

THERMAL ANALYSIS AND KINETIC STUDY OF DECOMPOSITION PROCESSES OF SOME COMMERCIAL PESTICIDES

I. Triazine derivatives

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Abstract

The thermal behaviour of some commercial pesticides was studied by means of simultaneous TG–DSC measurements. Kinetic parameters relating to liquid–gas-phase transition processes were determined via a dynamic TG technique. Gas chromatography-mass spectrometry were used to make measurements on the gaseous products.

The liquid–gas-phase transition processes of these compounds seem to be influenced by the substituent groups rather than by the side-chains.

A chlorine substituent destabilizes some compounds, bringing closer together the temperatures of melting and liquid–gas-phase transition processes.

Keywords: enthalpy, GC–MS measurements, kinetics, simultaneous TG–DSC, thermal stability, 1,3,5 triazine derivatives

Introduction

Pesticides have been subjected to numerous studies, involving various techniques. As these compounds are poorly soluble in water, they are usually present in the solid phase in the soil. Due to their low reactivity, they can remain unchanged in the environment for a long time, causing gradual pollution [1–10]. The important question is the natural degradation of these compounds. One factor influencing this process is the temperature [11–15].

Hence, a knowledge of the thermal behaviour of pesticides may provide information on the fates of these derivatives in the environment.

Further, large amounts of herbicides, insecticides and fungicides are stored and transported for agriculture. In the event of accidents, and especially fires, it is of great importance to know the thermal stabilities of these compounds.

Thermoanalytical methods have been utilized in recent investigations of pesticides [16–22]. Our laboratory too has carried out the thermal analysis of pesticides, using simultaneous TG–DSC measurements, and kinetic calculations of their liquid–gas-phase transition processes by a dynamic TG technique [23].

Our goal is a systematic study of commercial pesticides in order to acquire more information on the thermal processes which occur during heating of the pure compounds. The present work relates to the thermal behaviour of some 1,3,5-triazine derivatives [24–27], other compounds (1,3,5-triazine-2,4-dione derivatives) with structures similar to those of the triazines, and DIURON, a chloroorganic pesticide.

This was performed by studying the influence of side-chains and substituent groups on the thermal stabilities, enthalpies of melting and kinetic activation energies of liquid–gas-phase transition processes. GC–MS studies were also carried out on the compounds.

Experimental procedure

The experimental measurements were carried out on a Stanton-Redcroft 625 simultaneous TG–DSC instrument connected to an Olivetti 250 computer.

As regards the calibration of temperature, the use of several standards allows the determination of a linear temperature function. This function is used to calculate the correction to be added to the sample temperature.

As concerns DSC calibration, after production of a baseline curve with sapphire, subsequent experiments are used to convert the raw data counts to rates of heat transfer. Calibration experiments on the fusion of standard materials (lead, tin, zinc and benzoic acid) are used to 'fine tune' the data collected.

For decomposition studies under dynamic conditions, the TG–DSC apparatus was set up as follows: samples (6–8 mg) were weighed in aluminium pans. To avoid oxidative decomposition of the samples, the TG–DSC system was flushed with nitrogen gas both below (at a flow rate of 50 ml min⁻¹) and above (at a flow rate of 30 ml min⁻¹) the open pan. In this way, the gases evolved during the thermal decomposition experiments were removed continuously. The heating rate was always 10 K min⁻¹ and at least two runs were made for each compound.

All the thermodynamic quantities were calculated by using the Stanton-Redcroft Acquisition System Trace, version 4.

Thermal analysis included the extrapolated temperatures of decomposition onset, the percentage mass losses and the enthalpy values of the various processes (melting, crystallization, polymorphic changes, decomposition, and chemical reactions) occurring as the temperature was raised.

Simultaneous TG–DSC is a very useful tool for investigating organic compounds, as it combines, in a single run, mass loss and heat change processes, so that transformations that occur even with small mass changes (chemical reac-

tions, decomposition, vaporization and oxidation processes) can be distinguished from those occurring without mass change (melting, crystallization and polymorphic changes). Thus, consistent TG and DSC values can be obtained even for small samples.

During heating, all compounds can undergo a solid-liquid-phase transition (without molecular decomposition) and a liquid-gas-phase transition (with possible molecular decomposition).

The thermal stabilities of pesticides can be tested by means of GC-MS measurements.

The gaseous products of thermal processes were adsorbed into carbon trap adsorbent tubes (Supelco), desorbed into an organic liquid (CS₂) and injected into a Hewlett-Packard 5890 GC coupled to a Hewlett-Packard MS 5971 Selective Detector.

The capillary column used was made of PTE, 30 m long×0.25 mm id, with a stationary phase film thickness of 0.25 μm (Supelco).

The GC oven was held at 343.15 K for 2 min, and then ramped at 10 K min⁻¹ to 553.15 K.

The carrier gas (helium) flow rate was 0.8 ml min⁻¹.

MS determination was performed with the SCAN technique, using electron impact ionization at 70 eV, and the transfer line was maintained at 553.15 K.

Finally, a kinetic TG-dynamic study of the liquid-gas-phase transition processes for the compounds was carried out by the method of McCarty & Green [28]. The kinetic analysis included the kinetic energy of activation E_a relating to the liquid-gas-phase transition processes, the frequency factor $\ln A$, and the reaction order. This implementation of the McCarty & Green method is restricted to first-order reactions.

The initial equation for this technique is Eq. (1):

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{-E_a/RT} (1-\alpha) \quad (1)$$

where α percentage conversion (reaction progress), A pre-exponential factor (min⁻¹), β heating rate (K min⁻¹), E_a activation energy (kJ mol⁻¹), R gas constant (8.316 kJ mol⁻¹), and T temperature (K).

Rearranging Eq. (1) and integrating yields

$$-\ln(1-\alpha) = \left(\frac{AE_a}{\beta R} \right) p(x) \quad (2)$$

where x substituted variable for the quantity E/RT , and $p(x)$ represents a series expansion approximating the resulting integral:

$$p(x) \approx \left(\frac{x+3}{x(x+1)(x+4)e^x} \right) \quad (3)$$

On taking natural logarithms of both sides of Eq. (2), we obtain

$$\ln(-\ln(1-\alpha)) = \ln\left(\frac{AE_s}{\beta R}\right) + \ln p(x) \quad (4)$$

Assigning $F(\alpha) = \ln(-\ln(1-\alpha))$ and then differentiating with respect to x :

$$\frac{dF(\alpha)}{dx} = \frac{d\ln(p(x))}{dx} \quad (5)$$

Substituting for dx where $\frac{dx}{d(1/T)} = ER$ yields

$$E = R \frac{dF(\alpha)/dT^{-1}}{d\ln(p(x))/dx} \quad (6)$$

The numerator in Eq. (6) is the slope of a plot of $F(\alpha)$ vs. $1/T$. The data for the construction of this plot are taken from the TG curve. The denominator can be estimated from the series

$$\frac{d\ln(p(x))}{dx} = \frac{1}{x+3} - \frac{1}{x} - \frac{1}{x+1} - \frac{1}{x+4} - 1$$

Since the numerator is also a function of E_a , the software uses an initial guess of $125.56 \text{ kJ mol}^{-1}$ for the activation energy. A series of iterative calculations is performed to refine the value of E_a to within 0.42 J . Once E_a has been determined, the pre-exponential factor A is calculated via Eq. (2).

