naphthoisoxazole **169** is formed. A further product probably is *o*-xylene derivative **170**.

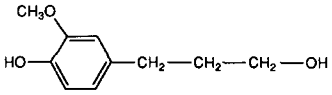


168

169

170

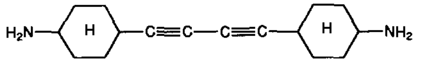
Various phenylpropanol derivatives which were substituted by hydroxyl and methoxy groups were investigated with the help of DTA and DTG analysis [116]. The products, which were partially characterized by IR spectroscopy or their melting points, result from the radical fragmentation of the starting materials such as, for example, from 3-(4-hydroxy-3-methoxyphenyl)propanol **171**.



171

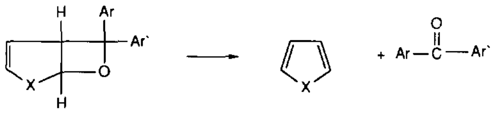
The decomposition of these compounds takes place both by exothermic and endothermic reactions.

In a static air atmosphere 1,4-bis(4-aminocyclohexyl)-butadiyne **172** shows, after melting, a strong exothermic DSC effect above 200 ° C which is accompanied by a loss of mass at the same time [117]. A further TG step appears between about 300 ° C and 500 ° C. There are no statements about the evidence of stable intermediate products which may have been formed.



172

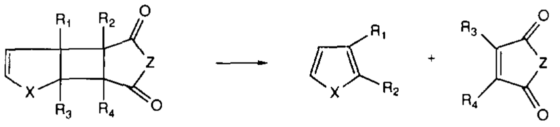
3.4.7.2. Heterocyclic compounds. Bolivar and Rivas [118] could prove with only one DSC run that differently substituted oxetanes **173** undergo endothermic melting followed by exothermic decomposition to the five-membered heterocycles **174** and carbonyl compounds **175**. Additionally, the reaction products were analysed by mass spectroscopy.



173 174 175

X = O, S, N-CO-Ph

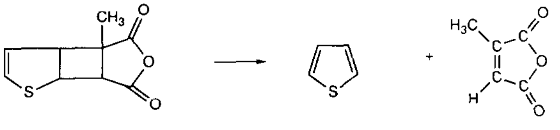
The corresponding substituted five-membered heterocycles **177** and the anhydrides or maleimides **178** were formed in a retro-[2 + 2]-cycloaddition [119] during the thermal decomposition of heterocycles of the general formula **176** (with X ≡ S or O and Z ≡ O or NH) although these reactions are not allowed thermally according to the Woodward–Hoffmann rules.



176 177 178

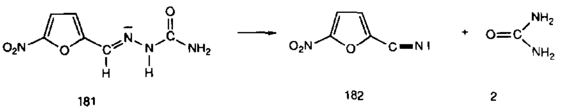
X = S or O; Z = O or NH

The published TG curves show a two-step decomposition process, and the DSC curves generally show two endothermic effects for the fusion and evaporation and partly for the decomposition of the compound **176**. For some derivatives of **176** also exothermic signals were obtained. The thermal decomposition of 6-methyl-2-thia[3,2,0]bicyclohept-3-en-6,7-dicarboxylic anhydride **179** results in methylmaleic acid anhydride **13** and thiophene **180** which were analysed by GC/MS.

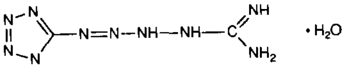


179 180 13

DTA, DSC and TG curves also exist for 5-nitro-2-furaldehydesemicarbazone **181** [120]. The semicarbazone **181** decomposes at about 245 °C in an exothermic reaction with a simultaneous mass loss of about 67%. Further temperature increases cause a mass loss of 100% as well as the appearance of further endothermic and exothermic signals. It is possible that at first the relatively volatile nitrile **182** arises from **181** in an elimination reaction which perhaps could explain the first TG step with a mass loss of about 70% in comparison to the initial material. It can only be speculated about the primary formation of urea **2**, as the decomposition products of **181** were not analysed further.



As an example of a large number of investigations on organic explosives, the DSC investigations of tetracene **183** [121] and different substituted tetrazole-5-yl-hydrazones **184** [122] should be mentioned. For the thermal decomposition of both compounds exothermic signals were of course registered, whereas in contrast to **184** two peaks were obtained for the decomposition of **183**. No statements were made about the primarily formed decomposition products or their identification.



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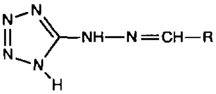

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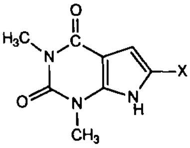
The DSC curves of some 6-substituted-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrrolo[2,3-*d*]pyrimidines **185** show endothermic effects in a nitrogen atmosphere for the melting and the degradative volatilization of the melts. In an oxygen atmosphere, however, exothermic effects were measured for the oxidative decomposition of **185** [123]. No statements were made about stable decomposition products which may have been formed.

