

THERMAL ANALYSIS AND KINETIC STUDY OF DECOMPOSITION PROCESSES OF SOME PESTICIDES

*F. Rodante, G. Marrosu and G. Catalani**

DEPARTMENT OF CHEMICAL ENGINEERING, RAW MATERIALS AND METALLURGY,
UNIVERSITY OF ROME, VIA DEL CASTRO LAURENZIANO 7, 0061 ROMA, ITALY
*ISTITUTO REGINA ELENA, VIALE REGINA ELENA 293, ROMA, ITALY

The thermal analysis of some pesticides using simultaneous TG-DSC measurements and kinetic calculations by the dynamic TG technique have been carried out.

With this technique it was attempted to group compounds with similar structures according to the shape and number of peaks of their thermoanalytical curves and to characterize their features by means of thermodynamic and kinetic quantities.

Small variations in the structure of the components of a class make larger variations in the thermodynamic and kinetic values being in close agreement with the observed differences in their biological behaviour.

Keywords: kinetics, pesticides, thermodynamics

Introduction

The pesticides have been the object of numerous studies, based on various techniques. As these compounds are poorly soluble in water, they are usually present in solid phase in the soil. Thus the behaviour of pesticides in the solid phase gives very interesting information on their influence on the environment. This depends, in turn, on the soil features and on a number of factors such as wind, sunlight, rain and temperature [1-3].

The last parameter affects the chemical degradation reactions of pesticides [4, 5] and thermal analysis can give important information on the thermal behaviour.

Herbicides and insecticides are two classes of pesticides [6] which can influence the environment.

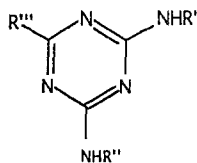
The most important compounds of the former class are represented by the 1-3-5 triazine derivatives [7-10]. A large number of compounds based on this ring system have been synthesized and tested. Among them, the highly active triazines

are characterized by having two substituted amino groups, with the third position usually being occupied by chloro, alkoxy and alkylthiogroup.

Within the active series, small changes in the substitution pattern produce important differences in the biological activity.

The compounds of this class used in this work were 2-chloro-4, 6-bis (isopropylamino)-s-triazine (Propazine), 2, 4-bis-(isopropylamino) 6-methylthio-s-triazine (Prometryn), 2, 4 bis-(isopropylamino)-6-methoxy-s-triazine (Prometon), 2-chloro-4, 6-bis-(ethylamino)-s-triazine (simazine) and 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine).

These compounds are shown in Table 1.



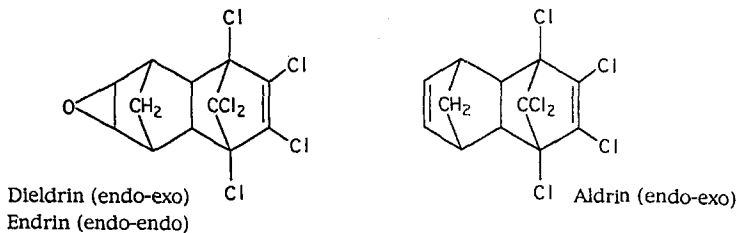
Scheme 1 1-3-5 triazine derivatives

Table 1 Structures of herbicidal 1, 3, 5-triazines

Compounds	R'	R''	R'''
Propazine	Pr ⁱ	Pr ⁱ	Cl
Prometryn	Pr ⁱ	Pr ^j	SCH ₃
Prometon	Pr ⁱ		OCH ₃
Simazine	Et	Et	Cl
Atrazine	Pr ⁱ	Et	Cl

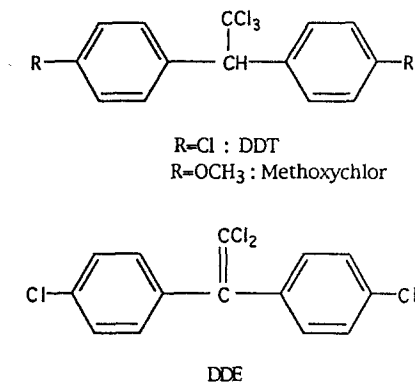
For the insecticides two different groups are considered: tricyclopentadiene and diphenylethane derivatives.

