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THERMOANALYTICAL INVESTIGATIONS OF SOME CHLORO-ORGANIC PESTICIDES AND RELATED COMPOUNDS *

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ABSTRACT

The thermal features of several chloro-organic pesticides, namely lindane, HCB, PCNB, p,p'-DDT, dicofol and p,p'-methoxychlor, as well as some related compounds were studied using thermoanalytical methods (DTA, TG, DTG) and by the application of standard procedures to identify some of the reaction products. Heating of the compounds at a constant rate leads to their total volatilization. Most of the compounds studied undergo simple evaporation or sublimation with rising temperature. The volatilization of p,p'-DDT, o,p'-DDT, dicofol and p,p'-methoxychlor is, however, accompanied by chemical changes in the system. It has been revealed that the primary step in the decomposition of p,p'-DDT is the elimination of HCl and formation of p,p'-DDE. The decomposition of o,p'-DDT and p,p'-methoxychlor presumably begins with an analogous process.

In the case of the compounds exhibiting simple volatilization patterns, the thermodynamics and kinetics of the process were examined on the basis of the TG curves. The enthalpy of volatilization was evaluated from the Clausius–Clapeyron equation. The kinetics were analysed using a standard approach assuming that the rate is described by an equation comprising the term characterizing a kinetic model for the process and the Arrhenius term accounting for the influence of temperature on the process. This procedure revealed that the rate determining step is well represented by the Polanyi–Wigner model without any activation barrier over that resulting from the thermochemical requirements.

The enthalpies of formation of some of the compounds were evaluated on the basis of the Benson's group additivity scheme. These characteristics together with the information on the thermal behaviour of these derivatives enabled the possible pathways for the thermal decomposition of DDT isomers, α-chloro-DDT, dicofol and p,p'-methoxychlor to be revealed.

INTRODUCTION

Chloro-organic pesticides belong to the group of compounds which were first used on a large scale [1–3]. Owing to their relatively high stability and

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distinct biological activity, they seemed to be very promising derivatives for wide application. Unfortunately, after a few years of their use many negative features of the compounds were revealed [4–11]. One of these is their behaviour in environmental conditions. Due to the low reactivity of the compounds they can remain unchanged in the environment for a long time causing its gradual pollution [1–3,10–16]. Of course, the immensely important problem is the natural degradation of the compounds. One of the factors influencing environment is temperature. Hence, a knowledge of the thermal behaviour of the pesticides may provide information on the fates of these derivatives in the environment. There is a general policy now towards total restriction on the use of chloro-organic pesticides. So far, several of them have been withdrawn from application, e.g. DDT [1–3]. Nevertheless, considerable amounts of some of these compounds are still stored in magazines. Thus, the problem of their utilization remains relevant [17–19]. Thermoanalytical investigations may also be helpful in discovering methods of degradation or incineration of these derivatives.

The thermochemistry and thermal properties of some of these compounds have been examined in the past [20–27]. However, extensive studies concerned several other aspects, namely the problems regarding volatilization of the compounds [28–37], also in natural conditions [38–40], their dehydrochlorination [41–43], the decomposition of the compounds at high temperatures [44–47], e.g. in tobacco smokes [44,48], their isomerization [42,49–53], their thermal degradation [47,49,54–57], their thermal degradation in the presence of additives [54–57], their thermal degradation in soil [34,58–60], etc. To our knowledge, in only a few works have thermoanalytical methods been involved in the investigations [61–64].

The aim of the present work was to gather more information on the character and pathways of the thermal processes occurring during heating of the pure compounds, to reveal the thermal and thermochemical characteristics for these derivatives and to analyse the kinetics of those processes exhibiting a simple nature. Such studies should shed more light on the thermal behaviour of chloro-organic pesticides. They may also be helpful in understanding problems regarding the chemistry of the environment.

