THERMAL ANALYSIS AND NON-ISOTHERMAL KINETIC STUDY OF SOME PESTICIDES
Part II. Chlorinate derivatives

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Abstract

The thermal behaviour of some commercial pesticides was studied by simultaneous TG/DSC measurements. Kinetic parameters, related to solid-gas phase transition processes, were also carried out by using dynamic TG technique.

The kinetics were analysed by using Arrhenius, Satava and Harcourt-Esson equations. The choice of the mathematical expression to insert in these equations was influenced by the shape of the TG plot and other thermal analysis signals. The compounds studied undergo a fusion process followed by a single vaporization process. The latter is well represented by a diffusive process (D_1, D_2 or D_3). The variation of the activation energy values within the range of temperature where the vaporization processes occur was calculated. The enthalpy values of vaporization were also evaluated by using the Clausius-Clapeyron equation.

Keywords: Arrhenius, Satava and Harcourt-Esson equations, non-isothermal kinetics, simultaneous TG-DSC, vaporization processes, variation of activation energies

Introduction

The class of chlorinated hydrocarbon pesticides includes three major, structurally different, groups of chemicals. The first group is represented by DDT and its analogues. The second, relatively younger group is that formed by cyclodienes. The third group is represented by γ-hexachlorocyclohexane (γ–HCH) also called Lindane or benzene hexachloride (BHC). These compounds have been used in the last few years by virtue of their high stability and biological activity [1–3] but some negative features [4–11] have caused a restraint of their use.

Thermodynamic and kinetic investigation on the solid gas phase transition processes with rising temperature for some of the cited compounds have been examined in the past [12, 13]. However, as the problem of their utilization in agriculture is not

completely solved, thermal analysis may be helpful in suggesting suitable conditions for the degradation of these compounds [14–16].

As considerable amounts of chlorinated pesticides are still stored in repositories, it is important to know the thermal behaviour of these compounds in case of fire. In our laboratory a thermal analysis of some cyclodiene derivatives (Endrin, Dieldrin, Aldrin) and dichlorodiphenylethane derivatives (DDT, DDE, methoxychlor) was carried out [17].

The work aims at stressing the thermal and kinetic behaviour of six chlorinated pesticides (Endosulfan, Heptachlor, Lindane, Diuron, Dichlorobenil and Quintozene).

As, in the case of fire, the loss of pesticides from agricultural land and that of other toxic organics from waste disposal sites through the vapour phase is the main pathway [18], a non-isothermal kinetic study on the vaporization process of some of them attempts to determine the most probable mechanism and the kinetic parameters involved.

This may be helpful in understanding some problems regarding the chemistry in the environment.

The suitable choice of a mathematical expression representing a proper mechanism for all the compounds examined can be narrowed down by considering that both the shapes of each α-T plot and of its derivative $d\alpha/dT$ *vs.* temperature curve (that are obtained from the TG and DTG curves) are affected by kinetic behaviour [19–22].

The activation energy and the pre-exponential factor for all compounds examined can be obtained by using both differential (Arrhenius equation) and integral (Satava equation [23]) methods. As in many solid state reactions kinetic data show more linear relationships, the dependence of specific reaction rate and thus of the activation energy upon the temperature [24–26] must be tested.

Experimental

The experimental measurements were carried out on a Stanton Redcroft 625 simultaneous TG-DSC connected to an Olivetti 290 computer. Calibration of this instrument was performed with standard indium, lead, tin, zinc, naphthalene and benzoic acid samples of known temperatures and enthalpies of melting. The metals possess over 99.99% purity and the organic compounds over 99.95%. The chlorinate pesticides (Polyscience) were used without purification and their purity (99%) was more than that required for the application of DSC [27, 28]. Their purity was checked by gas chromatographic-mass spectrometry measurements. Their common names and the chemical classifications are listed in Table 1.

To carry out solid-gas phase transition process studies under dynamic conditions, the TG-DSC apparatus was set up as follows. Samples (8–10 mg) were weighed in aluminium pans placed in an argon-filed dry box. The TG-DSC system was flushed with argon gas below (at flow rate of 50 ml min^{-1}) and above (at flow rate of 30 ml min^{-1}) the open pan. In this way the gas evolved during the thermal solid-gas phase process was removed continuously. The heating rate used were 2.5, 5, 10, 15 and 20 K min^{-1} and at least

Table 1 Nomenclature of chlorinate pesticides

Compounds	Chemical nomenclature
Endosulfan	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide
Heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-endomethanoindene
Dichlorobenil	2,6-dichlorobenzonitrile
Quintozene	pentachloronitrobenzene
Diuron	3-(3,4 dichlorophenyl)-1,1-dimethylurea
Lindane	gamma-1,2,3,4,6-hexachlorocyclohexane

three runs were made for each compound. All the thermodynamic quantities were calculated using the Stanton-Redcroft Data Acquisition System, Trace 2, Version 4.