The molecules of the first group, 1, 2, 3, 4, 10, 10-hexachloro-1, 4, 4a, 5, 8, 8a-hexahydro-endo-exo-1,4:5, 8-demethanonaphthalene (Aldrin), 1, 2, 3, 4, 10, 10-hexachloro-6, 7-epoxy-1,4, 4a, 5, 6, 7, 8, 8a octahydro-endo-exo-1, 4: 5, 8-dimethanonaphthalene (Dieldrin) and 1, 2, 3, 4, 10, 10-hexachloro-6, 7, epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-endo-endo-1, 4: 5, 8-dimethanonaphthalene (Endrin) show a structure with six atoms of chlorine.



Scheme 2

The second group of insecticides is formed by 1, 1, 1-Trichloro-2, 2bis-(p-chlorophenyl)ethane (DDT), 1, 1,-di-chloro-2, 2bis-(p-chlorophenyl) ethylene (DDE) and 1, 1, 1-trichloro-2, 2bis-(p-methoxyphenyl) ethane (Methoxychlor) (Scheme 3).



Scheme 3

This work aims at stressing how the thermal behaviour of the components of the two classes sometimes is indicative of different structural conformations. Indeed often even minimal variations in similar structures (substituents groups, single-double bonds, stereoisomers) determine rather different thermal behaviour. It is well known that thermal analysis of solid phases provides physical measurements of thermal decomposition process for organic compounds but gives no chemical information in the process studied. However, this technique can supply useful information on the characterization of some compounds with similar structures. In this manner, it was possible [11] to group some α -amino acids by the shape of their thermoanalytical curves and related thermodynamic quantities.

Experimental and procedure

The experimental measurements were carried out on a Stanton-Redcroft 625 simultaneous TG-DSC connected to an Olivetti 250 computer. Instrument calibration was performed with standard indium and tin samples of known fusion temperatures and enthalpies of fusion. For decomposition studies under dynamic conditions, the TG-DSC apparatus was set up as follows.

Samples (2–3 mg) were weighed in aluminium pans placed in a nitrogen-filled dry-box. In order to avoid oxidative decomposition of the samples, the TG-DSC system was flushed with nitrogen gas both below the open pan (at flow rate of 50

during the thermal decomposition experiment were continuously removed. The heating rate was always $10 \text{ deg}\cdot\text{min}^{-1}$, and at least two runs were made for each compound. All the thermodynamic quantities were calculated using the Stanton-Redcroft acquisition system Trace, version 4. A dynamic (non-isothermal) TG technique was used in the kinetic study of the decomposition reaction.

The compounds (Polyscience) were used without purification as their purity (99%), is larger than that needed for the application of DSC [12–14]. The purity of all compounds in Refs [12–14] is also 99%.

Thermal and kinetic analyses were used to characterize the various compounds.

Thermal analysis includes the onset temperature of decomposition, the weight percent loss and the enthalpy values of the various processes (melting, crystallization, polymorphic changes, decomposition, chemical reactions) occurring as the temperature increases.

Kinetic analysis includes the kinetic energy of activation E_a related to the decomposition process, the half-life and the percent conversion times both at fixed temperatures.

Results and discussion

Trends of thermal behaviour in the compounds examined are shown in Figs 1–11.

The values of the thermodynamic and kinetic quantities related to the TG and DSC measurements are reported in Tables 2–7.

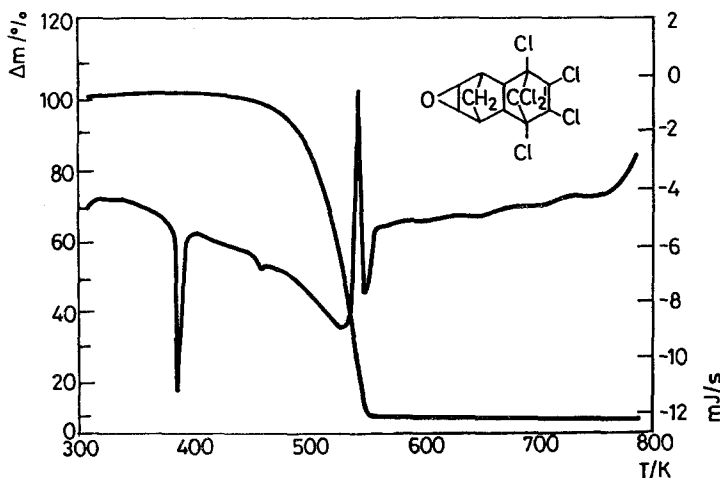


Fig. 1 DSC and TG curves of Endrin

Table 2 Thermodynamic parameters for thermal degradation, fusion and transition processes of some tricyclopentadiene derivatives from TG-DSC measurements