EXPERIMENTAL

α-BHC, β-BHC, γ-BHC, p,p'-DDT, o,p'-DDT and p,p'-DDE, all from P.O.Ch. (Poland), were of analytical grade (GC analytical standards) and were used as received. HCB, from Fluka AG and Busch SG, and PCNB, from Aldrich, both of pure grade, were subjected to vacuum sublimation before use. Other compounds examined were synthesized by methods described in the literature. Thus 1,1′-(tetrachloroethylidene)bis(4-chlorobenzene) (α-chloro-DDT) and p,p'-DDE were prepared according to Grummitt et al. [65]. Dicofol was obtained by a slight modification of the method described in ref. 66. Lastly, 1,1′-(dichloroethenylidene)bis(4-methoxybenzene) was synthesized as described by Haris and Frankforter [67]. All pesticide reference standards, as well as standards of related compounds, were supplied by the U.S. Environmental Protection Agency.

The thermal analyses were carried out on OD-103 and Q-1500 derivatographs (Monicon) with α-Al_2O_3 as reference. All analyses on the OD-103 derivatograph were performed in a dynamic atmosphere of nitrogen with samples placed on a flat platinum crucible (see e.g. ref. 68, Appendix 1, No. 4). Other operating conditions on this instrument were: the sample mass, 50 mg; the heating rate, approx. 5 K min^{-1}; and the sensitivities of the DTG, DTA, and TG galvanometers, 0.1, 0.5–0.2 and 50 mg respectively. Analyses on the Q-1500 derivatograph were carried out in a standard Q mode. The samples weighing 50 mg were placed in a special labyrinth platinum crucible which assures a self-generating atmosphere above the condensed phase [69]. The sensitivity of the TG measurements was adjusted taking into account the expected weight loss of the sample. Lastly, the mass loss rate, $\mathrm{d}m/\mathrm{d}t$, was set at values equal to 1–2 mg min^{-1}.

In order to identify the products of the thermal decomposition, the experiments were carried out in isothermal conditions in a manner described previously [70]. Thus, the heating of samples was performed in a quartz reactor with a cold finger inside it. In this way, volatile products were removed from the reaction zone in an inert gas stream, whereas non-volatile products were trapped on the cold finger. The gaseous phase was checked for the presence of HCl. The residue at the bottom of the reactor and the residue condensing on the cold finger were analysed by IR and NMR spectroscopy, GC and HPLC methods, and by performing elemental analyses. All GC analyses were carried out on a Mera–Elwro model N504 (Poland) chromatograph using a 3.2 m long glass column (i.d. = 0.004 m) packed with 1.5% OV-17 + 1.95% OV-210 phase coated on Chromosorb WAW (100/120 mesh). The column was treated with a sylating reagent (trimethylchlorosilane) and high concentrations of pesticides prior to use. The HPLC analyses were performed on a HPP 5001 chromatograph (Czechoslovakia) using a 0.15 m column (i.d. = 0.0033 m) packed with Sepazon SCX C_{18}. A $CH_3CN : H_2O$ mixture (1 : 1) was the mobile phase. IR spectra were obtained on a Specord 71 IR spectrophotometer. NMR spectra were recorded on a Tesla BS 487C spectrometer (80 MHz). Elemental analyses were carried out on a Carlo Erba model 1106 elemental analyser.

The thermochemical and kinetic examination of the thermal process for those compounds showing a simple volatilization pattern (compounds listed below in Table 3, see also Fig. 1A) was based on the numerical values of the temperature (T) corresponding to certain values for the extent of reaction (α). For each such compound, a set of α against T data points was

TABLE 1

α versus T for the volatilization of lindane (A), PCNB (B) and p,p'-DDE (C)

	T (K) at $\alpha =$										
	0.1	0.18	0.26	0.34	0.42	0.50	0.58	0.66	0.74	0.82	0.9
A	457.4	471.0	480.7	487.3	492.9	497.2	501.3	505.0	508.1	511.0	513.6
B	447.5	462.0	471.5	477.5	483.5	489.0	493.0	496.5	499.5	503.0	507.0
C	475.8	491.8	501.5	509.5	515.5	520.8	525.8	529.1	532.8	536.1	