The gaseous products of thermal processes were adsorbed into suitable adsorbent (Supelco) tubes: Chromosorb, Glass Fiber Filter, coconut charcoal and activated silica gel. Subsequently these tubes were desorbed into an organic liquid (CS_2) and injected into a Hewlett-Packard 5890 GC coupled to a Hewlett-Packard MS 5971 Selective Detector. The capillary column used was a PTE, 30 m length×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, then it was scanned at 2.5 K min^{-1} to 553.15 K. Carrier gas (helium) flow was 0.8 ml min^{-1}. Mass Spectrometry (MS) determinations were performed with the SCAN technique using electron impact ionization at 70 eV and the transfer line was maintained at 553.15 K.

Procedure

TG/DSC measurements mainly aim at stressing the evaluation of extrapolated onset temperatures, the mass loss percentage (mass loss %) and the enthalpy values of any process occurring at rising temperature (melting, crystallization, polymorphic changes, decomposition, chemical reactions).

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

The thermodynamics of the processes regarding the compounds which exhibit only liquid-gas phase transition (without decomposition) can be examined assuming that the system attains equilibrium at any stage.

When the equilibrium is achieved, the extent of the mass loss at a given temperature (α) can be described by the ratio of the equilibrium vapour pressure P to the atmospheric pressure P^0.

The volatilization process can be described by the integral of Clausius-Clapeyron equation:

$$\ln\frac{P}{P^0}=\ln\alpha=\frac{\Delta H_v}{R}\frac{1}{T_v}-\frac{\Delta H_v}{R}\frac{1}{T} \tag{1}$$

where T_v and ΔH_v are related to the vaporization process and P^0 to the boiling temperature. Substituting P/P^0 with the experimental α values and plotting $\ln\alpha$ *vs.* $1/T$ one can determine ΔH_v and T_v and compare them with those obtained by TG/DSC curves to point out if only vaporization process occurs.

The kinetic goal is to determine the most suitable mechanism to describe liquid-gas phase transition processes using both non-isothermal integral and differential approaches and to determine and compare the activation energies E and the pre-exponential factors A evaluated with those methods.

In order to study chemical and physical properties variation related to non-isothermal processes a mathematical relationship is normally associated with a particular model mechanism; however there are several model giving the same mathematical expression and the same model can be described by two or more different expressions [29].

Dollimore and co-workers [19–21] have written a computer program that plots a theoretical α-T curve using the equation

$$\frac{d\alpha}{dT}=\frac{A\exp(-E/RT)f(\alpha)}{\beta} \tag{2}$$

where $\beta=dT/dt$ is the heating rate and when the hypothesized mechanisms $f(\alpha)$ and the suitable values of both A and E are introduced.

This approach may be considered as the reverse of the Arrhenius non-isothermal kinetics in which A and E are calculated from α-T plots and by assuming a proper mechanism. The shape of the theoretical curve obtained in this way proves to be only a function of the mechanism and makes it possible to determine the following parameters:

i) the initial (T_i) and final (T_f) temperatures of the TG curves as diffuse (*d*) or sharp (*s*)

ii) the half width defined as the peak width on the differential plot of $d\alpha/dT$ *vs.* T measured at half height

iii) the value of α_{max} at the maximum rate of the process (at T_p) on the α-T plot.

The comparison of these characteristic quantities (half width, α_{max}, T_i and T_f) for our experimental curves with those reported in literature [19, 20] showed more than one possible mechanism for each compound.

In order to select the appropriate mechanism for each compound and to determine the kinetic parameters A and E, the following method was used.

The α values, calculated from the TG curves as a function of temperature, together with those of $d\alpha/dT$ were inserted in the mathematic expressions of $f(\alpha)$ and used in the Arrhenius differential equation

$$\ln\frac{(d\alpha/dT)\beta}{f(\alpha)}=\ln k=\ln A-\frac{E}{RT} \tag{3}$$

where $k=[(d\alpha/dT)\beta/f(\alpha)]$ is the specific reaction rate.

The α values were also inserted in the mathematical expression of $g(\alpha)$ and used in the Satava integral equation [24]:

$$\log[g(\alpha)] = -0.4567\frac{E}{RT} - 2.315 + \log\frac{AE}{R\beta} \tag{4}$$

where Doyle's approximation is valid in a temperature range of 100 K.