In this study, we considered mass losses consistently lower than 10% for the calculation of activation energy. Indeed, it was usually considered [14] that the initial portion of the TG curves can be fitted by a first-order reaction equation.

Table 1 Names and chemical specifications of some pesticides

Terbutylazine: 2,4-diamino-6-chloro-N-(1,1-dimethylethyl)-N'ethyl-1,3,5-triazine
Terbutryn: 2,4-diamino-N-(1,1-dimethylethyl)-N'-ethyl-6-methylthio-1,3,5-triazine
Cyanazine: 2-methyl-(4-chloro-6-ethylamino-1,3,5-triazin-2-yl-amino)-propionitrile
Ametryn: 2,4-diamino-N-ethyl-N'-(1-methylethyl)-6-methylthio-1,3,5-triazine
Simetryn: 2,4-diamino-N-N'-diethyl-6-methylthio-1,3,5-triazine
Dipropetryn: 2,4-diamino-6-ethylthio-N, N'-bis(1-methylethyl)-1,3,5-triazine
Trietazine: 2,4-diamino-6-chloro-N, N, N'-triethyl-1,3,5-triazine
Anilazine: 2-amino-4,6-dichloro-N-(2-chlorophenyl)-1,3,5-triazine
Metamitron: 4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Metribuzin: 4-amino-6-(1,1-dimethylethyl)-3-methylthio-1,2,4-triazin-5(4H)-one
Diuron: 3-(3,4-dichlorophenyl)-1,1-dimethylurea

The compounds (Polyscience) were used without purification; their purities (99%) were higher than that needed for the application of DSC [29–31]. The purities of the compounds were checked by HPLC measurements. Their common names and the chemical classifications are listed in Table 1.

Results and discussion

The trends in thermal behaviour of the examined compounds are given in Figs 1–11. The values of the thermodynamic and kinetic quantities relating to the TG and DSC measurements are reported in Tables 2 and 3.

Thermal stability and enthalpy

Terbutylazine (Fig. 1) was chosen as reference compound; its liquid–gas-phase transition follows a simple curve (extrapolated onset temperature 488.49 K with a mass loss of 98.08%). The compound melts at an extrapolated onset temperature of 451.30 K, with an enthalpy of 32.92 kJ mol⁻¹, the peak temperature being at 454.02 K (in good accordance with the literature [31]).

Terbutryn (Fig. 2) differs from Terbutylazine in the substituent group (SCH₃ instead of Cl).

This compound displays a mass loss of 6.55% at an extrapolated onset temperature of 347.30 K (with an enthalpy of 11.40 kJ mol⁻¹ at an extrapolated onset temperature of 337.23 K), followed by a fusion process ($\Delta H=21.16$ kJ mol⁻¹ with an extrapolated onset temperature of 377.87 K), in good accordance with the lit-

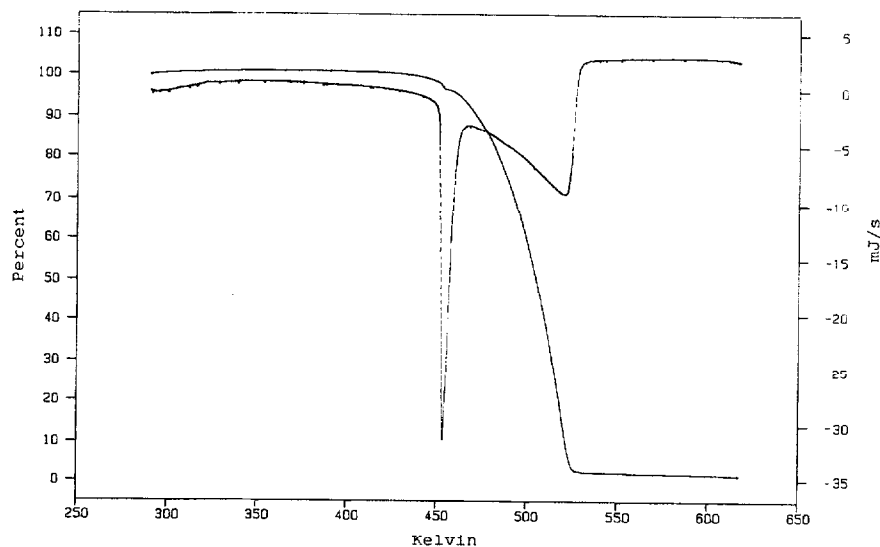


Fig. 1 DSC and TG curves of Terbutylazine

erature [31] ($21.43 \text{ kJ mol}^{-1}$ at 375.89 K) and a liquid–gas-phase transition process with a mass loss of 90.52% .

Cyanazine undergoes a fusion process (extrapolated onset temperature of 440.65 K , $\Delta H=30.66 \text{ kJ mol}^{-1}$, peak temperature 442.19 K), followed by five steps in the liquid–gas-phase transition process.

