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DECOMPOSITION STUDIES OF PHOTOADDITION PRODUCTS DERIVED FROM FIVE-MEMBERED HETEROCYCLICS AND MALEIC ANHYDRIDE AND MALEIMIDE DERIVATIVES BY DSC, TG AND MS

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ABSTRACT

Differential scanning calorimetry, thermogravimetry and mass spectral analysis studies as a function of temperature were carried out for the photoproducts derived from the photosensitized cycloaddition reactions between different furan and thiophene derivatives and methyl substituted maleic anhydrides and maleimides. It was found that the photoproducts melt with partial decomposition followed by evaporation of the undecomposed material as well as the decomposition products. This investigation may serve to establish a general pattern in the thermal behaviour of this family of compounds containing as a common feature a four-membered ring between a five-membered heterocycle and a five-membered anhydride ring.

INTRODUCTION

In the course of an investigation on the photoaddition of citraconic anhydride and 2,3-dimethyl maleimide to furan, and of citraconic and 2,3-dimethylmaleic anhydride to several thiophene and benzo(b)thiophene derivatives sensitized by benzophenone, the corresponding (2 + 2) cycloaddition products have been isolated according to the general reaction [1—5] given in Fig. 1. These compounds (Tables 1 and 2) have been found to be generally thermally stable.

They are chemically interesting substances due to the fact that the four-membered ring formed in the (2 + 2) cycloaddition reaction leads to two stereoisomers, *syn* and *anti*, the *anti* being the predominant isomer when the photolysis is carried out at —20°C [6]. Since, previously [7], useful correlations were found in the thermal behaviour of oxetanes derived from carbonyl compounds and five-membered heterocyclics, it appeared interesting

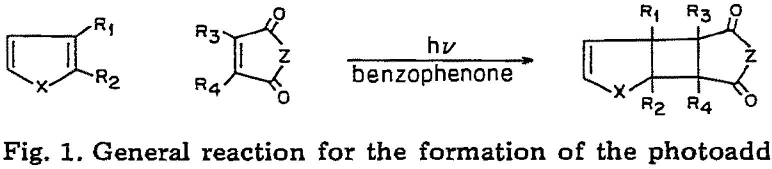
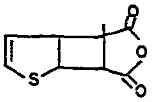
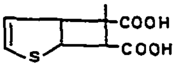
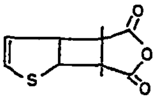
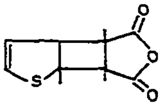
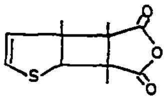
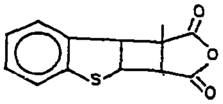
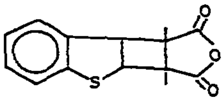
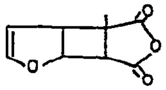


Fig. 1. General reaction for the formation of the photoadducts I—X, X = S or O, Z = O, NH.

TABLE 1

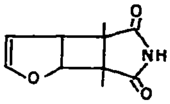
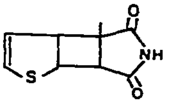
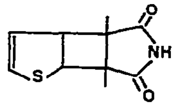
Photoaddition products from methyl-substituted maleic anhydrides and five-membered heterocycles studied by DSC

Heterocycle	Anhydride	Photoaddition product		Ref.
Thiophen	Citraconic		I	1
			Ia	
Thiophen	2,3-Dimethyl maleic		II	1
2-Methyl thiophen	2,3-Dimethyl maleic		III	1
3-Methyl thiophen	2,3-Dimethyl maleic		IV	1
Benzo(b) thiophen	Citraconic		V	2
Benzo(b) thiophen	2,3-Dimethyl maleic		VI	2
Furan	Citraconic		VII	5

to study by means of differential scanning calorimetry and related techniques the physical and chemical transitions undergone under heating by this series of compounds containing a four-membered ring with no heteroatom in it. The series of compounds studied is illustrated in Tables 1 and 2.