By considering the best fit of the linear relationship of log $[g(\alpha)]$ *vs.* $1/T$ (higher values of correlation coefficients) and comparing the E and A values obtained with the previous two methods the most likely mechanism for each compound is obtained.

The kinetic parameters A and E for all the compounds examined were calculated from the slope and the intercept of Eqs (3) and (4).

Finally, to test the dependence of the specific reaction rate (k) upon the temperature, the relationship between the Harcourt-Esson and the Arrhenius equations was used:

$$k = CT^m = A\exp\left(\frac{-E}{RT}\right) \tag{5}$$

To evaluate the change in activation energy values in the range of temperature where the process occurred, the Eq. (5) was used at two different temperatures T_1 and T_2:
writing

$$\left[\frac{T_1}{T_2}\right]^m = \frac{\exp(-E/RT_2)}{\exp(-E/RT_1)}$$

or in a logarithmical form

$$m\ln\frac{T_1}{T_2} = \frac{E}{R}\frac{\Delta T}{T_1 T_2} \tag{6}$$

where ΔT is $T_2 - T_1$.

Using Eq. (6) the variation of activation energy values in the entire temperature range where the processes occur can be calculated considering the ΔT increments as a function of the constant degree of conversion (α) increments.

The values of m were calculated using the Hartcourt-Esson relationship in differential

$$\log\frac{(d\alpha/dT)}{f(\alpha)} = \log C + m\log T \tag{7}$$

and in the integral form

$$\log[g(\alpha)] = (m+1)\log T + \log B \tag{8}$$

where B is equal to $C/[\beta(m+1)]$.

Results and discussion

To establish which compound undergoes simple volatilization (without decomposition) gas chromatographic-mass spectrometry spectra on their gaseous products are performed as reported in the experimental part (Figs 1a–2b).

The MS spectra of gaseous products (obtained after the thermal analysis of each compound) are compared with those of the pure compounds reported in some spectral libraries and their match quality (utility) are reported in Table 2.

Table 2 Match quality (utility) of the spectra of gaseous products for chlorinate pesticides studied

Compounds	Utility	
	spectra from 1st peak	spectra from 2nd peak
Endosulfan	95	
Heptachlor	99	
Dichlorobenil	97	
Quintozene	99	
Diuron	96	83

The trends in the thermal behaviour of the compounds are given in Figs 3–8b. The values of the thermodynamic parameters related to TG and DSC measurements (only those obtained at $\beta=10$ K min^{-1}) are reported in Table 3.

Temperatures and enthalpies directly determined by DSC curves are compared in Table 4 with the values obtained by using the Clausius-Clapeyron equation and the TG-DSC data at a heating rate of 2.5 K min^{-1}.

GC-MS measurements

For Endosulfan the peak of the gaseous product is present at retention time 10.94 min. Comparison of the corresponding mass spectra (Fig. 1a) with the one reported in literature for α-Endosulfan (Fig. 1b) reveals that the compound undergo a simple volatilization without decomposition. The match quality (in percentage) reported in Table 2 is a measure of the correspondence of the two mass spectra compared. Heptachlor, Dichlorobenil and Quintozene show the same behaviour (the spectra of gaseous products are equal to those reported in spectral libraries for the same compounds). On the contrary the mass spectra of Diuron gaseous compounds (relating to peaks at retention times 9.16 and 10.94 min) show the presence of two decomposition products: Benzene 1,2-dichloro-4-isocyanate (Fig. 2a) and Benzeneamine 2,3-dichloro (Fig. 2b). No spectra were found for the carbonaceous residue of Lindane.