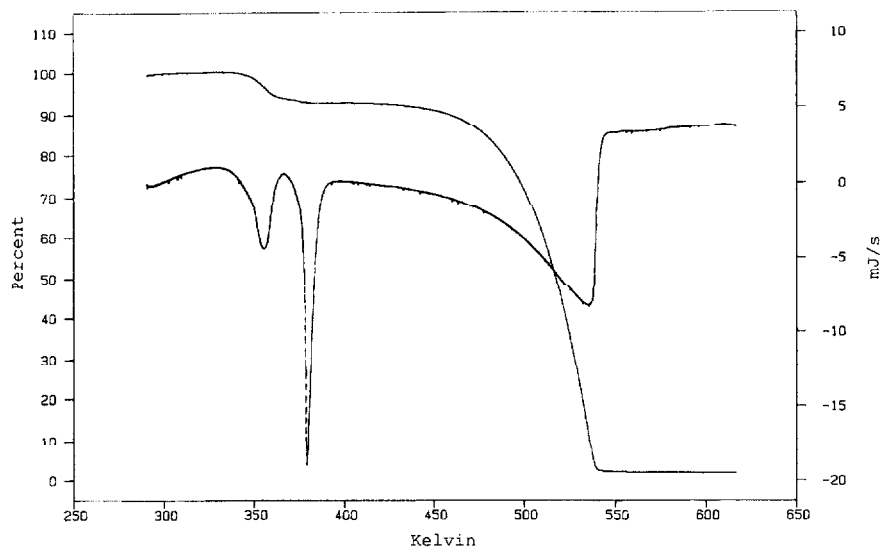


Fig. 2 DSC and TG curves of Terbutryn

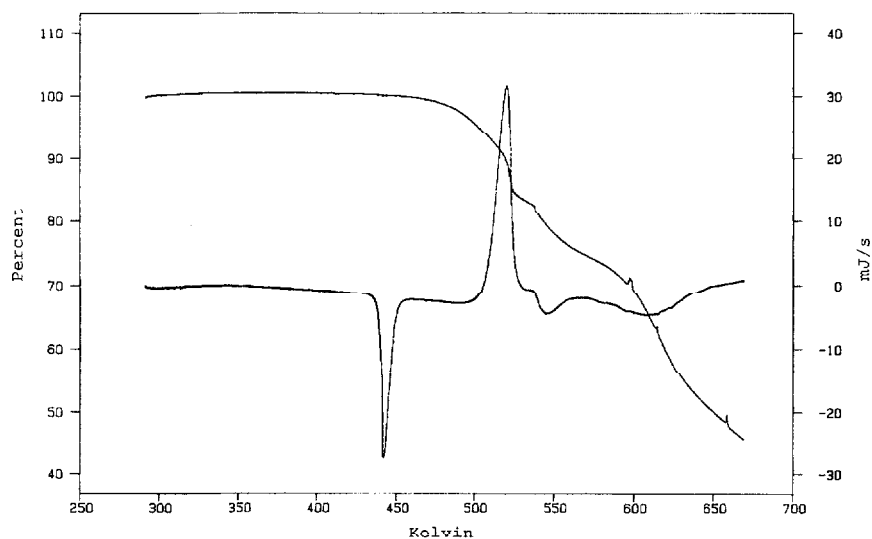


Fig. 3 DSC and TG curves of Cyanazine

The exotherm due to the second step is often characteristic of a thermal decomposition involving the formation of stable compounds [32]. At 673.15 K for Cyanazine, the mass loss is 52.30%, with a carbonaceous residue.

Ametryn and Simetryn exhibit very similar thermal behaviour. For the former, there is a fusion process (extrapolated onset temperature 361.80 K, $\Delta H=$

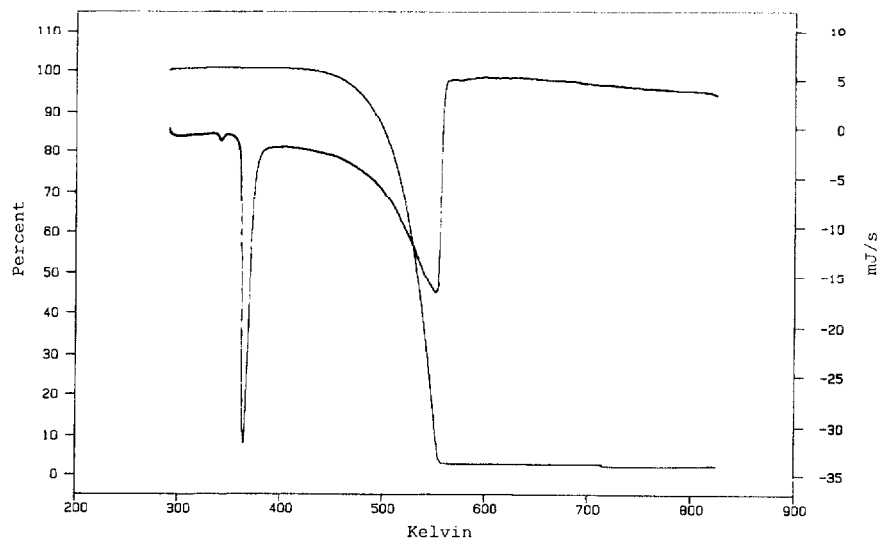


Fig. 4 DSC and TG curves of Ametryn

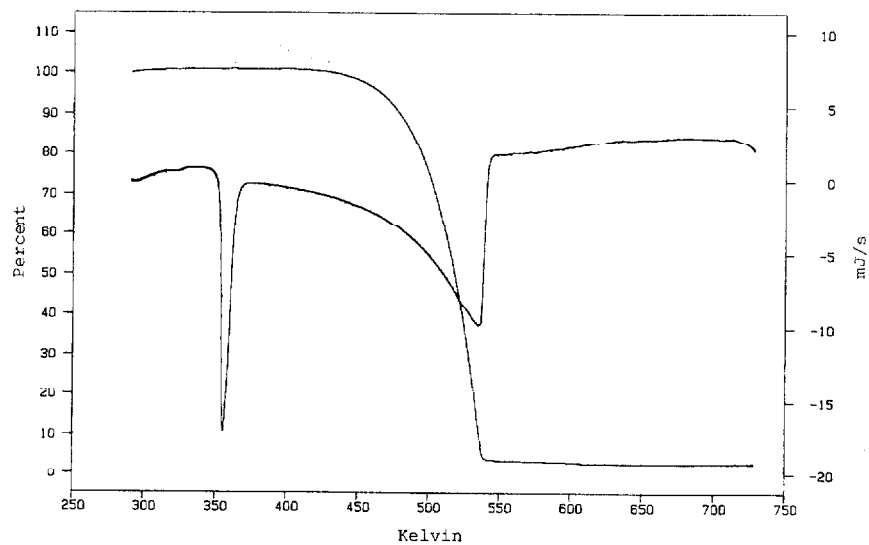


Fig. 5 DSC and TG curves of Simetryn

26.13 kJ mol⁻¹, peak temperature 364.37 K), followed by a liquid-gas-phase transition process (97.24% mass loss and extrapolated onset temperature 509.23 K). For the latter, the fusion process (extrapolated onset temperature 353.00 K, $\Delta H=24.11$ kJ mol⁻¹) is followed by a liquid-gas-phase transition process (96.16% mass loss, extrapolated onset temperature 497.34 K).