Compounds	TG			DSC		
	Stages	Temp. onset / K	W/ %	Temp. onset / K	$\Delta H /$ $J \cdot g^{-1}$	Peak / K
Endrin	I	501.2	90.4	383.4	41.0	386.4
	II			533.6	-53.6	539.6
Dieldrin	I	494.0	93.2	391.6	37.2	400.8
	II			443.2	278.2	525.2
Aldrin	I	468.4	92.6	336.6	49.4	340.6
	II			376.2	2.9	381.2
	III			385.8	286.6	495.8

Table 3 Thermodynamic parameters for thermal degradation, fusion and transition processes of some diphenylethane derivatives from TG-DSC measurements

Compounds	TG			DSC		
	Stages	Temp. onset / K	W/ %	Temp. onset / K	$\Delta H /$ $J \cdot g^{-1}$	Peak / K
DDT	I	496.2	95.5	384.8	86.2	386.2
	II			493.2	25.5	495.2
	III			500.2	1.7	505.5
	IV			510.2	118.0	533.2
DDE	I	501.8	100.0	343.6	4.2	347.2
	II			361.6	69.9	364.2
	III			443.2	424.7	533.2
Methoxychlor	I	451.4	50.7	359.2	69.5	362.6

Endrin and Dieldrin are stereoisomers and have one atom of oxygen that is lacking in the third compound. In spite of the equal stoichiometric composition, the thermal stability and the kinetic parameters of decomposition processes of Endrin and Dieldrin are influenced by the spatial position of the atoms.

A fusion process or a crystalline phase transition (onset temperature of DSC curve at 383.4 K) and exotherm decomposition process (onset temperature at 553.6 K), probably due to the interaction of two endo groups with release of hydrochloric acid occur in the Endrin thermal behaviour.

The isomer Dieldrin shows a transition phase (onset temperature at 391.6 K) between two crystalline forms (in agreement with the values of the literature [12-14]) but the fusion process is absent. Aldrin shows a phase transition between two crystalline forms (onset temperature at 366.6 K) and a fusion of the

Table 4 Thermodynamic parameters for thermal degradation, fusion and transition processes of some 1, 3, 5 substituted triazines from TG-DSC measurements

Compounds	TG			DSC		
	Stages	Temp. onset / K	W/ %	Temp. onset / K	ΔH / $J \cdot g^{-1}$	Peak / K
Propazine	I	471.2	92.1	493.2	613.0	496.2
Prometryn	I	475.2	93.8	394.2	105.4	397.2
	II			475.2	585.8	501.2
Prometon	I	464.4	90.4	367.4	118.8	372.2
	II			408.4	546.4	491.8
Simazine	I	481.6	94.2	503.0	764.0	507.6
Atrazine	I	471.2	89.0	452.2	143.9	454.2
	II			467.6	256.1	497.2

Table 5 Kinetic parameters of thermal degradation of some tricyclopentadiene derivatives

Compounds	T / K	E_a / $kJ \cdot mol^{-1}$	$\ln A$	B / min	C / min
Endrin	323.2–564.2	64.0	13.3	60	23
Dieldrin	433.2–546.2	62.3	13.2	41	17
Aldrin	383.2–509.2	56.1	12.6	13.5	7

B: Half-life at 433 K

C: 90% of conversion at 493 K

Table 6 Kinetic parameters of thermal degradation of some diphenylethane derivatives

Compounds	T / K	E_a / $kJ \cdot mol^{-1}$	$\ln A$	B / min	C / min
DDT	427.2–542.2	69.0	14.8	24	3.8
DDE	438.6–540.6	66.5	14.0	25	4.5
Methoxychlor	434.4–557.8	36.4	6.9	11	7.4

B: Half-life at 453 K

C: 90% of conversion at 543 K

second form (onset temperature at 376.2 K) both in agreement with the values of the literature [12–14].

The scales of thermal stability referred to the onset temperature of decomposition, to the kinetic energy of activation values for the same process and to the

half-life and percentage conversions times show the same order Endrin > Dieldrin > Aldrin.