From this experimental evidence it can be concluded that for these compounds, with the exception of Diuron and Lindane, processes of liquid-gas phase transition without decomposition may occur.
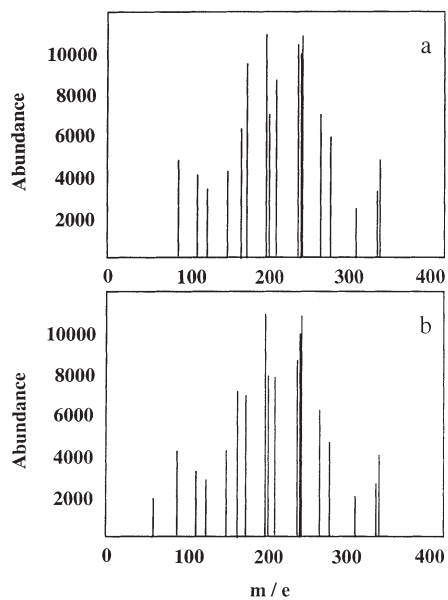
Fig. 1 Mass spectra of the gaseous product of α-Endosulfan (a) and of α-Endosulfan itself (reference from spectral library) (b)
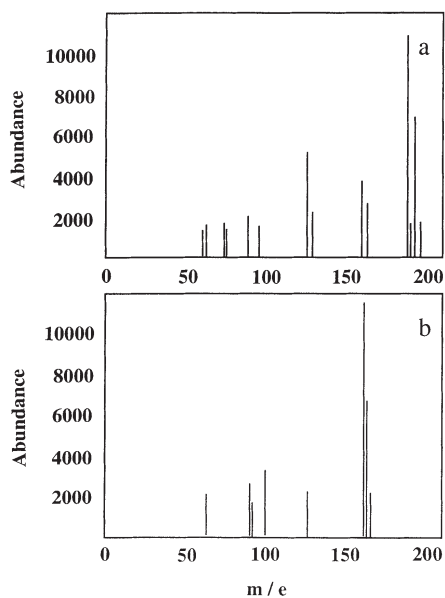

Fig. 2 Mass spectra of the gaseous products of Diuron: Benzene 1,2-dichloro-4-isocyanate (a) and of Benzeneamine 2,3-dichloro (b)

Table 3 Thermodynamic parameters for the fusion and vaporization processes of the chloro-organic pesticides from TG-DSC measurements (β=10 K min^{-1}) and comparison with literature data

| Compounds | TG measurements vaporization | | DSC measurements | | | | | | | | |
| | | | fusion | | | | | | vaporization | | |
	T_e/K^a	Mass loss/ %	T_e/K^a	T_p/K	T_e/K^b	ΔH^c/ kJ mol^{-1}	ΔH^b/ kJ mol^{-1}	Refs	T_e/ K	ΔH/ kJ mol^{-1}	peak/ K
Endosulfan	505.9	99.29	359.0	368.0	380.0	16.52	10.00	[30]	415.1	80.50	540.0
Heptachlor	477.6	97.98	355.5	362.2	369.0	20.72	–	[28]	445.4	64.32	501.0
Dichlorobenil	433.0	98.28	418.6	421.2	416.7	24.56	25.94	[28]	418.3	74.33	471.2
					417.2		26.17	[30]			
					417			[31]			
Quintozene	475	99.01	420.1	421.8	417.4	21.89	17.68	[30]	453.3	77.25	507.2
					417			[31]			
Diuron	515.0	98.47	433.2	435.1	430.5	25.28	30.47	[30]	500.5	190.11	543.2
Lindane	455.1	77.74	388.1	389.6	386.8	22.8	22.13	[30]	443.3	–241.10	480.9
					386.0			[32]			

^{a}Extrapolated onset temperature from this work
^{b}Data from other works
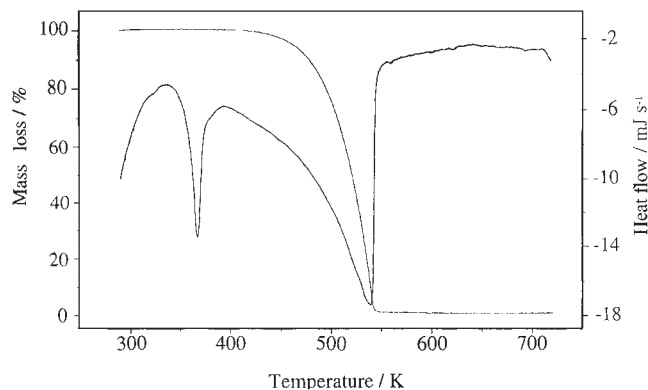^{c}Enthalpy values from this work

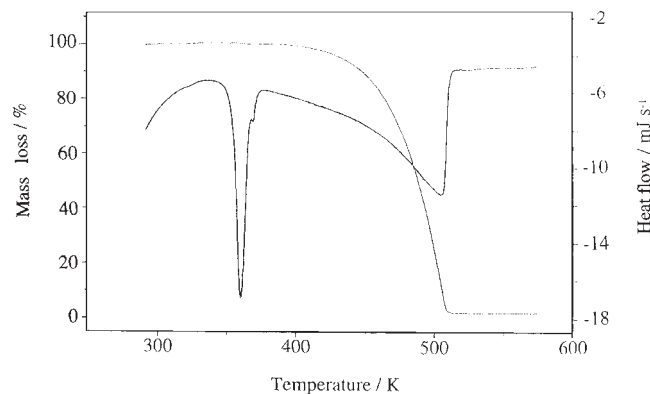**Fig. 3** Simultaneous DSC and TG curves of Endosulfan

Fig. 4 Simultaneous DSC and TG curves of Heptachlor

Features of the thermal processes

By comparison of TG/DSC curves for all compounds (with the exception of Lindane) (Figs 3–8b) it can be seen that there are two endothermic processes: the former corresponds to the fusion, as can be concluded from comparison with literature data for the same compounds [28, 30–32] (Table 3), the latter is a vaporization process (with or without decomposition).