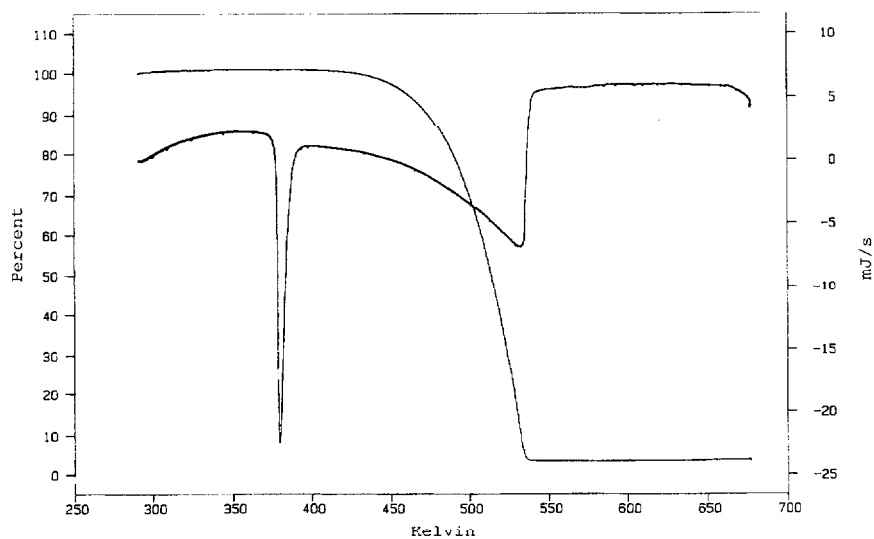


Fig. 6 DSC and TG curves of Dipropetryn

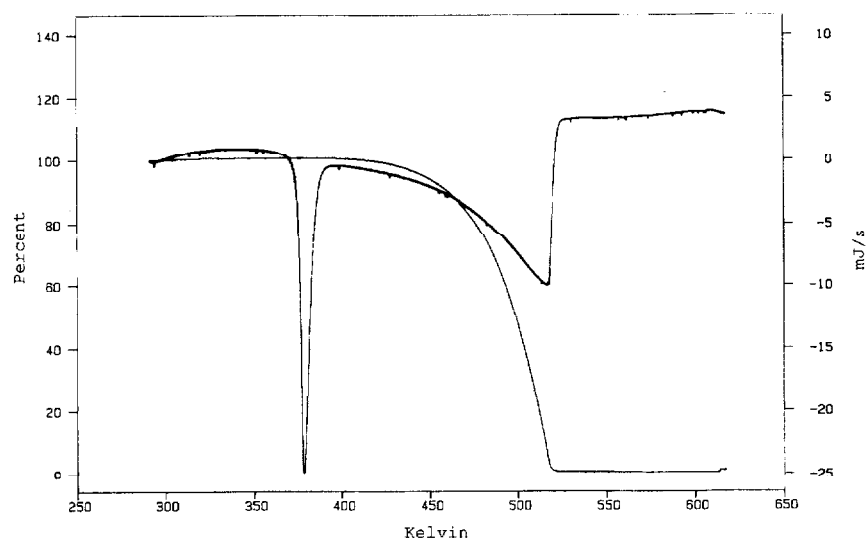


Fig. 7 DSC and TG curves of Trietazine

Dipropetryn undergoes a fusion process (extrapolated onset temperature 377.62 K, $\Delta H=30.80 \text{ kJ mol}^{-1}$, peak temperature 379.69 K), followed by a liquid-gas-phase transition process (97.24% mass loss, extrapolated onset temperature 495.69 K).

The fusion process of Trietazine (Fig. 7) (extrapolated onset temperature 375.70 K, $\Delta H=30.79 \text{ kJ mol}^{-1}$, peak temperature 378.00 K) is followed by a liq-

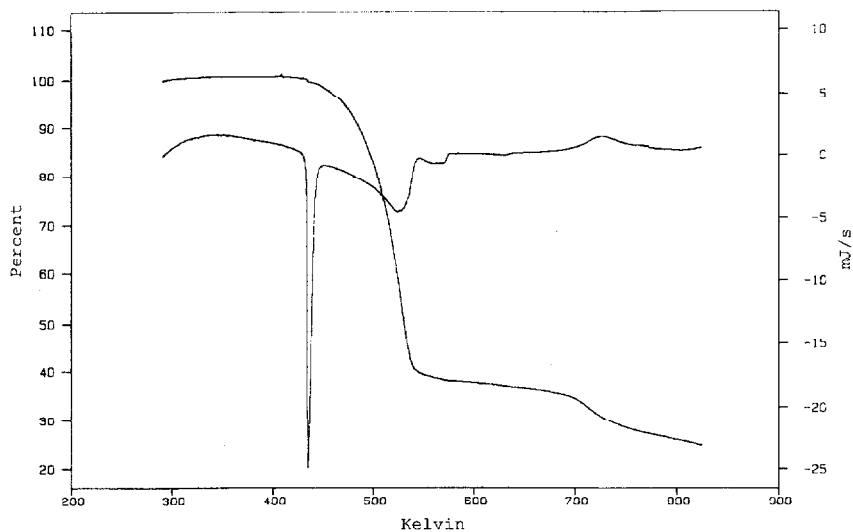


Fig. 8 DSC and TG curves of Anilazine

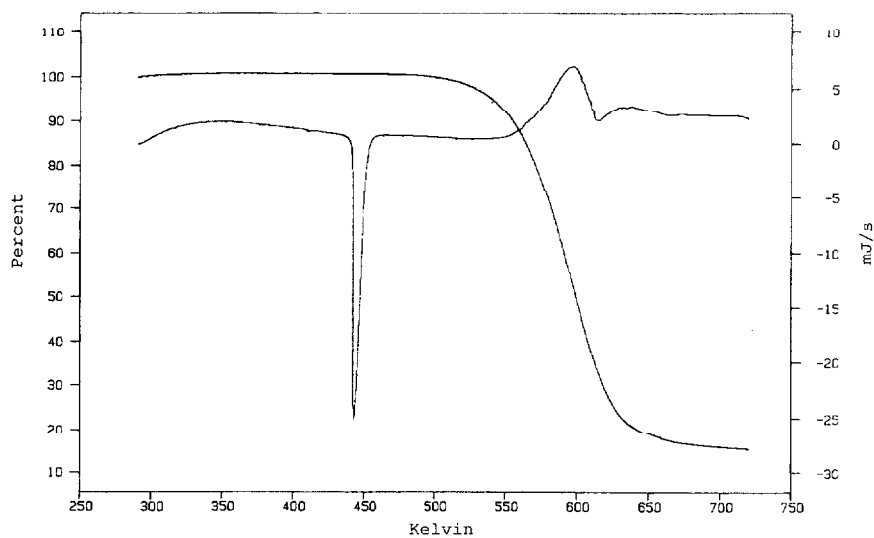


Fig. 9 DSC and TG curves of Metamitron

uid-gas-phase transition process (99.60% mass loss, extrapolated onset temperature 483.35 K).