TABLE 2

Photoaddition products from maleimides five-membered heterocycles studied by DSC

Heterocycle	Maleimide	Photoaddition product		Ref.
Furan	2,3-Dimethyl		VIII	3
Thiophene	Citraconimide		IX	3
Thiophene	2,3-Dimethyl		X	3

EXPERIMENTAL

Synthesis of the photoproducts

The general procedure for the preparation of the photocycloaddition products was essentially that of Schenck et al. [8] and may be described as follows. A solution of 0.045 mole of the anhydride and 0.01 mole of benzophenone in 80 ml of the corresponding thiophene derivative was placed in a 100 ml reaction vessel. A double-walled quartz immersion well, containing a pyrex filter sleeve and a Hanovia 450 W lamp, was fitted into the reaction vessel; the lamp was cooled at —20° C and nitrogen was bubbled through the solution before and during irradiation. At the end of 15 h the irradiation was stopped and the liquid portion distilled under vacuum. In some cases the residue crystallized immediately but in most cases it was necessary to leave the residue in the ice box for 24 h. The crude crystals were washed with carbon tetrachloride to eliminate the benzophenone and other impurities and the solids were crystallized from appropriate solvent mixtures such as carbon tetrachloride—ethanol (3 : 1). When the thiophene derivative is not a liquid, as in the case of the benzo(b)thiophene, the irradiation was carried out at 40° C just above the melting point of the thiophene derivative. For more experimental details it would be useful to refer to previous papers from this laboratory [1—5].

The diacid Ia was obtained by dissolving 0.83 mmole of the adduct I in 3 ml of an acetone—water mixture and refluxing for 12 h. The purity of all the photoproducts obtained was verified by their mass spectra.

Scanning calorimetry

Differential scanning calorimetry (DSC) was carried out in a Du Pont DSC module used in conjunction with the analyzer Model 990 console; a heating rate of 5°C min^{-1} was used in the temperature range 22—550° C. Non-hermetic pans were used. The DSC was calibrated by performing melting curves with metallic indium. The photoproducts were recrystallized from suitable solvent systems [1,2] and dried under vacuum. Samples ranging from 4.0 to 10.0 mg with an accuracy of within ±0.01 mg were weighed. The reversibility of the melting point was verified by taking the melting point twice in succession for the same sample. That is to say, after the first determination the temperature was allowed to go up 5°C higher, then the sample was cooled and the melting point determined once more. If the value corresponding to the area of the fusion peak after the second determination is smaller than that after the first one it is inferred that the compound melts with decomposition. It was observed that all these photochemical adducts I—X showed a decrease of the area of fusion in the second determination relative to the first. Therefore, it is likely that all these compounds melt with decomposition.

Furthermore, it is well known that when a compound melts with decomposition its melting point changes with the rate of heating [9]. Thus, after calibration of the instrument with indium (m.p. 156.6°C), samples of these compounds (5—8 mg) were heated at heating rates of 100, 50 and 5°C min^{-1}, respectively. The shifting of the vertex corresponding to the melting point was observed as expected. For example, for compound I the vertex of the melting point peak was shifted from 103 to 101 and to 99°C, respectively. Moreover, by thermogravimetric analysis a 5—10% decrease in weight was observed at the melting point of the compounds I—VII.

Thermogravimetry

Thermogravimetry (TG) was carried out in a Du Pont 951 analyzer module coupled to the same analyzer Model 990 console used for DSC. The rate of heating was 5°C min^{-1} and the experiments were performed in an open thermobalance with no special gas flow. The samples used ranged between 4 and 10 mg.

Mass spectrometry

Mass spectrometric analyses were performed in a Du Pont 21-492B mass spectrometer in conjunction with a Du Pont 21-094B computer system. As soon as the samples were introduced in the ionizing chamber heating was started and kept at a rate of 20°C min^{-1}, beginning at 30°C and ending at 330°C. The intensity data of the most significant fragments (*m/e* 18, 28, 44 and 84) were stored for further reference (Fig. 5).