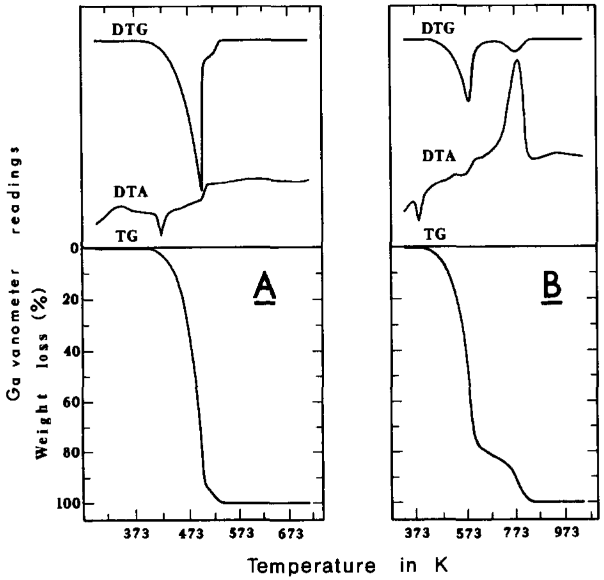

Fig. 1. Thermal analyses of PCNB (A) and p,p'-methoxychlor (B).

determined from at least three replicate measurements [71]. Examples are given in Table 1.

RESULTS AND DISCUSSION

General features of the thermal process

Thermoanalytical curves recorded by both derivatographs for three compounds chosen as examples are shown in Figs. 1–3. Table 2 shows the characteristic parameters resulting from the examination of the thermal analysis curves, along with the information available from the literature.

The thermal processes of all the compounds studied have a multi-step pattern. Relatively simple thermolysis courses are exhibited by compounds **1–5**, **8**, **11** and **12** (Table 2). Thermoanalytical curves for these derivatives are characterized by regular, smooth shapes (Fig. 1A). Complementary studies involving the identification of the reaction products demonstrated that the substance transferred to the gaseous phase (condensed on the cold finger) and that remaining at the bottom of the quartz reactor are both identical with the original sample. An exception is α-chloro-DDT which decomposes slightly upon volatilization to p,p'-DDE and presumably chlorine. All the above facts indicate that, in most cases, the compounds mentioned above are exclusively volatilized with rising temperature. The results of our studies are in accordance with several literature reports

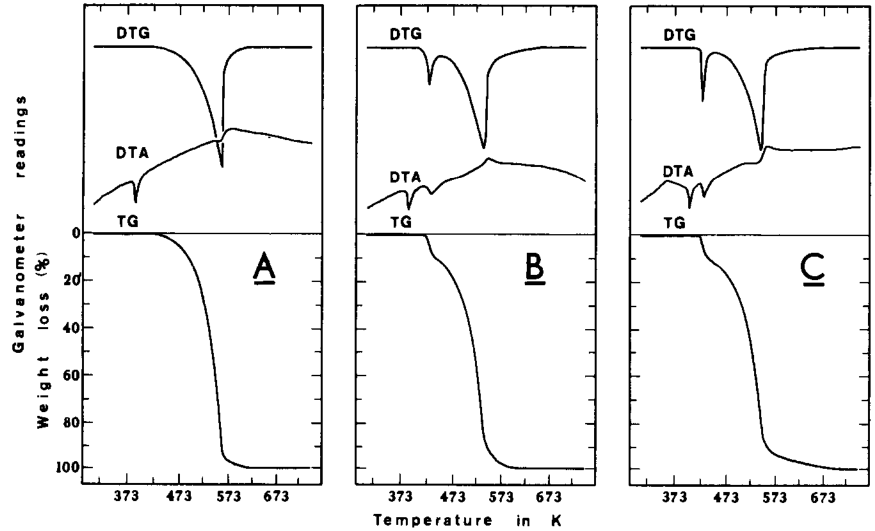

Fig. 2. Thermal analyses of p,p'-DDT recorded on an OD-103 derivatograph: A, sample ground in an agate mortar; B, unground crystals; C, sample ground in a ceramic mortar (see Table 2, footnotes f, h and i respectively).

regarding the thermal behaviour of some of the compounds of this group (see e.g. refs. 25, 28–30, 32, 33, 36, 37 and 46). However, we were not able to confirm a rather complicated pattern of thermal changes of isomers of BHC which has been observed by Venugopal et al. [63]. It is probable that, in the