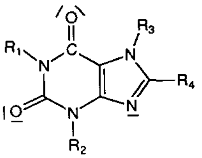


X = $COCF_3$, $COCCl_3$, $COCH_3$
CHO, $CONH_2$, $COOH$, $COOC_2H_5$

185

At the end of this review there are still some remarks to be made concerning the thermoanalytical investigations of some natural substances (purine derivatives, carbohydrates and nucleosides).

There are numerous publications by Salas-Peregrin and others about the thermoanalytical investigations of *purine derivatives* **186**.



186

For example, DSC, TG and DTG curves were measured for the following purine derivatives **186**:

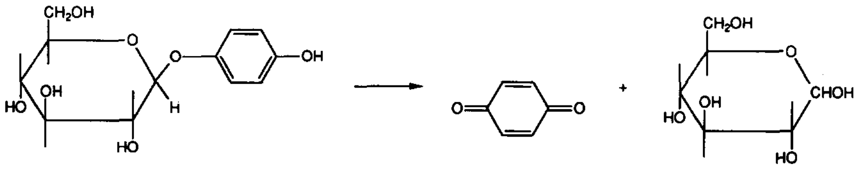
xanthine (2,6-dioxopurine) $R_1 = R_2 = R_3 = R_4 = H$ [124]

8-ethylxanthine	$R_4 = Et, R_1 = R_2 = R_3 = H$ [125]
8-ethyl-3-methylxanthine	$R_4 = Et, R_2 = Me, R_1 = R_3 = H$ [125]
8-ethyl-1-methylxanthine	$R_4 = Et, R_1 = Me, R_2 = R_3 = H$ [126]
8-ethyl-1,3-dimethylxanthine	$R_4 = Et, R_1 = R_2 = Me, R_3 = H$ [126]
theophylline	$R_1 = R_2 = CH_3, R_3 = R_4 = H$ [127]
8-substituted theophyllines	$R_1 = R_2 = CH_3, R_3 = H, R_4 = Et$, propyl, isopropyl, Ph [128]
theobromine	$R_2 = R_3 = CH_3, R_1 = R_4 = H$ [129]
caffeine	$R_1 = R_2 = R_3 = CH_3, R_4 = H$ [130]
xanthosine	[131]
hypoxanthine (6-hydroxypurine)	[132]

In general, both endothermic and exothermic effects during the thermal decomposition of purine derivatives **186** could be detected. Nothing was reported about the formation of stable intermediates or the identification of the decomposition products.

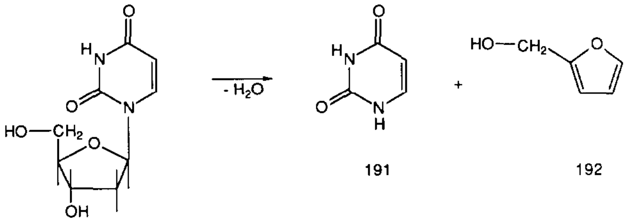
The reactions accompanying the pyrolytic decomposition of *carbohydrates* are also very complex. The DTA or DSC curves of carbohydrates show both endothermic and exothermic effects [133–136]. An identification of the decomposition products was absent in most of the thermoanalytical investigations of carbohydrates.

For the decomposition of the monosaccharide arbutin **187**, however, among the various decomposition products hydroquinone **188** and α- as well as β-D-glucose **189** can be definitely identified as primary products of the pyrolytic decomposition of **187** by GC analysis and IR spectroscopy [136].



187 **188** **189**

Some of the thermoanalytically investigated *deoxynucleosides* also exhibit exothermic and endothermic effects in the corresponding DTA/DSC curves [137–141]. The exothermic effects partly appear directly after the melting of the deoxynucleosides, but sometimes some can additionally be found far above the melting peak of the educts. The appearance of the exothermic effects directly after the melting process of deoxynucleosides can be explained by the cleavage of the glycosidic bond via pyrolytic elimination and the subsequent formation of stable products. The newly formed products could either be identified by their melting points directly after their formation using DSC or by additional methods of analysis such as MS, IR, UV and GC. Thus, for example, uracil **191** and furfuryl alcohol **192** were identified as products of the thermal decomposition of 2′-deoxyuridine **190** [139].



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192

4. CONCLUSIONS

We have seen that thermoanalytical methods, especially DTA/DSC, TG and DTG, are suitable for determining the thermal stability of organic compounds and for observing their phase transitions as well as decompositions. In addition, in many cases thermoanalytical methods can successfully characterize the course of chemical reactions where new and well-defined products are formed which are successfully identified.

The application of thermoanalytical methods to so-called "one-pot reactions" succeeds in those cases where both the formation and the identification of the products formed can be achieved by only one measurement. It should be emphasized that the "one-pot method" can only be applied with success if the melting and boiling points of the products lie above the temperature of their formation.

In many cases additional methods of analysis, such as GC, IR, MS, UV, etc., complement the identification of the primarily formed products if this is not possible by thermal analysis only.

It can be seen from the increasing number of publications which deal with the application of thermoanalytical methods when investigating organic substances, that in future thermoanalytical techniques in the field of organic chemistry will become more and more important.

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