RESULTS AND DISCUSSION

All the photoadducts studied (Table 1) exhibited a common pattern in the DSC curves which consist of two endothermic peaks, as illustrated in Fig. 2. They correspond to the fusion and evaporation temperatures which match those measured independently by using a melting point apparatus. Further-

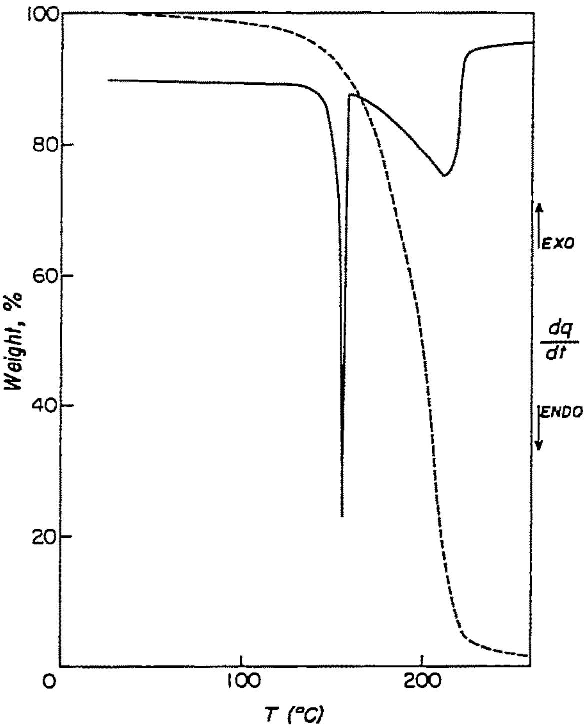


Fig. 2. Typical thermoanalytical curves for the anhydrides I—VII (Table 1). ———, DSC; - - - - - -, TG.

more, they agree with the melting points already reported in the literature [1—5].

The heats of fusion and evaporation for these adducts could not be determined by DSC as was done previously in this laboratory for a series of oxetanes derived from five-membered heterocyclics and benzophenone [7]. The reason for not being able to obtain this helpful information was that these compounds I—X melt with partial decomposition, as may be inferred from the following: (a) the broadness of the evaporation peak is suggestive of the decomposition process (Fig. 2); (b) the thermogravimetry curve reveals a weight loss in the sample of about 10% by the end of the fusion process (Fig. 2); and (c) when a sample of adduct I was heated to the melting point in a sealed tube [10] and then analyzed by GLC—MS, only the thiophene was detected [11,12].

It is possible that the decomposition mechanism undergone during the DSC determination may be the same as that observed for these compounds under electron impact in the mass spectrometer [13], namely a retro-Diels Alder process (Fig. 3).

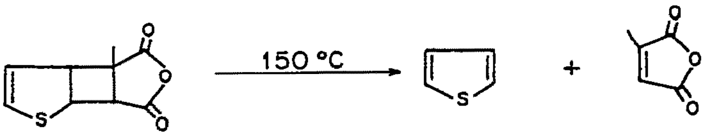


Fig. 3. Thermal decomposition of the adducts I.