Table 7 Kinetic parameters of thermal degradation of some 1, 3, 5 substituted triazines

Compounds	T / K	E _a / kJ·mol ⁻¹	ln A	B / min	C / min
Propazine	435.2–515.2	101.7	23.9	38	4.2
Prometryn	421.8–515.2	69.0	15.7	16	5.5
Prometon	407.6–501.8	67.8	15.8	10	3.7
Simazine	444.2–515.2	114.6	26.5	33 ^e	1.9 ^f
Atrazine	403.2–523.2	83.7	18.8	9 ^e	1.6 ^f

B: Half-life at 443 K

C: 90% of conversion at 503 K

e: Half-life at 453 K

f: 90% of conversion at 523 K

The absence of the oxygen atom destabilizes Aldrin from both the thermodynamic and kinetic point of view (see onset temperatures of the decomposition, energies of activation and half-life times in Tables 2 and 5), so this compound quickly decomposes as the temperature reaches high values.

An attempt to explain the decomposition processes can be made by referring to the spectra of the compounds obtained by MS technique [15]. Although these spectra relate to the fragmentation ions of the reagents, some prediction concerning the thermal processes can be made with their help. Indeed, the peaks obtained

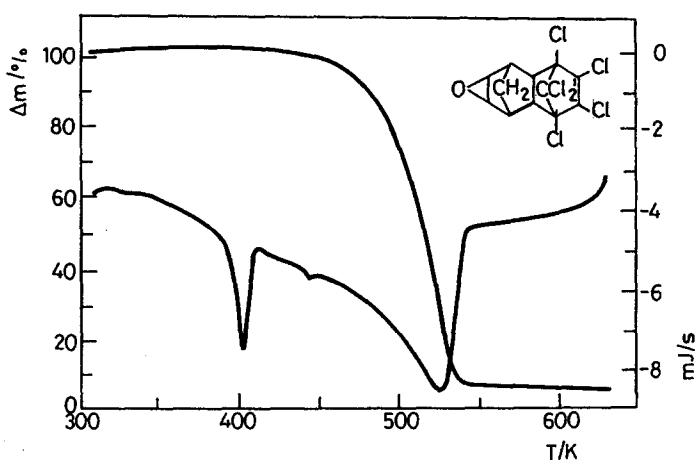


Fig. 2 DSC and TG curves of Dieldrin

with this technique are due to the fragmentation of the molecules by preferred cleavage of those bonds which led to energetically more favoured (i.e. more stable) positive ions. The base peaks of Endrin, Dieldrin and Aldrin are related respectively to ions C_4H_3O ($m/e = 67$), C_5H_3O ($m/e = 79$) and C_5H_6 ($m/e = 66$), so it can be noted how the first two compounds decompose giving stable oxygenated compounds while the abundance of HCl for Endrin (15.9%) confirms the hydrochloric acid loss for the first compound.

