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THERMOANALYTICAL INVESTIGATIONS ON HETEROCYCLIC ORGANIC COMPOUNDS. PART II. THERMAL DECOMPOSITION OF SUBSTITUTED 1,4-DIHYDRO-2,4-DIOXO-2*H*-3,1-BENZOXAZINE

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ABSTRACT

The thermal decomposition of substituted 1,4-dihydro-2,4-dioxo-2*H*-3,1-benzoxazine involves a decarboxylation reaction and the formation of dimeric products that arise by a Diels–Alder reaction involving the ketenimine as diene and dienophile. Significant destabilization of the oxazinedione ring was manifested in the thermal decomposition of 3,4-dihydro-1,3-dioxo-1*H*-pyrido (3,2-*d*)(1,3) oxazine (V). The shape of the thermogram is dependent on the experimental conditions. Further decomposition of the dimers leads to dark glassy materials of polymeric nature.

INTRODUCTION

The thermolysis of organic heterocyclic compounds in the solid state may be studied with the aid of TG, DTG, DTA and DSC techniques. This can be a useful synthetic route to numerous ring systems, particularly those accessible by thermally allowed bond reorganization [1]. Furthermore, the thermoanalytical data can be used to determine a mechanistic postulate which can elucidate the thermal decomposition and speed of detonation of organic compounds [2,3]. The structure of substituted oxazinediones allows the loss of a carbon dioxide molecule to give products of a polymeric nature [4]. Smalley and co-workers [5] reported the decomposition of isatoic anhydride, [(I), R = H] in a solvent of high boiling point to give 2-(*o*-aminophenyl)-4*H*-3,1-benzoxazine-4-one (III) with the evolution of carbon dioxide. The product was considered to arise by a Diels–Alder type of reaction involving the ketenimine [(II), R = H] which is valence-isomeric with the corresponding benzazetidinone as diene and dienophile.

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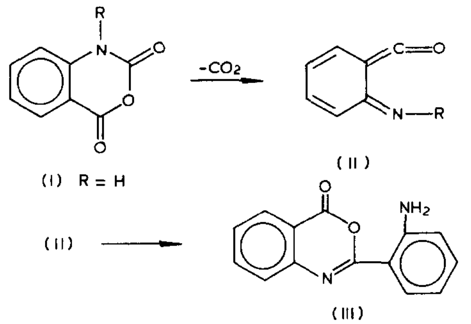


The aim of the present work is to study the thermolysis of several substituted oxazinediones, namely, 1,4-dihydro-2,4-dioxo-2*H*-3,1-benzoxazine (I), *N*-methyl isatoic anhydride (IV), 3,4-dihydro-1,3-dioxo-1*H*-pyrido (3,2-*d*) (1,3) oxazine (V), and 7-nitroisatoic anhydride (VI). Whenever possible, intermediate products were isolated and identified. The results are used to postulate a mechanism for the decomposition reactions of these compounds.

EXPERIMENTAL

Melting points were determined on a Kopfler hot bench apparatus and are uncorrected. Infrared spectra were recorded on a Pye-Unicam SP-1100 infrared spectrophotometer (Table 1). The elemental analyses were performed by Alfred Bernhardt Laboratories, West Germany and the Central Laboratories of the Iraqi National Oil Company (INOC), Baghdad, Iraq. The results of the analysis are listed in Table 2. Trimethylsilyl azide was purchased from Fluka AG, Switzerland.

TABLE 1

Infrared spectral data for the oxazinediones (I–VI)

Compound no.	N–H (cm^{-1})	$C{=}O_{(asym.)}$ (cm^{-1})	$C{=}O_{(sym.)}$ (cm^{-1})	C–H in-plane deformation	C–H out-of-plane deformation
(I)	3240m	1840s	1770s	1448s, 1342s, 1265m, 1225s, 1025s, 980s	840m, 826s, 775s, 733s, 715s
(IV)		1795s	1723s	1423s, 1352s, 1280m, 1225s, 1033s, 1010s	835m, 788s, 773s, 750s, 710s
(V)	2850–2950m	1791s	1742s	1450s, 1348s, 1275m, 1223s, 1025m, 990s	830m, 785s, 748s, 713s
(VI)	3015m	1785s	1748s	1452s, 1350s, 1282s, 1225m, 1033s, 995s	842m, 792s, 753s, 720s