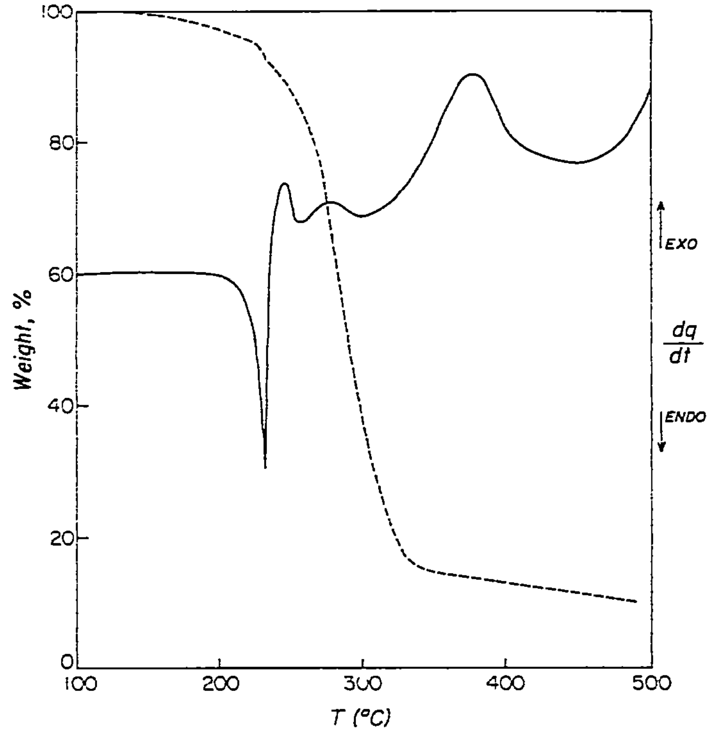


Fig. 4. Thermoanalytical curves for the diacid Ia (Table 1). ———, DSC; - - - - - -, TG.

The DSC thermogram (Fig. 4) for the dicarboxylic acid Ia is more complicated than those obtained for the anhydride [5] (Fig. 2). It consists of four peaks, one endothermic, followed by three exothermic peaks. The endotherm corresponds to the fusion of the dicarbocyclic acid Ia; it is followed by a first step in the decomposition which represents approximately a 12% loss in weight. The major weight loss is associated to the second and third exothermic peaks and finally a residue remains which corresponds to about 15% of the total weight. The latter is relatively thermally stable.

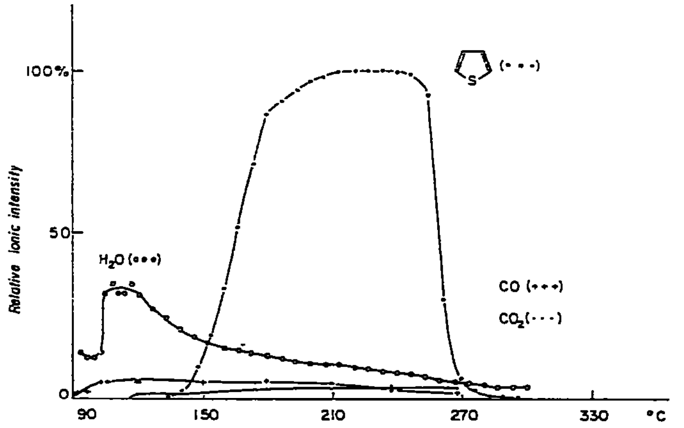


Fig. 5. Typical patterns of ionic intensity for *m/e* 18, 28, 44 and 84 for the diacid Ia. Heating rate 20—30°C min^{-1} [14].

The mass spectrometric analysis [14] as a function of temperature (Fig. 5) shows that the intensity of the peak corresponding to the *m/e* 18 (H_2O ions) decreases as temperature increases. This fact may suggest that the first step in the decomposition of the diacid Ia is a dehydration followed at higher temperature by increased evolution of thiophene. The latter is probably the major decomposition process at temperatures higher than the melting point. The decarboxylation and decarbonylation seem to be less important processes in the thermal decomposition of the diacid Ia. In other words, after the loss of water the anhydride is re-formed and it then proceeds to decompose by the retro-Diels Alder mechanism previously described.

The maleimide derivative exhibits the same behaviour as the maleic anhydride derivatives when subjected to heating under DSC conditions (Table 2).

So far, the sulphur and oxygen heterocycles have been investigated; other five-membered heterocyles are expected to be investigated in this connection.

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10 The sample was heated in a sealed tube at 150°C for 10 h.
11 A 5 m. GLC column 15% carbowax 20 M on chromosorb 20 mesh was used at 150°C and 20 ml min^{-1}.
12 Citraconic anhydride was retained in the GLC column used for the analysis. It was verified by injecting an authentic sample of citraconic anhydride. A separate DSC determination for citraconic anhydride showed that it evaporates with decomposition. This information is more evidence to help understand the fact that only thiophene as decomposition product is detected by GLC—MS.
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