TG/DSC curves of Endosulfan and Heptachlor (Figs 3 and 4) show a fusion process followed by volatilization (without decomposition as determined by GC-MS measurements). In the TG/DSC curves this last process is associated with a broad endothermic effect (Figs 3 and 4). The fusion processes for Dichlorobenil and Quintozene (Figs 5 and 6) appear just at the beginning of the volatilization process. This phenomenon is evident from the superimposition of the two endothermic effects in their DSC curves. By virtue of this fact, the ΔH values of vaporization are obtained by subtracting the enthalpy of
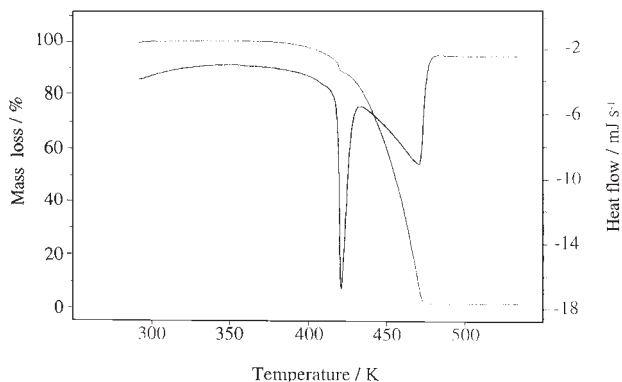
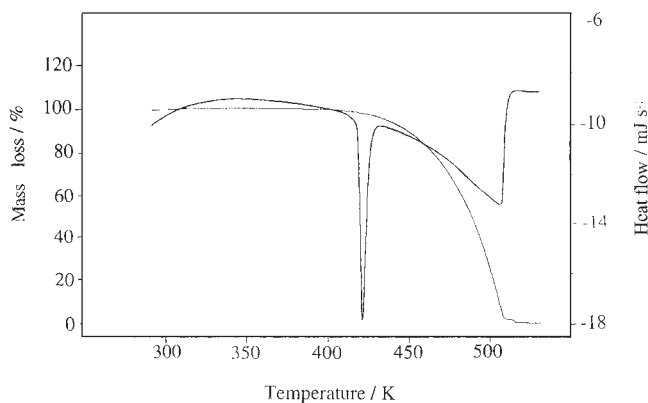**Fig. 5** Simultaneous DSC and TG curves of Dichlorobenil

Fig. 6 Simultaneous DSC and TG curves of Quintozene

melting from the overall enthalpy of the two processes. The extrapolated temperatures of vaporization and ΔH values calculated from linearizating Eq. (1) are in agreement with the experimental ones for Endosulfan, Heptachlor, Dichlorobenil and Quintozene (Table 4).

Fusion and volatilization processes for Diuron (Fig. 7) are fairly separated (about 100 K from the two endothermic peak temperatures). However GC-MS measurements reveal that the latter is a decomposition process with the formation of benzene 1,2-dichloro-4-isocyanate and Benzeneamine 2,3-dichloro. Moreover, the enthalpy value of the decomposition process as calculated from the DSC curve (Table 3) is more than two times higher than that extrapolated from the linearization of the Clausius-Clapeyron Eq. (1) revealing that a further energy contribution, due to decomposition process, is required [12].

**Table 4** Thermodynamic parameters for vaporization processes calculated by means of TG/DSC curves and Eq. (1)

Compounds	T^a	T_v^b	$\Delta H/$kJ mol$^{-1\,c}$	$\Delta H/$kJ mol$^{-1\,d}$
Endosulfan	540.1	542.4	80.50	78.09
Heptachlor	501.0	517.6	64.32	66.87
Dichlorobenil	480.0	471.0	74.33	74.60
Quintozene	513.1	507.0	77.25	76.40
Diuron	553.0	560.0	190.11	92.73
Lindane	453.1	559.4	−233.64	35.34