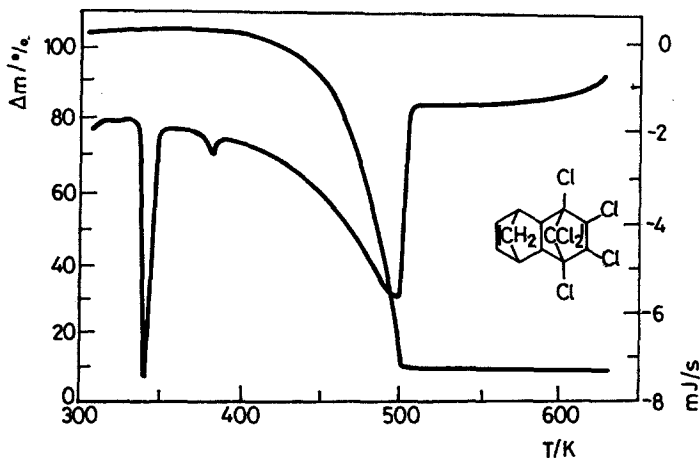


Fig. 3 DSC and TG curves of Aldrin

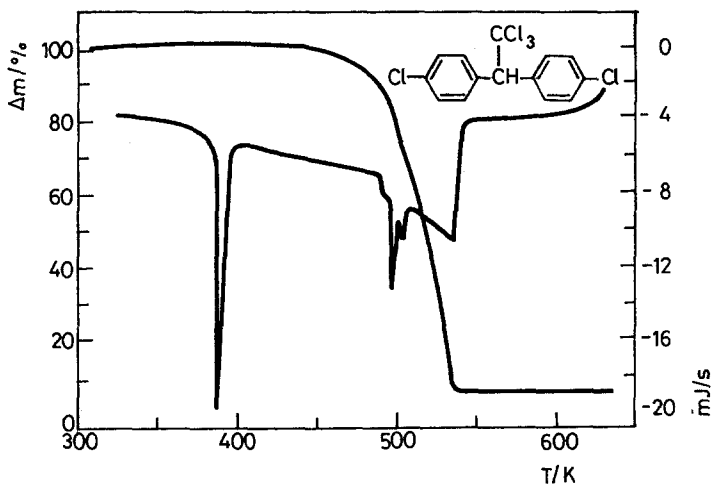


Fig. 4 DSC and TG curves of DDT

Another group of insecticides with similar structure is formed by DDT, DDE and Methoxychlor. DDT has a different substituent with respect to Methoxychlor and differs from DDE by virtue of a double bond.

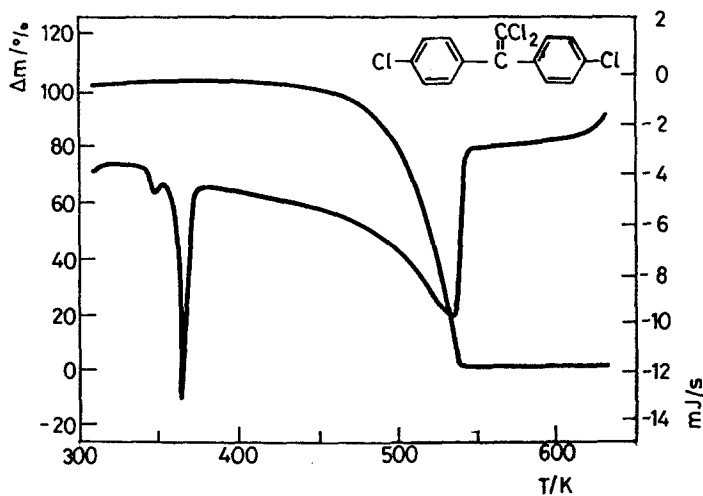


Fig. 5 DSC and TG curves of DDE

The fusion processes of the three compounds (onset temperatures of DSC curves at 384.8, 361 and 359.2 K) are in good agreement with those of the literature [12–14]. DDE shows a transition process between two crystalline forms (onset temperature at 343.6 K) and Methoxychlor decomposes without heat exchange.

The scale of thermal stability referring to the onset temperature follows the order DDE > DDT > Methoxychlor while the kinetic energy of activation scale is DDT > DDE > Methoxychlor.