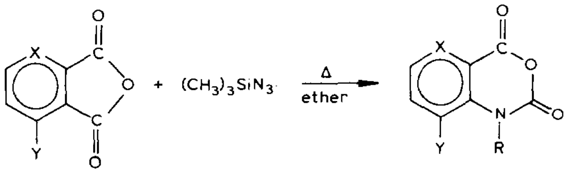
TABLE 2

Elemental analysis data

Compound no.	C (%)	H (%)	N (%)
III	Found 70.11	3.96	11.61
	Calcd. 70.58	4.20	11.76
IV	Found 60.96	3.94	7.88
	Calcd. 61.01	3.95	7.90
V	Found 51.32	2.42	17.02
	Calcd. 51.21	2.43	17.07
VI	Found 45.86	1.99	13.60
	Calcd. 46.15	1.95	13.41

General procedure for the synthesis of the oxazinediones(I–VI)

A solution of the corresponding anhydride in ether was heated with a slight excess of trimethylsilyl azide until gas evolution slowed. Cooling of the solution to room temperature and hydrolysis with 95% ethyl alcohol gave the corresponding oxazinediones (I–VI) (cf. refs. 6 and 7).



(I) X = C, R = H, Y = H
(IV) X = C, R = CH_3, Y = H
(V) X = N, R = H, Y = H
(VI) X = C, R = H, Y = NO_2

Thermal analysis

The simultaneous TG, DTG and DTA measurements were carried out in a MOM derivatograph (Hungarian Optical Works). 40–60 mg samples were heated in platinum crucibles of the type used by Jasim et al. [8], at a rate of 10°C min^{-1} under a static (air) atmosphere. The reference material for the DTA measurements was α-Al_2O_3 heated to 500°C. The evaluation was based on thermograms obtained from 2–3 runs for each sample to ensure reproducibility. The DSC measurements were carried out on a Heraeus TA 500 thermal analyser system.

RESULTS AND DISCUSSION

The TG and DTG curves, and the DTA curves for the compound 1,4-dihydro-2,4-dioxo-2*H*-3,1-benzoxazine (I), and the effect of the shape of the sample holder are shown in Figs. 1 and (2), respectively. The DSC curve of compound (I) is shown in Fig. 3. The TG, DTG and DTA curves of compounds IV, V and VI are given in Figs. 4–6. The decarboxylation reaction is a characteristic feature of these compounds.

It is clear from Fig. 1 that decarboxylation commences with a slow induction period between 195 and 211°C, whereafter, it proceeds at a much faster rate. The rate of decomposition attains a maximum at 238°C (average of six runs). This reaction could be considered a topochemical and autocatalytic reaction. Similar observations were reported by Wesolowski [9] involving the decarboxylation of *para*-aminosalicylic acid. However, the decarboxylation starts earlier when the multiplate sample holder [10] was used