[a]Extrapolated temperature from TG curves for vaporization process
[b]Extrapolated temperature of vaporization from linearization of $\ln\alpha$ *vs.* $1/T$
[c]Enthalpies values of vaporization process from DSC curves
[d]Enthalpies values of vaporization process extrapolated from $\ln\alpha$ *vs.* $1/T$
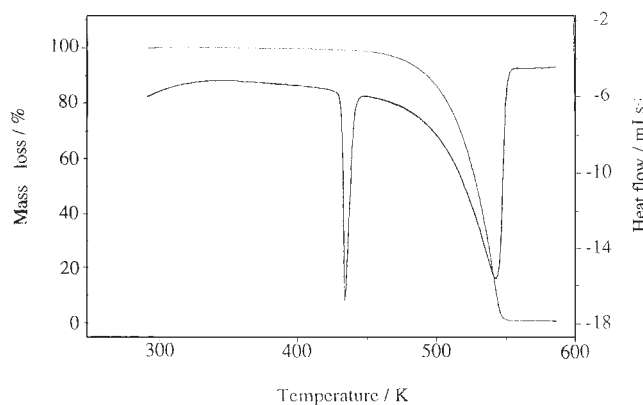
Fig. 7 Simultaneous DSC and TG curves of Diuron

In Fig. 8a the TG/DSC curves of Lindane are reported. After the fusion, with a corresponding endothermic effect on the DSC curve at about 390 K, this compound undergoes a rapid, strong and sharp exothermic process. After this thermal effect the apparent decrease in the sample temperature recorded on the TG curve as the heating scan goes on (Fig. 8a) is anomalous and unreal as it disappears when the TG/DSC curves are reported as a function of time (Fig. 8b). From Table 4 it can be seen that Lindane has the lowest value of enthalpy obtained from Eq. (1). For this compound this relationship was applied before the appearance of the exothermic effect on the DSC curve ($\alpha < 0.65$). Comparison of the above cited value with the thermochemical one (from the DSC curve) is meaningless as the latter is a negative value probably due to an oxidation process.

In order to explain the thermal behaviour of Lindane, different samples (Polyscience, Aldrich) were tested at different heating rates β (2.5, 5, 15 and 20 K min^{-1}) (Table 5). All the ΔH values lie in a small range thus confirming the same side pro-
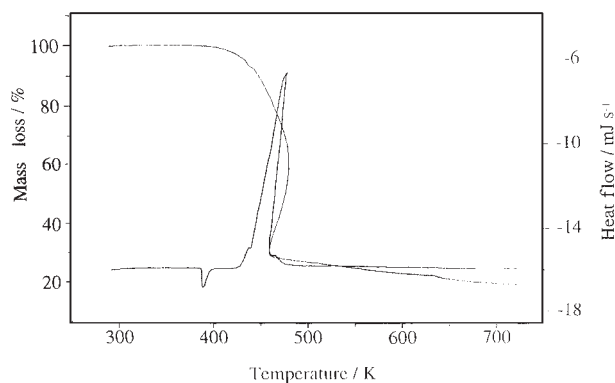
Fig. 8a Simultaneous DSC and TG curves of Lindane
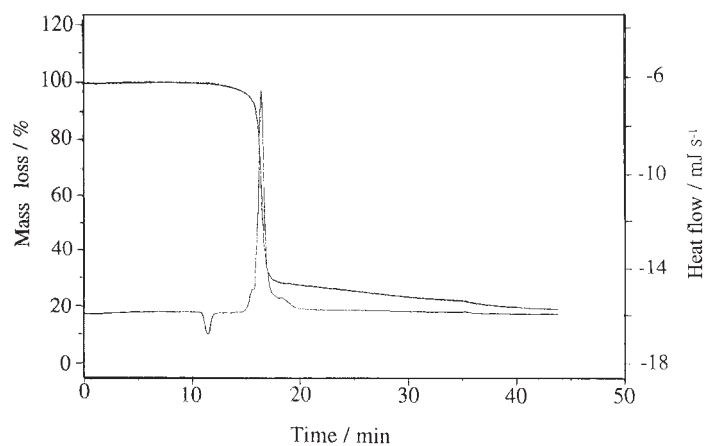
Fig. 8b Simultaneous DSC and TG curves of Lindane *vs*. time

Table 5 Onset, peak temperature and enthalpy values from DSC curves related to melting and liquid-gas phase transition processes for Lindane at various heating rates β

β/K min⁻¹	Fusion			Vaporization		
	T_e/K	T_p/K	ΔH/kJ mol⁻¹	T_e/K	T_p/K	ΔH/kJ mol⁻¹
2.5	387.0	388.8	21.5	416.0	489.7	−226.5
5	387.8	389.4	24.3	425.6	501.0	−228.1
10	388.1	389.6	22.8	436.6	504.0	−241.1
15	387.9	390.4	22.7	437.8	512.0	−223.1
20	387.9	390.5	20.5	448.4	519.0	−199.8