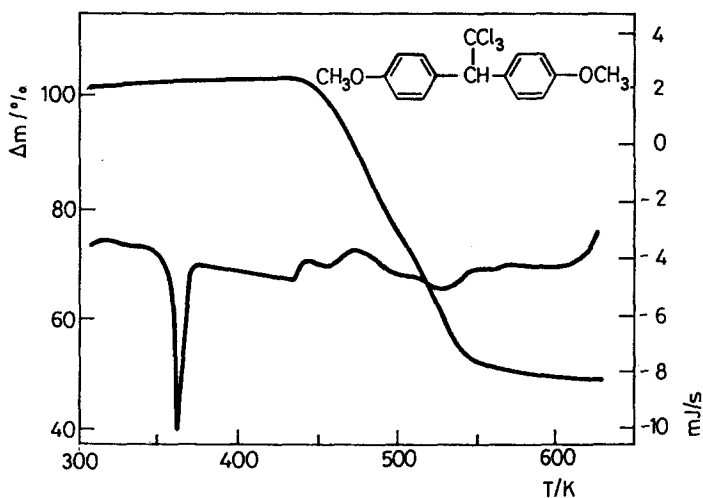


Fig. 6 DSC and TG curves of Methoxychlor

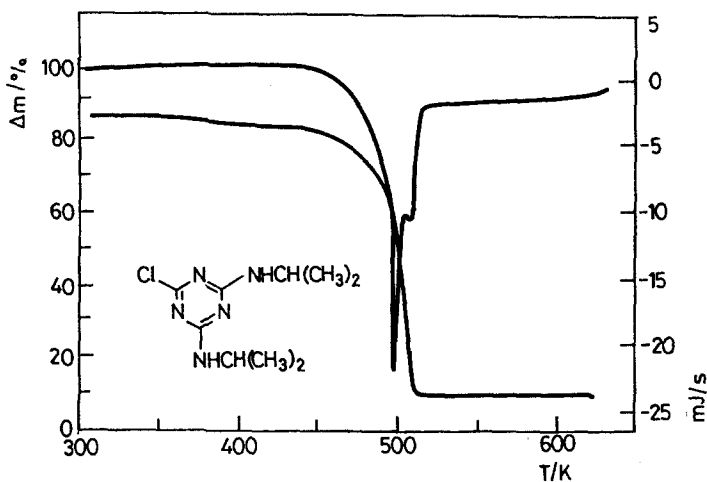


Fig. 7 DSC and TG curves of Propazine

By comparing the structures which differ only by a substituent or a double bond, the following considerations can be made. Thermodynamic and kinetic data (reported in Tables 3 and 6) show that the chlorine atom stabilizes the common structure more than the methoxy group and the structure of DDE is more stable than that of DDT in spite of the presence of a double bond. It can be hypothesized, in agreement with the complementary studies involving the identification of the reaction products [16], that DDT and Methoxychlor lose hydrochloric acid as can be observed from the respective first stage of decomposition. (9.70% onset temperature of decomposition at 496.2 K and 5.30% onset

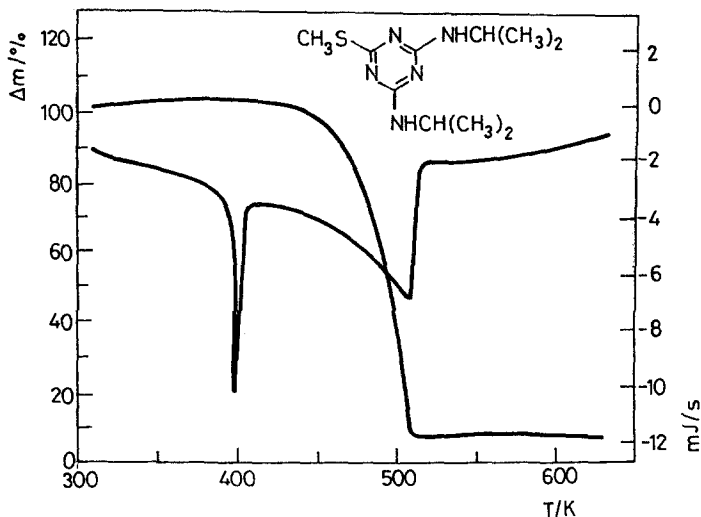


Fig. 8 DSC and TG curves of Prometryne

temperature at 451 K.) Thus DDT changes [16] into DDE in the solid phase and shows a similar thermal behaviour; Methoxychlor also becomes similar to DDE, but, as it bears two methoxy groups instead of the chlorine atoms, it shows a large difference in the thermal behaviour: these compounds volatilize and decompose with a weight loss of 50% while DDE starts to volatilize (onset temperature 501.8 K) without decomposition, [16] as can be observed from the weight loss (100%).

Let us consider now pesticides of 1-3-5 triazine derivatives class.