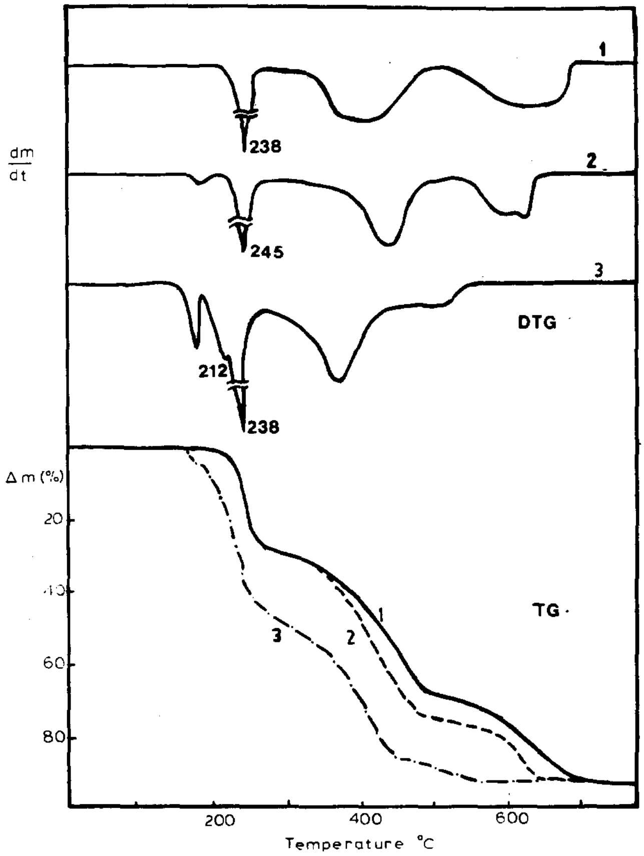


Fig. 1. TG and DTG curves of oxazinedione (I). 1, Open crucible; 2, covered crucible; 3, multiplate sample holder.

instead of the normal crucible. This can be attributed to the partial vacuum condition which is furnished by the multiplate sample holder [8]. Moreover, the process is terminated far beyond the predicted amount of CO_2. The corresponding DTG curve (Fig. 1, curve 3) clearly shows that the decarboxylation process attains a maximum rate at 212°C and is followed by a step which proceeds at a faster rate showing a maximum at 238°C.

The products obtained from the decarboxylation reactions were analysed to obtain the elemental composition and the results were fitted well to the predicted structures. These products could be considered to form via a Diels–Alder type of reaction, with the corresponding ketenimine, which formed initially, acting as diene and dienophile [5]. The IR spectrum clearly revealed the NH stretching vibration in the region of 3μ.

The DTA curve (Fig. 2, curve 1) indicates that the process is endothermic with a peak at 238°C and terminates slightly higher than the general base line. A closer look at the thermodynamic nature of the reaction was made with the aid of DSC using a relatively small sample weight. It can be seen from Fig. 3 that the induction period starts as early as 165°C and corresponds to ~ 1.5% of the overall extent of the reaction (based on peak area ratio). The DSC peak maximum appears at 233°C which is in agreement with the DTA and DTG peaks. The endothermic process is immediately succeeded by an exothermic one between 238 and 270°C with a peak

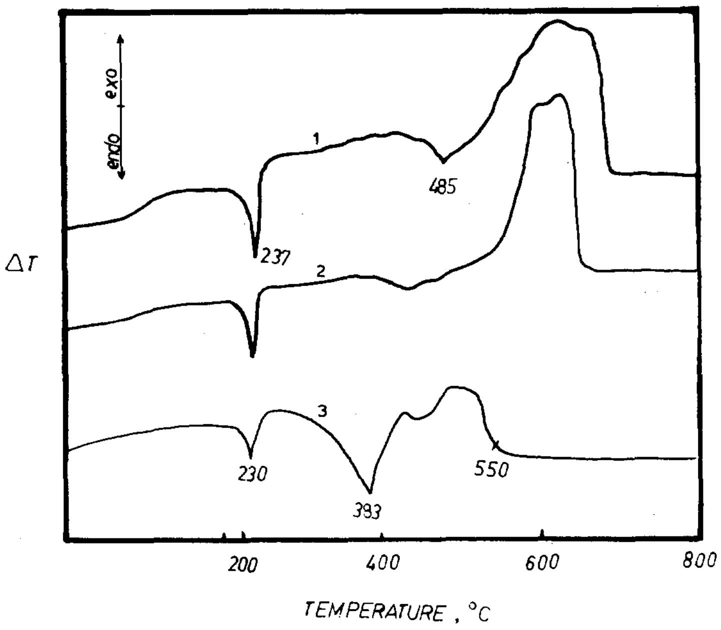


Fig. 2. DTA curves of oxazinedione (I). 1, Open crucible; 2, covered crucible; 3, multiplate sample holder.