Table 6 Parameters related to mechanism-characteristic features for the vaporization process of chloro-organic pesticides from TG/DTG curves

Compounds	From TG curves characteristic features of T_i and T_f	α_{max}	From DTG curves					Kinetic model
			T_i/K	T_{max}/K	T_f/K	$\Delta T_{Lo}/\Delta T_{Hi}$	half width/K	
Endosulfan	T_i diffuse, T_f sharp	0.90	425.9	539.8	553.4	6.6	33.1	D_1, D_2
Heptachlor	T_i diffuse, T_f sharp	0.90	396.5	514.2	521.6	7.2	30.8	D_1, D_2
Dichlorobenil	T_i diffuse, T_f sharp	0.90	383.4	469.7	474.9	11.9	26.4	D_1, D_2
Quintozene	T_i diffuse, T_f sharp	0.85	400.2	503.9	519.3	10.7	25.8	D_2
Diuron	T_i diffuse, T_f sharp	0.80	485.6	553.6	566.4	2.7	33.7	D_2, R_2
Lindane	T_i diffuse, T_f sharp	0.65	318.5	504.0	456.1	2.1	32.6	D_3, R_3

Table 7 Classification of the mathematical expressions chosen from the evaluation of reaction mechanisms

Kinetic classification	$g(\alpha)=\int d\alpha/f(\alpha)=kt$	$f(\alpha)=1/K(d\alpha/dT)\beta$
Diffusion mechanisms		
D_1 one-dimensional	α^2	$1/2\alpha$
D_2 two-dimensional	$(1-\alpha)\ln(1-\alpha)+\alpha$	$[-\ln(1-\alpha)]^{-1}$
D_3 three-dimensional	$[1-(1-\alpha)^{1/3}]^2$	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
Based on geometrical models		
R_2 contracting area	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
R_3 contracting volume	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$

cess. At the end of each run some carbonaceous residues found in the crucibles make it possible to hypothesize that an oxidation process occurred.

Non-isothermal kinetics

It is shown that α_{max} is characteristic for any specific mechanism [20] and practically does not depend on Arrhenius parameters or the heating rate.

With further information offered by the width of the peaks of DTG curves at half height (the so-called half width) it is usually possible to narrow down the choice of the proper mathematical expression which describes the reaction examined. For this purpose all parameters related to the evaluation of the mechanism of vaporization (with or without decomposition) taken from TG/DSC curves are reported in Table 6. All the compounds examined show the same typical TG/DTG shapes: TG curves with a diffuse initial or onset temperature and a sharp final one and DTG curves with a ratio $\Delta T_{Lo}/\Delta T_{Hi}$ (that represents the asymmetry of the DTG curves) which is always greater than the unity.

By comparing our experimental α_{max} and half width values with the theoretical ones reported in literature by Dollimore and co-worker [19] one can conclude that only the following mechanisms are possible: R_2, R_3, D_1, D_2, D_3 (Table 6).

The kinetic procedure for Lindane was applied in the temperature range before the occurence of the exothermic effect on the DSC curve ($\alpha<0.65$).

The mathematical expressions of $f(\alpha)$ (used in the Arrhenius differential method) and $g(\alpha)$ (used in the Satava integral method) for the most probable mechanisms are reported in Table 7.

For each compound, with the exception of Quintozene, two mechanisms are again possible. The criterion used for the selection of the appropriate mechanism has been previously described in the procedure, that is the best fit of the linear regression analysis of Eq. (4).

The plots of the degree of conversion (α) *vs.* temperature (K) were constructed from TG curves. The $d\alpha/dT$ experimental values and the suitable mathematical expression of $f(\alpha)$ and $g(\alpha)$ were introduced respectively in Eqs (3) and (4).

Table 8 Kinetic parameters extrapolated from Eqs (3) and (4) and comparison with the temperature range obtained by means of Eq. (6). The most suitable mechanism is given in bold

