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STUDY OF THE THERMAL STABILITY OF 6-SUBSTITUTED-1,3-DIMETHYL-2,4-DIOXO-1,2,3,4-TETRAHYDROPYRROLO[2,3-*d*]-PYRIMIDINES

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ABSTRACT

1,3-Dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrrolo[2,3-*d*]pyrimidine is readily obtained from the reaction between chloroacetaldehyde and 1,3-dimethyl-6-aminouracil. Further treatment of this product with appropriate reagents leads to the formation of the desired 6-substituted-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrrolo[2,3-*d*]pyrimidine derivatives. Thermal analyses of these derivatives were performed between room and elevated temperatures under both oxygen and nitrogen atmospheres. Information was obtained on the thermal stability of these compounds and the thermal decomposition pattern they underwent.

INTRODUCTION

Thermoanalytical techniques are gaining much interest in the study of organic compounds referring to their stability, structure and polymorphorism, i.e., physical and chemical transitions [1–6]. The thermolysis of organic compounds in the solid state may be studied with the aid of differential thermal analysis, differential scanning calorimetry, thermogravimetry and differential thermogravimetry [7–9]. The pyrrolo[2,3-*d*]pyrimidine system is a skeleton of antibiotics which have found increasing application recently as potential antibacterial agents [10,11]. The aim of the present work is to study the thermal decomposition pattern in nitrogen and oxygen atmospheres of several 6-substituted-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrrolo[2,3-*d*]pyrimidines and related compounds. Phase transitions, thermal and thermogravimetric data were measured and briefly discussed.

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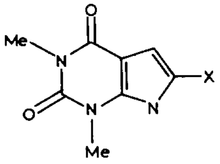
EXPERIMENTAL

Preparation

The general preparation of 6-substituted-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrrolo[2,3-*d*]pyrimidine was conducted by gradual addition of 30% chloroacetaldehyde and sodium acetate to a suspension of 1,3-dimethyl-6-aminouracil and sodium acetate at 75°C. The mixture was then stirred for 30 min at 80°C and cooled, filtered, washed with water and then crystallized from water. Further treatment of this compound with the appropriate reagent to yield the 6-substituted derivatives is performed as described earlier [12].

Thermal analysis

The TG, DTG and DSC measurements were carried out on a Heraeus TA 500 thermal analyser. For TG experiments, 3–7 mg powdered samples were placed in platinum crucibles and heated at a rate of 20°C min^{-1} under dynamic nitrogen atmosphere flowing at 15 cm^3 min^{-1}. For DSC experiments the sample holders were aluminium dishes with alumina as the thermal reference material. The samples were heated at a rate of 10°C min^{-1} under static oxygen and nitrogen atmospheres.



I-VII

Compound	I	II	III	IV	V	VI	VII
X	$COCF_3$	$COCl_3$	$COCH_3$	$CO_2C_2H_5$	CO_2H	CHO	$CONH_2$

RESULTS AND DISCUSSION

The DSC curves of the compounds **I–VII** performed between room temperature and 500°C in nitrogen and oxygen atmospheres are displayed in Figs. 1 and 2, respectively. The main features of the DSC curves recorded in the inert atmosphere of nitrogen gas (Fig. 1) are a major sharp endothermic peak which corresponds to the fusion transition of these compounds and the collapse of their crystal lattice structure. The values of the temperature maxima of this endothermic transition correlated well with the corresponding melting points of these compounds and as shown in Table 1. This

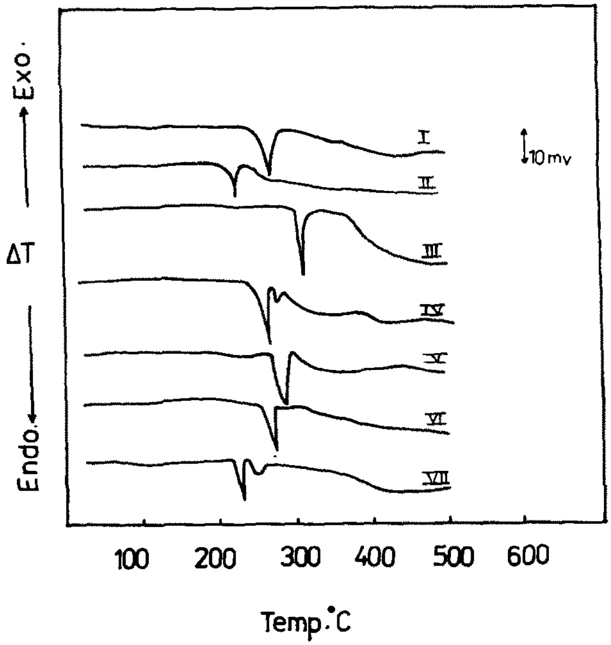


Fig. 1. DSC curves of compounds I–VII in nitrogen gas.