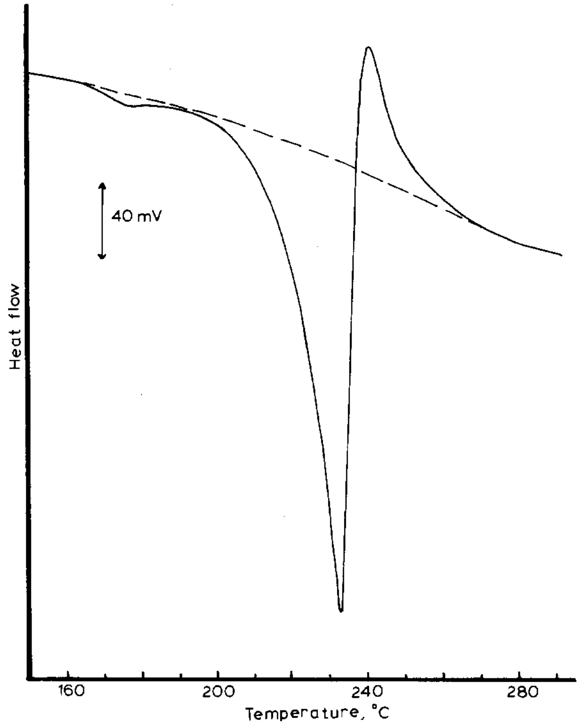


Fig. 3. Partial DSC curve of oxazinedione (I).

maximum at 242°C. The enthalpy of the decarboxylation of oxazinedione (I) assumes a value of 10.86 kJ mole^{-1}. The last exotherm corresponds to the dimerization of the ketenimine intermediate: Diels–Alder dienophile dimerization can be indicated on DTA curves [11] and, subsequently, in DSC curves. The enthalpy of the dimerization process is 2.12 kJ mole^{-1}. The calculated values of ΔH are subject to correction because of the expected overlap of the decarboxylation in the last stages with the dimerization. The activation energy of the decarboxylation was determined by applying the method of Piloyan et al. [12] to the DSC data of Fig. 3. The kinetic plot is shown in Fig. 4. The activation energy assumed a value of 233 kJ mole^{-1}.

The dimer, 2-(*o*-aminophenyl)-4*H*-3,1-benzoxazine-4-one (III) undergoes thermal decomposition into a dark glassy material at 500°C. The thermogram of the process varies depending on the type of crucible used, i.e. the extent of the weight loss for the uncovered sample holder was greater than that obtained for the covered sample holder (Fig. 1). The DTA curves indicate that a series of reversible reactions took place during the course of the decomposition. The homolysis of cyclic benzoxazinone (III) might generate a diradical intermediate (IIIa). Such modes of cleavage had been reported for cyclic peresters and peroxides [13–15]. The diradical intermediate (IIIa) initially formed, might undergo a decarboxylation reaction to the more

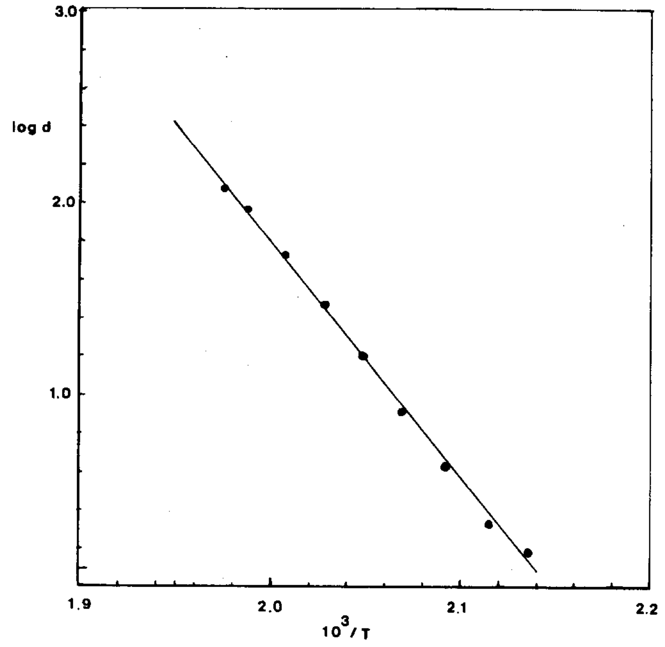
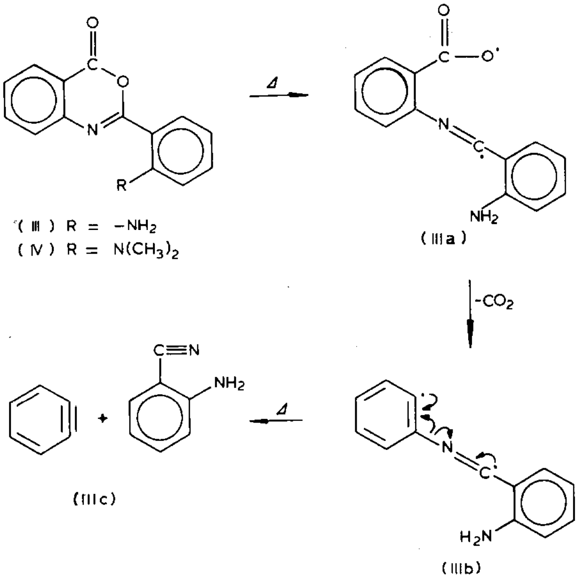