The extrapolated onset temperatures of melting and of liquid-gas-phase transition processes for Metamitron and Metribuzin are on average higher than those for 1,3,5-triazine derivatives.

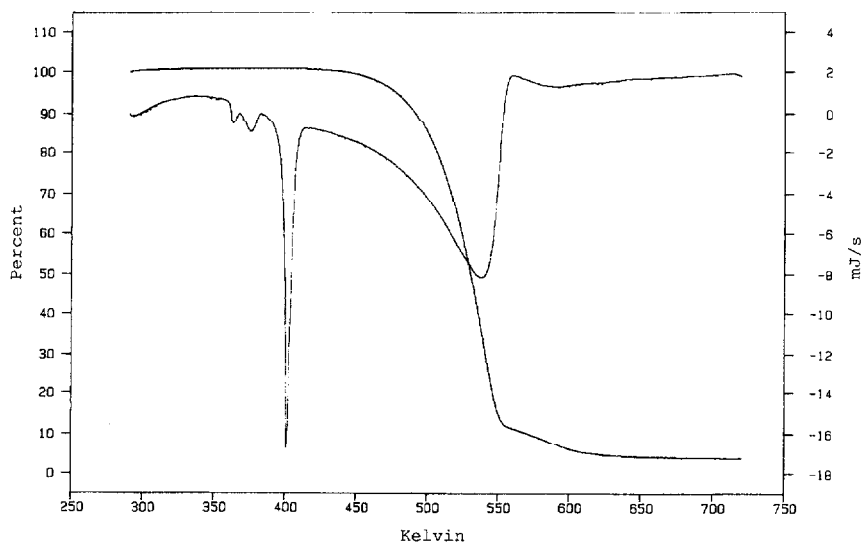


Fig. 10 DSC and TG curves of Metribuzin

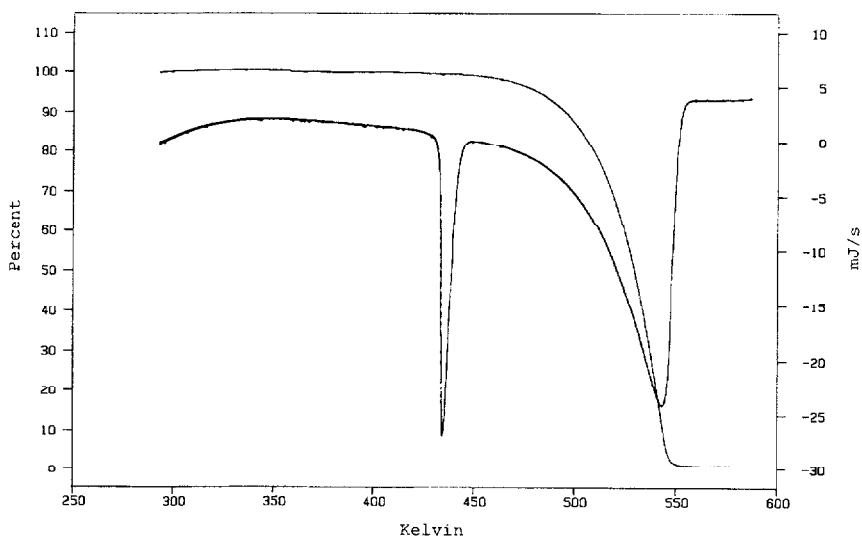


Fig. 11 DSC and TG curves of Diuron

Metribuzin and Metamitron have similar structures. Metribuzin melts at an extrapolated onset temperature of 398.07 K ($\Delta H=15.15 \text{ kJ mol}^{-1}$) and undergoes a liquid-gas-phase transition process at an extrapolated onset temperature of 506.87 K with a mass loss equal to 96.39%. The corresponding enthalpy value is endothermic ($\Delta H=90.53 \text{ kJ mol}^{-1}$).

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

Compounds	Stage	Extrap. onset temp./ K	Mass/%	Extrap. onset temp./ K	$\Delta H/ \text{kJ mol}^{-1}$	Peak/ K	ΔH overall/ kJ mol^{-1}
Terbutylazine	I	488.49	98.08	451.30	32.92	454.02	96.96
	II				64.04	521.26	
Terbutryn	I	347.30	6.55	337.23	11.40	355.45	152.61
	II	504.24	90.52	377.87	21.16	379.74	
	III			394.68	120.05	536.10	
Cyanazine	I	485.00	8.85	440.65	30.66	442.19	-33.50
	II		5.43	508.32	-64.15	520.22	
	III		1.78				
	IV		12.05				
	V		24.19				
Ametuyn	I	509.23	97.24	361.80	26.13	364.37	149.97
	II			439.04	123.84	550.84	
Symetryn	I	497.34	96.16	353.00	24.11	356.2	157.93
	II			450.00	133.82	535.85	
Dipropetryn	I	495.69	97.24	377.62	30.80	379.69	157.01
	II			446.00	126.21	532.00	
Trietazine	I	483.35	99.60	375.70	30.79	378.00	141.58
	II				110.79	513.00	
Anilazine	I	495.77	74.56	435.81	33.35	435.54	73.61
	II			482.91	40.26	516.72	
Metamitron	I	558.95	84.36	442.33	23.93	443.58	0.89
	II			564.18	-23.04	597.26	
Metribuzin	I	506.87	96.39	398.07	15.15	401.88	105.68
	II			464.00	90.53	538.00	
Diuron	I	516.59	98.77	433.08	30.89	434.49	221.99
	II			504.48	191.10	543.18	

Metamitron exhibits a melting process at an extrapolated onset temperature of 442.33 K, ($\Delta H=23.93 \text{ kJ mol}^{-1}$), followed by an exothermic liquid–gas–phase transition process (extrapolated onset temperature 558.95 K, mass loss 84.36%, $\Delta H=-23.04 \text{ kJ mol}^{-1}$).

Finally, diuron reveals a fusion process (extrapolated onset temperature 433.08 K, $\Delta H=30.89 \text{ kJ mol}^{-1}$, peak temperature 434.49 K) just below a liquid–gas–phase transition process (extrapolated onset temperature 516.59 K, mass loss 98.77%).

The values for the corresponding endothermic process are: extrapolated onset temperature 500.48 K, $\Delta H=191.10 \text{ kJ mol}^{-1}$ and peak temperature 543.18 K.