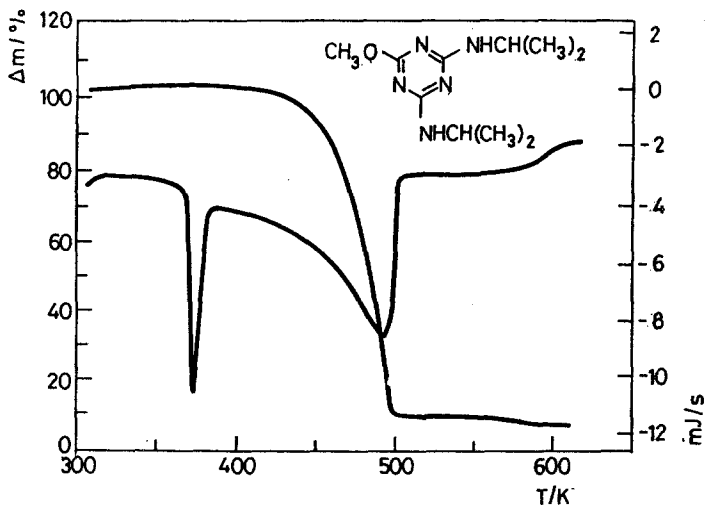


Fig. 9 DSC and TG curves of Prometon

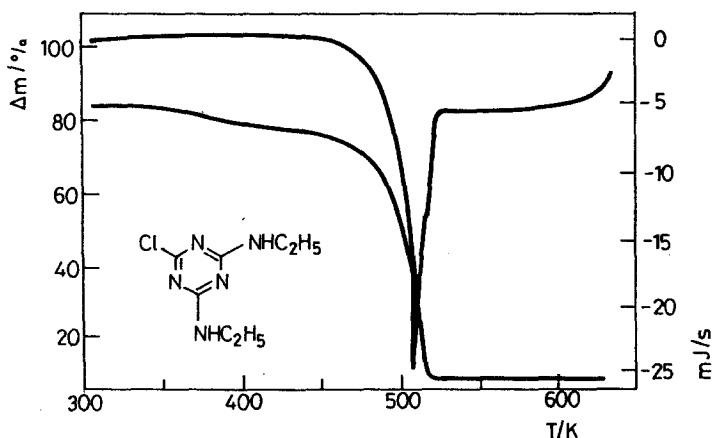


Fig. 10 DSC and TG curves of Simazine

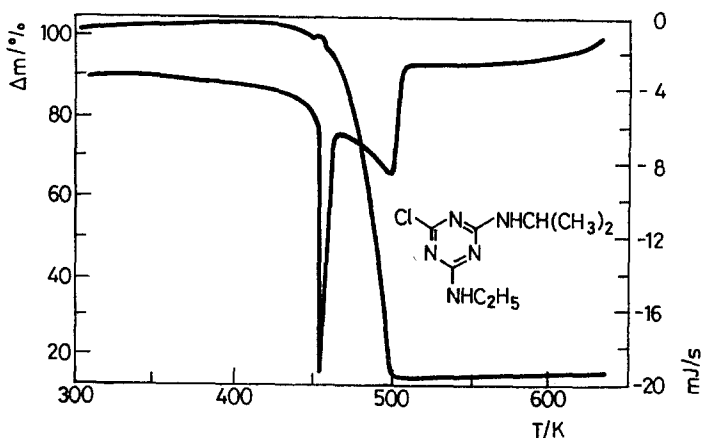


Fig. 11 DSC and TG curves of Atrazine

The thermal stabilities of the three compounds are in the following order: Prometryne > Propazine > Prometon and Prometryne and Prometon have enthalpy values of fusion processes ($105.4 \text{ J}\cdot\text{g}^{-1}$ and $111.8 \text{ J}\cdot\text{g}^{-1}$) close to those of the literature [12–14].

The activation energy values and the half-life times are in the order Propazine >> Prometryne > Prometon.

The chlorine atom stabilizes the first compound as can be seen from the absence of the fusion process and from the high kinetic values of Propazine degradation process with respect to those of Prometryne and Prometon (Table 7).

The S-CH₃ and O-CH₃ substituent make the behaviour of the other two compounds similar.

From the MS spectra [15], the following considerations can be made. The base peak of Prometryne is related to the ion of the undissociate molecule M ($m/e = 241$, abundance 99.9%).

Other fragments are M-15 ($m/e = 226$, abundance 61.9%), M-57 ($m/e = 187$, abundance 72%) and C₄H₂N₄ ($m/e = 106$, abundance 60.8%). For the side chains the ions C₃H₈N ($m/e = 58$, abundance 84.2%) and C₂H₅H ($m/e = 43$, abundance 57.8%) can be seen.

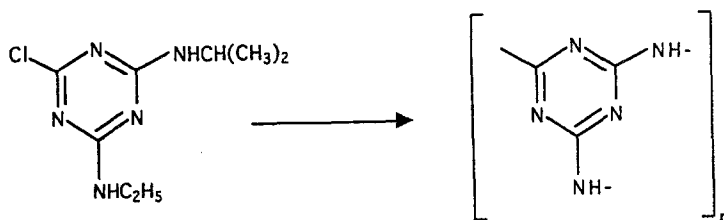
Prometon presents the fragments C₃H₈N ($m/e = 58$, abundance 99.9%), M-15 ($m/e = 210$, abundance 90.6%), M ($m/e = 225$, abundance 77.6%) and M-57 ($m/e = 168$, abundance 52.9%).