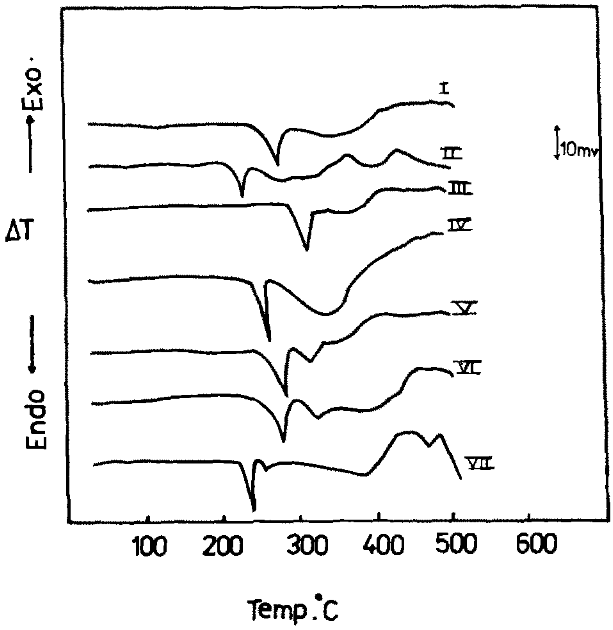


Fig. 2. DSC curves of compounds I–VII in oxygen gas.

TABLE 1

The peak temperature maxima recorded from DSC curves in N_2 gas and their corresponding melting points

Compound	T_m(°C)	M.p.(°C)	Compound	T_m(°C)	M.p.(°C)
I	279	281	**V**	290	282d
II	225	236	**VI**	275	284
III	315	313d	**VII**	235	239d
IV	270	274			

d = decomposition.

transition was followed by an endothermic offset from the baseline which could be attributed to the commencement of degradative volatilization of the melts of these compounds. The values of the onset temperature of volatilization recorded from the DSC traces correlated well with those recorded from their corresponding TG and DTG traces. Meanwhile, the DSC traces recorded in oxygen atmosphere (Fig. 2) exhibited yet again a sharp endothermic transition attributed to the fusion of these compounds. This was followed by another endothermic transition which is attributed to partial volatilization of the melts of these compounds and then a sharp exothermic effect related to oxidative degradation of these compounds.

The TG and DTG traces for compounds **I–VII** recorded between room temperature and 600°C in nitrogen gas are displayed in Figs. 3 and 4,

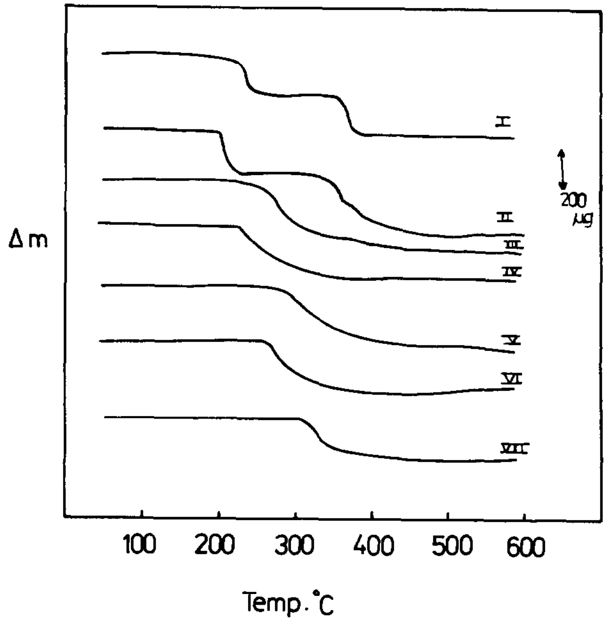


Fig. 3. TG curves of compounds **I–VII** in nitrogen gas.

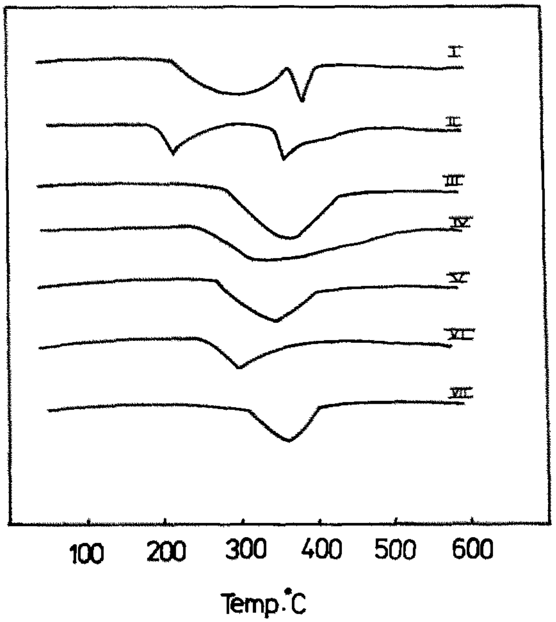


Fig. 4. DTG curves of compounds I–VII in nitrogen gas.

respectively. The degradation of these compounds proceeded with a well-defined single transition except for the fluoro and chloro derivatives where another transition is involved and is attributed to dehalogenation of these compounds prior to the major degradation step which involves total decomposition and volatilization of these compounds with no residual matters remaining. The initial (T_i), maximum (T_m) and final (T_f) temperatures of transition recorded from the DTG trace are displayed in Table 2. From the results obtained it can be concluded that the order of stability of these compounds is as follows: amide derivative > keto derivatives > carboxyl derivatives > halogeno keto derivatives.

TABLE 2

The temperatures of transition of the compounds (in °C) recorded from DTG curve in N_2 atmosphere

Compound	T_i	T_m	T_f	Compound	T_i	T_m	T_f
I	225	310	350	**IV**	225	315	500
	355	380	400	**V**	275	335	400
II	200	225	260	**VI**	260	300	375
	340	350	450	**VII**	325	365	400
III	275	375	425				

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