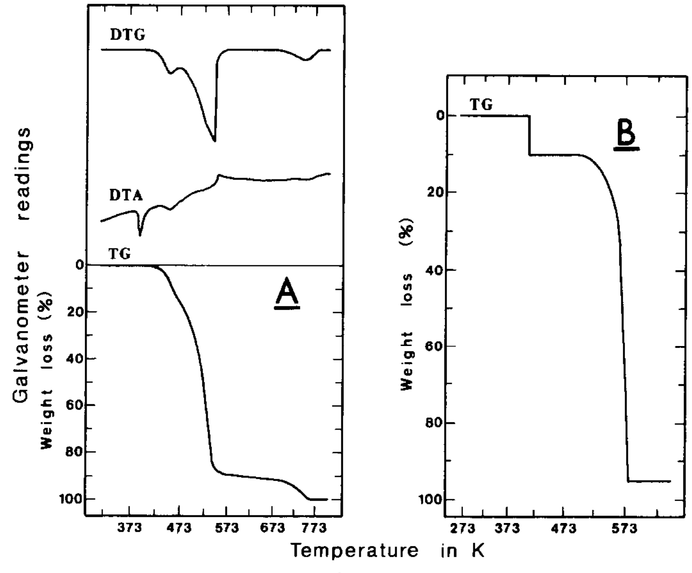

Fig. 3. Thermal analyses of p,p'-DDT: recorded on an OD-103 instrument (A) (see Table 2, footnote g) and on a Q-1500 derivatograph in Q mode (B).

experiments of the above-mentioned authors, the simple volatilization course of these derivatives was affected by some side processes.

Thermoanalytical curves for compounds **1–5**, **8**, **11** and **12** show another interesting feature; at the end of the process the rate slows down causing, in consequence, a characteristic "tail" on the TG curves. In the case of HCB and β-BHC, up to 18% and 16% respectively of the whole sample volatilizes in this slow, second stage. For the compounds whose volatilization is preceded by melting, i.e. the remaining compounds of this group, the effect is somewhat less pronounced. Nevertheless, the "tail" is still noticeable (Fig. 1A). It is worth mentioning that no chemical changes were noticed either in substances undergoing volatilization or trapped from the gaseous phase at temperatures corresponding to the second stage. All the above facts clearly indicate that the observed phenomenon is of a physical nature; its origin will be discussed below.

All the remaining compounds studied, i.e. isomers of DDT, *p,p′*-methoxychlor and dicofol exhibit more complex patterns of changes with heating. Examination of the thermal analysis curves indicates that in the case of the latter compounds also, several reaction steps can be revealed. The elucidation of the first step is particularly important as it can provide information on the nature of the primary processes. Thus, as well as standard thermal analysis measurements, we also undertook complementary studies in order to improve the resolution of the thermoanalytical investigations and to identify at least some of the reaction products.

The thermoanalytical studies of both isomers of DDT gave somewhat unusual results (Figs. 2 and 3, Table 2). Depending on the treatment of the sample before analysis, the course of thermolysis varies markedly. As is demonstrated in Fig. 2A, the thermal analysis curves of *p,p′*-DDT ground in an agate mortar are similar to those observed for compounds with simple volatilization pattern (Fig. 1A). Surprisingly, preparing the sample in the same way but using another agate mortar led to a completely different thermal decomposition pattern (Fig. 3A). Furthermore, the thermal analyses of unground crystals of *p,p′*-DDT (Fig. 2B) and of those ground in a ceramic mortar also differ from each other and are different from those described above. All these facts indicate that the results of thermoanalytical examinations of DDT isomers are strongly affected by the history of the sample. At present, we are not able to explain the nature of this phenomenon.