The MS spectrum of Propazine shows fragments C₃H₈N ($m/e = 58$, abundance 99.9%), M-15 ($m/e = 214$, abundance 83.6%), M ($m/e = 229$, abundance 52.9%) and C₂H₅N ($m/e = 43$, abundance 59.9%). From these data, it can be hypothesized that the three compounds lose their side chains as a primary process, while the aromatic nucleus remain, to a different extent undecomposed. The attitude of the decomposition process shows the same order of the thermal stability.

Finally Simazine and Atrazine have been considered.

These compounds, which are the most effective herbicides [10], differ only by the substituents of amino group (ethyl for simazine iso-propyl for atrazine). This makes a larger kinetic stability for the former ($E_a = 101.7 \text{ kJ}\cdot\text{mol}^{-1}$) with respect to the latter ($E_a = 83.7 \text{ kJ}\cdot\text{mol}^{-1}$). Indeed the decomposition of branched chains is easier than that of a straight one.

The simultaneous TA/MS investigations [17] for atrazine were performed in argon and air atmospheres. From these results, the degradation of Atrazine in argon atmosphere can lead to the cleavage of the side chains $\text{C}_3\text{H}_8\text{N}$ ($m/e = 58$, abundance 52%) and $\text{C}_2\text{H}_6\text{N}$ ($m/e = 44$, abundance 100%), while the degradation of Atrazine in air atmosphere can be seen as a polycondensation of the substance by the cleavage of the R-Cl bond with $R = \text{C}_2\text{H}_5$ or $R = \text{C}_3\text{H}_7$ (Scheme 4) followed by oxidation and coking of the polymer.



Scheme 4 Degradation of Atrazine in air

The MS spectra of Simazine [15] shows the following ion peaks $\text{C}_2\text{H}_6\text{N}$ ($m/e = 44$, abundance 99.9%), M ($m/e = 201$, abundance 77.7%), $\text{C}_2\text{H}_5\text{N}$ ($m/e = 43$, abundance 50.8%), $\text{M}-15$ ($m/e = 186$, abundance 50.6%) and $\text{M}-58$ ($m/e = 158$, abundance 25.4%) while the MS peaks of atrazine are $\text{C}_3\text{H}_8\text{N}$ ($m/e = 58$, abundance 99.9%), C_3H_7 and $\text{C}_2\text{H}_5\text{N}$ ($m/e = 43$, abundance 66.6%), C_3H_8 and $\text{C}_2\text{H}_6\text{N}$ ($m/e = 44$, abundance 55.5%), $\text{M}-15$ ($m/e = 200$, abundance 33.3%) and M ($m/e = 215$, abundance 19.4%).

These spectra confirm that the branched chain of Atrazine make easier thermal decomposition as previously seen.

Conclusion

In conclusion, the components of the two class of pesticides also in the cases of similar but not identical structures show different thermal behaviour (with the exception of the compounds bearing S- CH_3 and O- CH_3 substituents) contrary to what occurs for some standard α -amino acids [11]. Therefore, the TG-DSC curves represent a rapid tool enabling a first evidence for the presence of these compounds.

Since thermal analysis only supplies reliable physical quantities related to the decomposition process, the knowledge of the composition of the gas released is very important. Therefore in our laboratory a study of several pesticides by means of simultaneous thermal analysis /mass spectrometry is in progress.

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Zusammenfassung — Mittels simultanen TG-DSC-Messungen und kinetischen Berechnungen bei der DTG-Technik wurde eine thermische Analyse einiger Pestizide durchgeführt.

Mit dieser Methode wurde versucht, Verbindungen mit ähnlichen Strukturen anhand der Form und Anzahl von Peaks ihrer thermoanalytischen Kurven zu gruppieren und ihre Eigenschaften mittels thermodynamischen und kinetischen Mengen zu charakterisieren.

Geringe Änderungen in der Struktur der Komponenten einer Klasse verursachen größere Veränderungen der thermodynamischen und kinetischen Größen, was in enger Übereinstimmung mit den beobachteten Unterschieden ihrer biologischen Aktivität steht.