Fig. 4. The Piloyan kinetic plot from the DSC data of oxazinedione (I).

stable diradical intermediate (IIIb). The latter readily disproportionates into benzyne and 2-aminocyanobenzene (IIIc). It is obvious from Fig. 1, curve 3 that the rate of decarboxylation of the benzoyloxy radical is temperature-dependant, and it is faster at higher temperatures, i.e. the thermal environment facilitates the second decarboxylation reaction and, therefore, the ease of formation of the intermediate (IIIb). Similar observations for the calculation of the rate of decarboxylation of benzoyloxy radicals were reported by Bevington and Toole [16]. An additional evidence for the decarboxylation of the benzoyloxy diradical (IIIa) could be derived from the extent of the weight loss recorded for the compound, 1,4-dihydro-2,4-dioxo-2*H*-3,1-benzoxazine (I), using a multiplate sample holder (cf. Fig. 1, curve 3). The amount of weight loss is almost identical to that calculated as if three CO_2 molecules are lost per two molecules of the original compound (I). The intermediate (IIIc) can polymerize, under the experimental conditions, and undergoes thermal degradation into a dark-brown glassy material at 500°C. The elemental analyses of this product were: C = 71.18%, H = 3.39% and N = 11.36%. The composition differs from that predicted for the monomer (IIIc): this often occurs during the degradation of organic polymers, e.g. the degradation of (poly *N*,*N*′-4,4′-diphenyl ether) pyromellitimide, where, at only 2–3% weight loss, ~ 50% of the diphenyl ether and 30% of the pyromellitimide units in the original polymer chains had been chemically modified [17]. This approach can be applied to the present system where no



convenient method of chemical analysis is available at such high temperatures [18]. However, further studies are under investigation to determine the formula and structure of this glassy material. The material is unstable above 510°C and undergoes a combustion reaction in an atmosphere of static air.

Thermal decomposition of N*-methyl isatoic anhydride (IV)*

This compound undergoes a decarboxylation reaction between 172 and 245°C with a maximum rate at 197°C, to give the corresponding dimer (IVa). Similar results were reported by M.C. Ranninger et al. [19] and S. Zeman and Zemanova [20]: these authors report that *N*-substituted ring systems often decompose at temperatures lower than that recorded for the unsubstituted compounds. The dimer obtained from the decarboxylation of *N*-methylisatoic anhydride was equivalent to that obtained from the decarboxylation of compound (I), the only difference being the broadness of the DTA curve (cf. Fig. 2), which could be attributed to the difference in the type of group rearrangement for both compounds. Also, it appears that, through its hyperconjugation, the methyl group, as an electron-releasing group, enables the decarboxylation to proceed by induction with a lower thermal energy requirement than that needed for the *N*-unsubstituted oxazinedione (I).