Compounds	Kinetic model	From Eq. (6) ΔE/kJ mol^{-1} [a]	From Arrhenius Eq. E/kJ mol^{-1}	A/min^{-1}	From Eq. (6) ΔE/kJ mol^{-1} [b]	From Satava Eq. E/kJ mol^{-1}	A/min^{-1}	r
Endosulfan	D_1	127.4–155.2	144.9	$2.0 \cdot 10^{15}$	133.7–162.9	148.5	$1.2 \cdot 10^{14}$	0.9999
	D_2		170.3	$5.7 \cdot 10^{17}$		161.7	$1.8 \cdot 10^{15}$	0.9991
Heptachlor	D_1	110.1–136.9	126.8	$1.4 \cdot 10^{14}$	112.7–140.2	120.6	$2.0 \cdot 10^{13}$	0.9996
	D_2		148.4	$2.1 \cdot 10^{16}$		141.1	$2.6 \cdot 10^{15}$	0.9961
Dichlorobenil	D_1		136.5	$2.9 \cdot 10^{16}$		129.8	$3.9 \cdot 10^{15}$	0.9965
	D_2	151.8–180.3	172.6	$2.2 \cdot 10^{20}$	141.3–167.9	164.2	$3.0 \cdot 10^{19}$	0.9986
Quintozene	D_2	115.5–140.0	131.7	$4.3 \cdot 10^{14}$	143.4–173.7	158.4	$1.1 \cdot 10^{16}$	0.9997
Diuron	D_2	191.7–218.4	203.0	$2.2 \cdot 10^{20}$	186.2–212.1	191.9	$4.3 \cdot 10^{17}$	0.9981
	R_2		116.9	$1.1 \cdot 10^{12}$		69.3	$1.8 \cdot 10^{6}$	0.9914
Lindane	D_3	66.0– 85.6	88.9	$3.7 \cdot 10^{9}$	81.8–115.1	108.4	$4.5 \cdot 10^{9}$	0.9892
	R_3		31.8	$1.1 \cdot 10^{4}$		30.3	$6.3 \cdot 10^{3}$	0.9800

[a]According to Hartcourt-Esson differential method (Eq. (7))
[b]According to Hartcourt-Esson integral method (Eq. (8))

Table 9 Data for plots of log$k$ $vs.$ log$T$ and plots of log[$g(\alpha)$] $vs.$ log$T$ (according to relationships proposed by Hartcourt and Esson[a]) and comparison between values of m obtained from the two differential and integral methods

Compounds	Differential method			Integral method		
	log$C$	m_{diff}[b]	r	log$B$	m_{diff}[c]	r
Endosulfan	−93.01	34.52	0.9970	−101.80	36.24	0.9996
Heptachlor	−85.36	31.96	0.9989	−91.50	32.72	0.9989
Dichlorobenil	−121.89	46.09	0.9992	−117.54	42.92	0.9992
Quintozene	−88.80	33.22	0.9989	−114.38	41.23	0.9995
Diuron	−111.81	41.21	0.9988	−116.84	41.52	0.9996
Lindane	−60.20	22.42	0.9959	−79.19	27.80	0.9913

[a]From [26]
[b]From linear regression of log$k$ $vs.$ log$T$
[c]From linear regression of log[$g(\alpha)$] $vs.$ log$T$

Thus the more likely mechanisms (Table 8 in bold) and the corresponding E and A parameters were found.

It can be noted that kinetic parameters, obtained from Arrhenius and Satava methods are in good agreement with each other for each compound with the exception of Lindane and Quintozene.

The values of the constants m and c, contained in Eqs (5) and (6), are given in Table 9: values of m in integral and differential methods are close (with the exceptions of Lindane and Quintozene).

As previously reported in the procedure, by using Eq. (6) the variation of activation energies in the entire temperature range where the transition occurs can be calculated by taking the values of ΔT as increments corresponding to a constant increment (0.05) of α. The activation energies previously calculated with Arrhenius and Satava equations lie in the range of energy values calculated with Eq. (6) (Table 8), using, respectively, the parameter m obtained with differential and integral forms of the Harcourt-Esson equation (Table 9) thus showing the negligible variation of the activation energy in the studied processes.

Conclusions

The adopted procedure shows that all the compounds undergo vaporization processes with diffusive mechanisms: Endosulfan and Heptachlor, which undergo a simple volatilization process, follow a D_1 mechanism; Dichlorobenil and Quintozene, for which a fusion process overlaps the vaporization process, follow a D_2 mechanism, together with Diuron, which undergoes molecular decomposition while Lindane, in the range before the occurrence of the exothermic side process, follows a D_3 mechanism.

The hypothesis concerning a simple volatilization process for Endosulfan, Heptachlor, Dichlorobenil and Quintozene is confirmed from a thermodynamic point

of view by the agreement between the enthalpy values calculated by means of Eq. (1) and those obtained from DSC curves.

The difference between activation energy and enthalpy values shows that the latter is not the only one controlling the diffusive processes (Tables 4 and 8).

Finally it can be noted that the highest value of activation energy is that of Diuron (molecular decomposition) while the side process of oxidation greatly decreases the activation energy of Lindane.

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