Let us consider the following similar structures. Terbutylazine and Cyanazine differ from each other only in the CN and CH_3 -groups in the side-chains (the Cl substituent is the same), while Terbutylazine and Terbutryn differ only in the substituent groups (Cl and SCH_3). In spite of the fact that these compounds have somewhat similar structures, their thermodynamic parameters (extrapolated onset temperatures of liquid–gas–phase transition and enthalpies of fusion) are different, so it can be hypothesized that different mechanisms of thermal processes apply.

Ametryn and Simetryn, which differ by a CH_2 group in the straight-chain and branched side-chains, exhibit thermal behaviour similar to that of Dipropetryn, which in turn differs from the first two in chain and substituent groups.

In contrast, Trietazine and Terbutylazine, which differ from each other only in the straight-chain and branched side-chains, do not display similar thermal behaviour for the fusion or liquid–gas–phase transition processes.

Table 3 Kinetic parameters of liquid–gas–phase transition processes of some pesticides from TG measurements, assuming a first-order reaction

Compounds	$E_a/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$
Terbutylazine	67.21	14.62
Terbutryn	67.95	14.31
Cyanazine	67.43	13.98
Ametryn	63.68	12.85
Simetryn	62.89	13.14
Dipropetryn	60.89	12.77
Trietazine	60.95	13.25
Anilazine	59.12	12.16
Metamitron	68.22	14.57
Metribuzin	65.12	13.30
Diuron	83.37	17.63

Anilazine has a different structure from those of all the Triazines considered so far, and its thermodynamic parameters are significantly different from those of the other compounds (Table 2).

A complete scale of thermal stability referring to the extrapolated onset temperatures of the liquid–gas-phase transition can be written as: Ametryn > Simetryn > Dipropetryn > Anilazine > Terbutylazine > Cyanazine > Trietazine > Terbutryn.

The enthalpy values for the melting process follow the sequence: Anilazine > Terbutylazine > Dipropetryn > Trietazine > Cyanazine > Ametryn > Simetryn > Terbutryn, while for the enthalpy values of the liquid–gas-phase transition process the sequence is: Simetryn > Dipropetryn > Ametryn > Terbutryn > Trietazine > Terbutylazine > Anilazine > Cyanazine.

If the enthalpy values relating to the different ranges of temperatures are added, the overall enthalpy, i.e. the heat that the compound exchanges with the external system at constant pressure up to complete or partial decomposition, can be deduced.

The overall heat sequence is: Simetryn > Dipropetryn > Terbutryn > Ametryn > Trietazine > Terbutylazine > Anilazine > Cyanazine.

From this experimental evidence, it may be seen that the liquid–gas transition prevails in the enthalpic behavior.

As regards the two 1,3,5-triazine-2,4-dione derivatives, the following sequence was observed for the thermal stability: Metamitron > Metribuzin. The enthalpy values of the melting process follow the order: Metamitron > Metribuzin, while for the liquid–gas transition process values, the order becomes: Metribuzin > Metamitron.

The sequence of the overall enthalpy (Metribuzin > Metamitron) indicates that the liquid–gas transition process prevails in the enthalpic thermal behaviour.

Diuron exhibits thermal stability and overall enthalpy values higher than those of the triazine derivatives.

Kinetics

Terbutryn, Terbutylazine and Cyanazine have higher activation energies (E_a) than those of the other 1,3,5-triazine derivatives, which show similar values.

Finally, for the other compounds the sequence of the activation energy of decomposition is Metamitron > Metribuzin.

The activation energies and thermodynamic parameters indicate that the structures of these two compounds are on average more stable than those of the 1,3,5-triazine derivatives.

GC–MS measurements

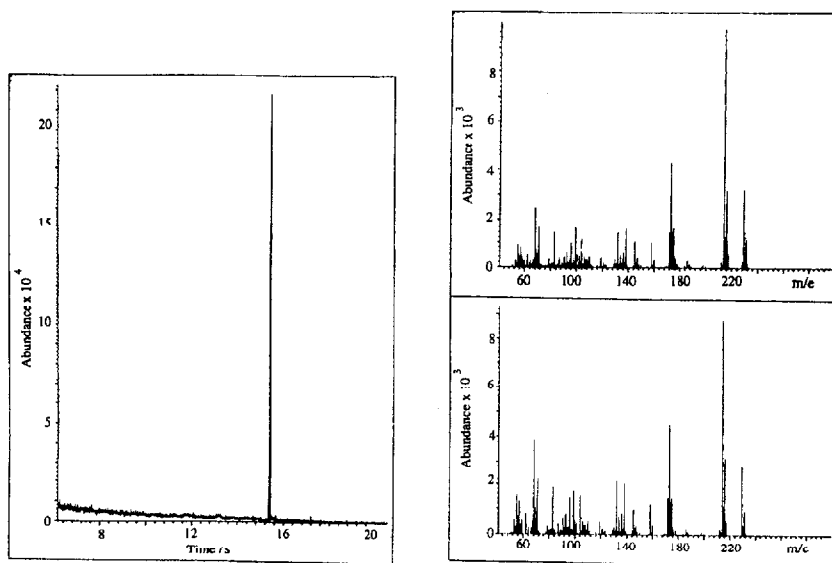
The total ion current chromatograms (TICs) and relative spectra of the gaseous products were recorded. The mass spectra throughout the scanning range were compared with those of the pure compounds reported in the literature; data on the match quality (utility) of the spectra are reported in Table 4.

Table 4 Match quality (utility) of spectra of gaseous products of some pesticides

Compounds	Utility	
	Spectra from 1st peak	Spectra from 2nd peak
Terbutylazine	98	
Terbutryn	78	
Cyanazine	49	83
Ametryn	99	
Simecryn	98	
Dipropetryn	99	
Trietazine	99	
Anilazine	99	
Metamitron	40	93
Metribuzin	97	
Diuron	96	83

From this experimental evidence, it can be concluded that Terbutylazine, Terbutryn, Symetryn, Ametryn, Dipropetryn, Trietazine, Anilazine and Metribuzin undergo liquid-gas-phase transition processes without decomposition.

For instance, the (TICs) and relative spectra for the gaseous products and pure Terbutylazine are reported in Fig. 12.