The second decomposition reaction is a complex endothermic process which involves about 30% weight loss of the original compound into a dark glassy material. However, the extent of the decomposition depends on the reaction conditions. The glassy material undergoes combustion above 450°C. The overall mode of the decomposition of *N*-methyl isatoic anhydride,

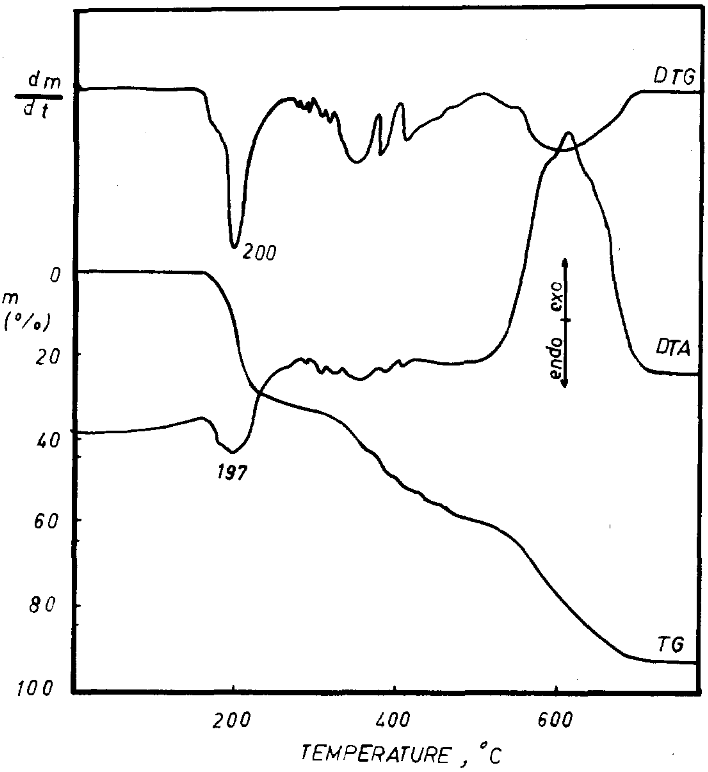


Fig. 5. TG, DTG and DTA curves of *N*-methyl isatoic anhydride.

therefore, is similar to that of the 1,4-dihydro-2,4-dioxo-2*H*-3,1-benzoxazine (I).

Thermal decomposition of 3,4-dihydro-1,3-dioxo-1H-pyrido(3,2-d)(1,3)oxazine (V)

The decarboxylation reaction of this compound occurs between 148 and 200°C with a maximum rate at 164°C, into a faint-brown material. The process is defined by a neat endothermic peak in the DTA curve with a maximum at 166°C (Fig. 6). It appears that a conjugative interaction of the lone pair on the nitrogen atom of the pyridine ring stabilizes the ketenimine, the initial product of the decarboxylation reaction that makes the oxazine ring system more susceptible to decomposition, if compared to the decomposition of 1,4-dihydro-2,4-dioxo-2*H*-3,1-benzoxazine. The thermoanalytical data of the succeeding steps were surprising and need further investigations to establish the mechanistic steps of the decomposition. They are to be included in the next communication of this series.