Despite the observed peculiarities of the decomposition of *p,p′*-DDT, the thermal processes can be outlined as follows. The compound begins to decompose at around 400 K with simultaneous loss of mass of the sample. The decomposition temperature mentioned above correlates well with those reported in the literature [41,56]. The first reaction step, marked by unresolved peaks on the thermoanalytical curves, is clearly separated from subsequent stages when analysis is performed in Q mode (Fig. 3B). The

TABLE 2

Thermal analysis data for chloro-organic pesticides and related compounds

Substance ^{a}		Temperature (K) and character of peaks ^{b,c}					Temperature ^{b}		Parameters of the onset of the second stage ^{d}	
No.	Common name	DTG	DTA				Of the onset of decom- position ($T_{0.01}$)	Of the comple- tion of decom- position ($T_{0.99}$)		
		T_p	Exo	Endo						
			T_p	T_m^{e}		T_p			α	T (K)
				This work	From literature (refs. in square brackets)					
1	α-BHC	504s,sh		443m,sh (423–430)	426–433 [28,42,61,73–80]	504m	415	540	0.90	505
2	β-BHC	546s,sh		(571d)	571–583 [28,42,61,74–77,81]	546m	460	640	0.84	555
3	γ-BHC (Lindane)	516s,sh		394m,sh (382–386)	385–387 [28,42,61,73–78, 80,82–84]	516m	400	535	0.96	515
4	HCB	507s,sh		(493–497d)	499–503 [85–88]	504m,sh	410	565	0.82	515
5	PCNB	505s,sh		424m,sh (415–418)	417–420 [62,89–91]	505m	415	535	0.94	510
6	p,p'-DDT	557s,sh ^{f}		391m,sh (379–381)	380–382 [42,67,80,92–95]	559m,b ^{f}	436 ^{f} 401 ^{j}	495 ^{f}	0.95 ^{f}	560 ^{f}
		450m,b; 543m,sh; 748m,b ^{g}	723w ^{g}			450m,b; 543m,b; 746w,b ^{g}	426 ^{g}	763 ^{g}		
		432m,sh; 539s,sh ^{h}				435m,b; 541m,b ^{h}	423 ^{h}	581 ^{h}		
		421m,sh; 541s,sh ^{i}				422m,sh; 543m,b ^{i}	417 ^{i}	613 ^{i}		

7	o,p'-DDT	481m,b; 536s,sh; 748w,b [g]	728w,b [g]	356m,sh (347–350)	346–347 [80,93]	475m,b; 533m,b;424 [j] 748w,b [g]	431 [g]	755 [g]		
		444w,sh; 540s,sh [h]				447w,b; 540m,b [h]	426 [h]	613 [h]		
		422m,sh; 545s,sh [i]				424m,sh; 543m,b [i]	411 [i]	618 [i]		
8	α-Chloro–DDT	555s,sh		376m,sh (365–367)	363–366 [65,93,96]	555m,b	445	605	0.89	560
9	Dicofol	474w,b; 546s,sh		357m,sh (342–345)	348 [62]	546m,b	445	645		
10	p,p'-Methoxychlor	557s,sh; 779m,b	778s,b	375m,sh (357–361)	358–367 [67,93,97,98]	578m,b	430 423 [j]	840		
11	p,p'-DDE	535s,sh		373m,sh (361–363)	359–362 [65,93,99]	537m,b	425	655	0.87	540
12	p,p'-DMDE	555s,sh		396m,sh (380–386)	383–386 [67,98,100,101]	556m,b	460	630	0.86	560

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[a] The chemical names of the compounds: **1** = 1α,2α,3β,4α,5β,6β-hexachlorocyclohexane (isomer α); **2** = 1α,2β,3α,4β,5α,6β-hexachlorocyclohexane (isomer β); **3** = 1α,2α,3β,4α,5α,6β-hexachlorocyclohexane (isomer γ); **4** = hexachlorobenzene; **5** = pentachloronitrobenzene; **6** = 1,1′-(2,2,2-trichloroethylidene)bis(4-chlorobenzene); **7** = 1-chloro-2-(2,2,2-trichloro-1-(4-chlorophenyl)ethyl)benzene; **8** = 1,1′-(tetrachloroethylidene)bis(4-chloro-benzene); **9** = 4-chloro-α-(4-chlorophenyl)-α-(trichloromethyl)benzenemethanol; **10** = 1,1′-(2,2,2-trichloroethylidene)bis(4-methoxybenzene); **11** = 1,1′-(dichloroethenylidene)bis(4-chlorobenzene); **12** = 1,1′-(dichloroethenylidine)bis(4-methoxybenzene).