**Fig 12** TIC chromatogram and mass spectrum of Terbutylazine

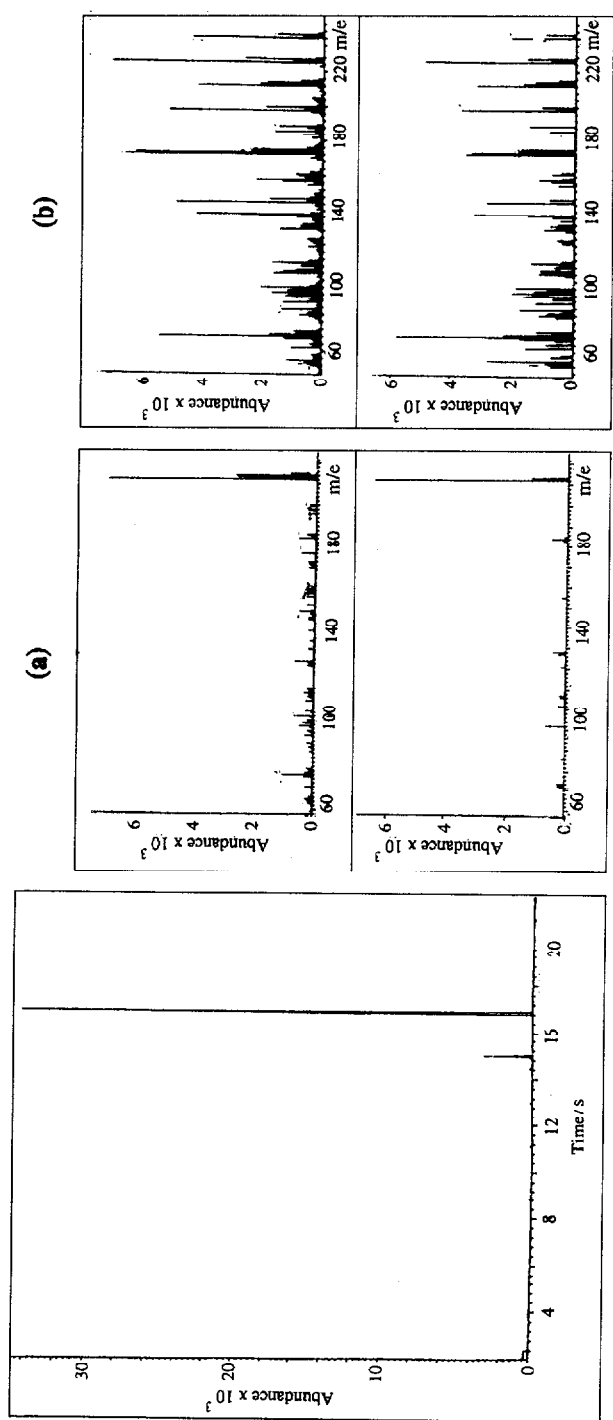


Fig. 13 TIC chromatogram and mass spectrum of Cyanazine

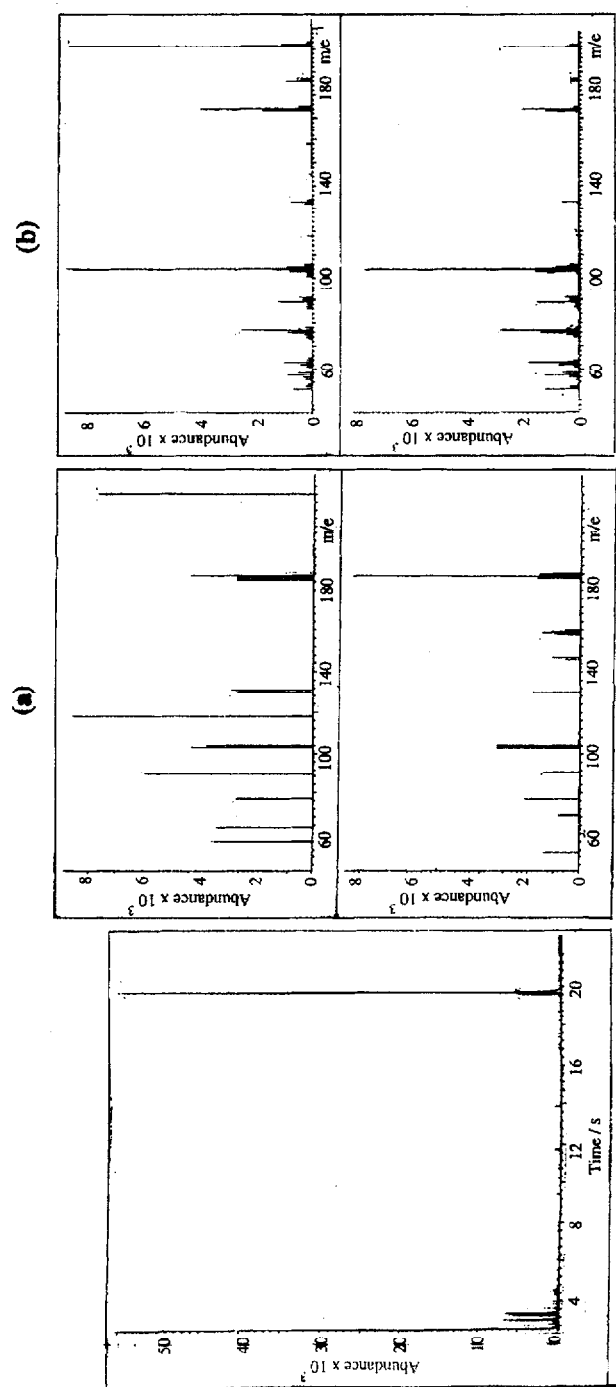


Fig 14 TIC chromatogram and mass spectrum of Metamitron

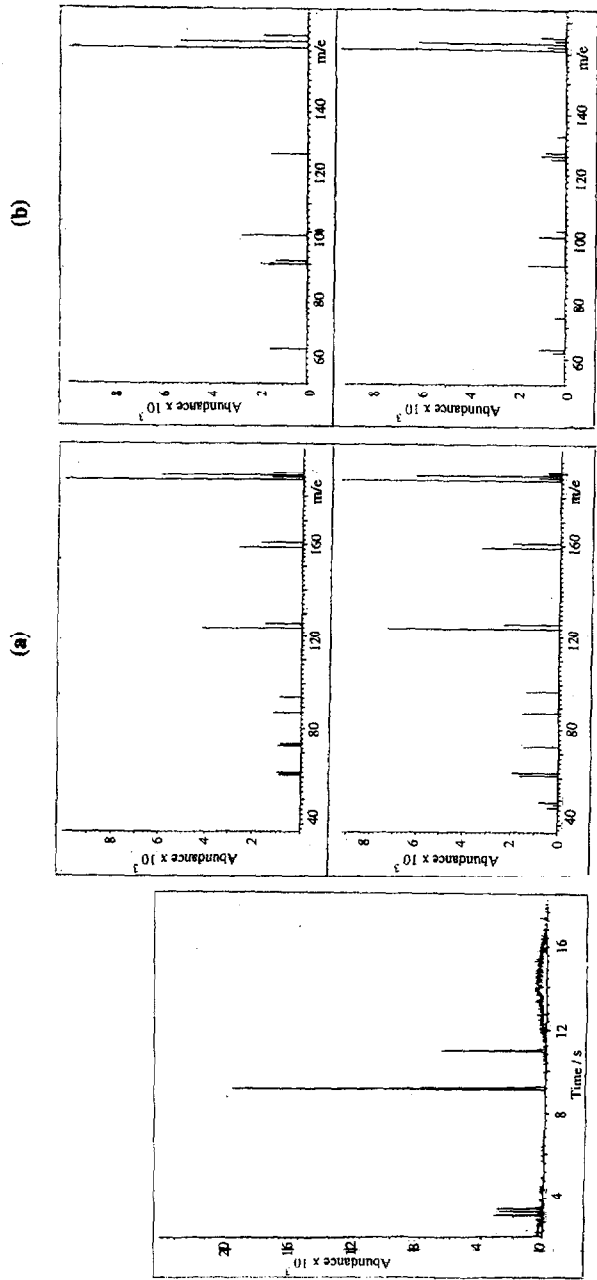


Fig. 15 TIC chromatogram and mass spectrum of Diuron

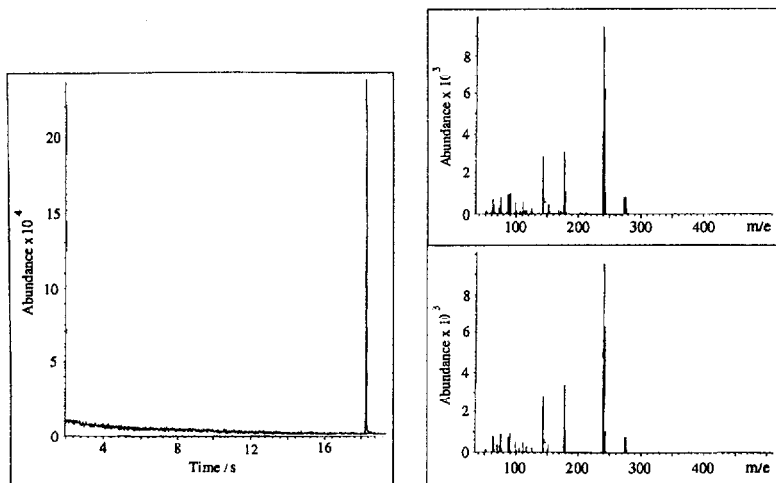


Fig. 16 TIC chromatogram and mass spectrum of Anilazine

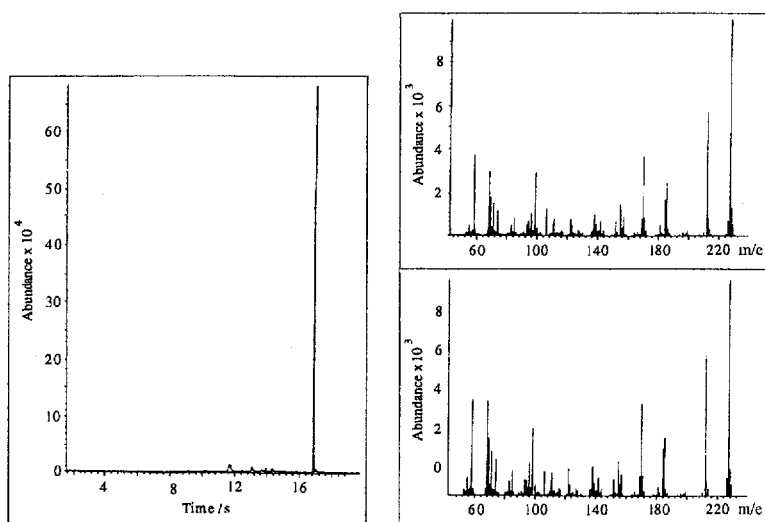


Fig. 17 TIC chromatogram and mass spectrum of Ametryn

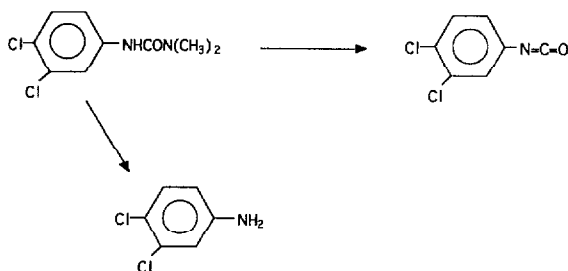
For Cyanazine, two peaks are present, at retention times of 14.98 and 16.88 min. The mass spectrum of the first peak (Fig. 13a) reveals the main ions M-28 ($m/e=212$, loss of N_2) and \dot{C}_4H_6N ($m/e=68$). The spectrum of the second peak is related to pure Cyanazine (Fig. 13b) and indicates the main ions M-28 ($m/e=212$), M-68 ($m/e=172$, loss of \dot{C}_4H_6N) and M-15 ($m/e=225$, loss of $\dot{C}H_3$).

This and the complex TG curve allow the hypothesis that some decomposition occurs during the liquid–gas-phase transition.

For Metamitron, two peaks are found, at retention times of 19.62 and 19.73 min. For the first peak, the spectra throughout the scanning range are identical, indicating (Fig. 14a) that decomposition occurred with subsequent formation of a stable unidentified compound (exothermic process). The spectrum of the second peak relates to pure Metamitron.

Diuron shows two peaks, at retention times of 9.16 and 10.94 min (Fig. 15). The spectra relating to the two peaks are those of benzene-1,2-dichloro-4-isocyanate (Fig. 15a) and 2,3-dichloro benzeneamine (Fig. 15b).

Accordingly, the following thermal decomposition of Diuron can be hypothesized:



Conclusions

Simultaneous TG–DSC investigations on these pesticides show that the majority of the products are stable to thermal stress.

The results of thermal analysis and GC–MS agree substantially: these compounds (with the exceptions of Cyanazine, Metamitron and Diuron) evaporate without decomposition in the liquid–gas-phase transition (Figs 16 and 17).

The components of this class of pesticides have similar, but not identical structures. However, they exhibit different thermal behaviour, in contrast with what is observed for some standard α -amino acids [29].

Only the chlorine substituent seems to influence the thermal stability of the triazine structures. Indeed, the fact that the liquid–gas-phase transition processes start at temperatures close to those of the melting processes (Terbutylazine, Anilazine and Cyanazine) or shifted towards them (Trietazine) allows the hypothesis that a chlorine substituent destabilizes these compounds (according to their position in the thermal stability sequence) with respect to the compounds bearing other substituents.

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