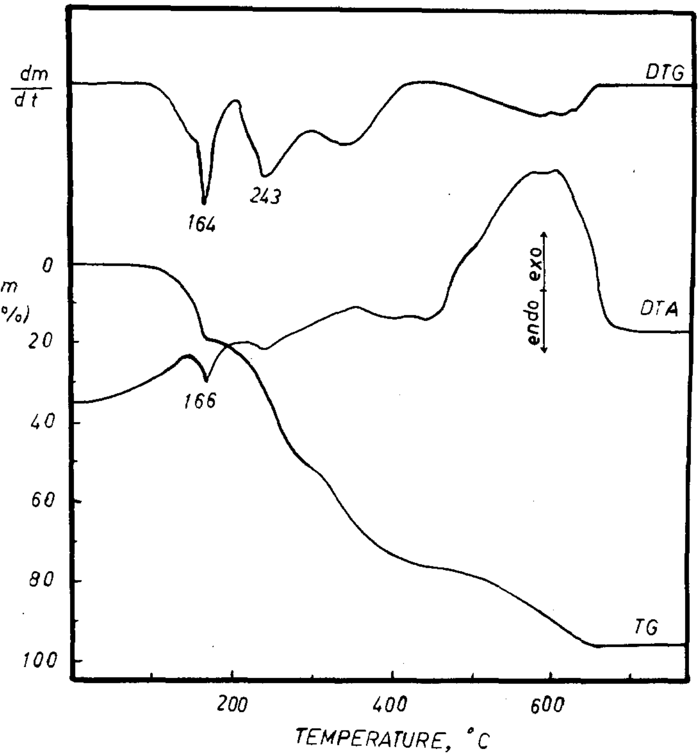


Fig. 6. TG, DTG and DTA curves of 3,4-dihydro-1,3-dioxo-1*H*-pyrido (3,2-*d*)(1,3) oxazine.

Thermal decomposition of 7-nitroisatoic anhydride (VI)

Attention was then turned to substituted 1,4-dihydro-2,4-dioxo-2*H*-3,1-benzoxazine, in order to study the ability of electron-withdrawing groups to destabilize the oxazinone ring. The decarboxylation reaction of this compound (VI) occurs between 155 and 225°C. The reaction starts slowly and attains a maximum rate at 208°C. A sample of this compound was heated in a hot-bench melting point apparatus and gas evolution was observed at 160°C while the sample was still in the solid state. When the temperature reached 205°C, the sample started to melt with fast evolution of gas bubbles and melting ceased at 218°C. This means that the largest fraction of the gas was evolved while the sample was in the molten state, which might suggest that the reaction cannot be first order, as it becomes faster in the liquid state.

The composition of the product resembles that of the unsubstituted 1,4-dihydro-2,4-dioxo-2*H*-3,1-benzoxazine (I) (vide supra) where a number of small steps from the overall 30% weight loss were recorded between 244 and 420°C. Further oxidative decomposition reactions (exothermic) occurred between 425 and 570°C. These decomposition reactions are not quite understood and further study may be required.

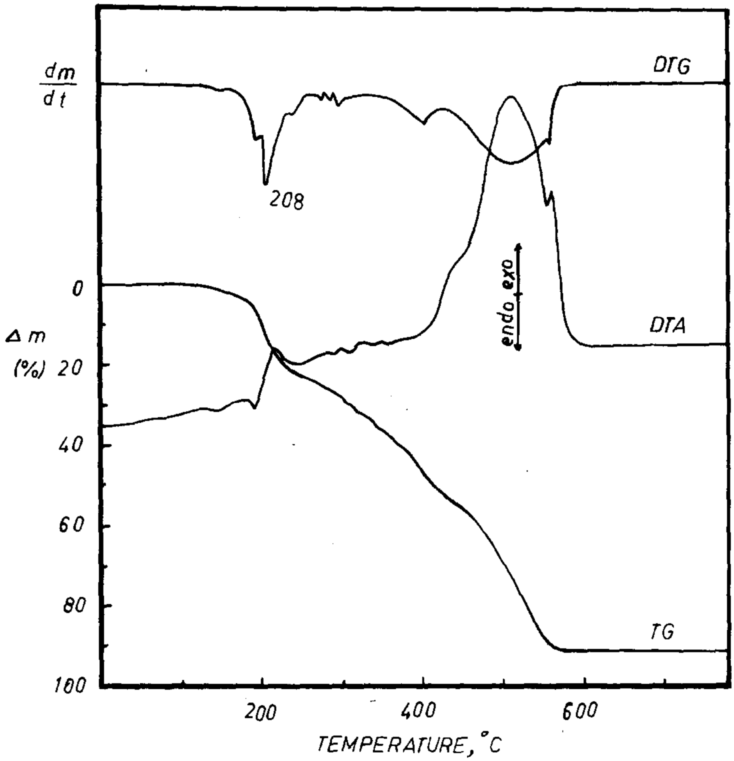


Fig. 7. TG, DTG and DTA curves of 7-nitroisatoic anhydride.

CONCLUSION

The decarboxylation reaction of the oxazinediones is affected by the experimental conditions and the electronic factors of the system. Steric interference by the substituent is not rate-determining since the more hindered compounds undergo easier decomposition.

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