[b] The symbols were taken from ref. 72. T_p = temperature of the peak, T_m = temperature of melting, and T_α = temperature at which the degree of conversion is equal to α (i.e. $T_{0.1} = T_{\alpha=0.1}$).

[c] w = weak, m = medium, s = strong, sh = sharp and b = broad.

[d] Characterizes substances undergoing simple volatilization upon heating.

[e] The m.p. determined by a standard capillary method is given in parentheses; d indicates that fusion is accompanied by the simultaneous mass loss of a sample.

[f] Sample ground in an agate mortar (in the case of p,p'-DDT see Fig. 2A).

[g] Sample ground in a different agate mortar (in the case of p,p'-DDT see Fig. 3A).

[h] Crystals not ground (in the case of p,p'-DDT see Fig. 2B).

[i] Sample ground in a ceramic mortar (in the case of p,p'-DDT see Fig. 2C).

[j] The decomposition point determined on the basis of thermogravimetric measurements performed on a Q-derivatograph (in Q conditions).

weight loss for this step corresponds exactly to the release of 1 molecule of HCl from 1 molecule of the substrate. Taking into account the above fact, as well as some literature reports [21,34,41,42,55,56,59,102–104], it is clear that the primary step in the thermolysis of *p,p'*-DDT is elimination of HCl accompanied by the formation of *p,p'*-DDE in the condensed phase. Indeed, the residue in the reactor and the deposit on the cold finger after heating *p,p'*-DDT at temperatures corresponding to the first step (425 K), were both identical with a sample of pure *p,p'*-DDE which tends to confirm the above assumption. Further stages in the thermolysis of *p,p'*-DDT should, therefore, be similar to those expected for *p,p'*-DDE; this was fully supported by a comparison of the thermoanalytical curves for *p,p'*-DDT and *p,p'*-DDE. The decomposition of both latter compounds was not examined in detail at higher temperatures. On the basis of the thermoanalytical data, it can be suggested that *p,p'*-DDE starts to volatilize at the onset of the process. However, at higher temperatures, side reactions sometimes also occur causing partial carbonization of the sample. The last step in the TG curve of *p,p'*-DDT (Fig. 3A) has an exothermic character and is presumably accompanied by oxidation of the residue. Because of the construction of the apparatus, oxygen from the air is always present in the reaction zone. It should be mentioned, however, that volatilization of pure *p,p'*-DDE was never accompanied by side processes at higher temperatures.

The course of the thermal decomposition of *o,p'*-DDT is similar to that described above for *p,p'*-DDT. The first thermolysis step is not as well separated as in the case of the *p,p'*-isomer; however, it is also accompanied by release of HCl. The decomposition of this isomer starts at a somewhat higher temperature than that of the *p,p'*-isomer.

p,p'-Methoxychlor begins to decompose at roughly the same temperature as *o,p'*-DDT. The elimination of HCl which could be expected on the basis of the investigations for DDT isomers, as well as some literature information [103,104], does not occur as a separate step (Fig. 1B). To clarify this stage, analysis was performed in Q conditions when the first stage at the onset of thermolysis of the compound became apparent although it was still not well separated. The weight loss for this stage was a little higher than that corresponding to the release of HCl. To analyse the reaction products, the process was stopped just at the end of this step, and the residue was subjected to various analyses. These investigations revealed that the solid residue is composed of at least 3 substances. The major product was identified as 1,1'-(dichloroethenylidene)bis[4-methoxybenzene]. Moreover, it was confirmed by a standard method that HCl is actually released at the onset of the overall decomposition process. The combination of these facts leads to the conclusion that the primary decomposition proceeds on at least three separate pathways. Among them is elimination of HCl accompanied by formation of *p,p'*-DMDE. As is shown in Fig. 1B, over 80% of original sample is evolved as gaseous products in the complex first period of the process. The release of gaseous substances is presumably associated with a partial carbonization of the solid phase. These non-volatile substances form the residue which undergoes oxidation accompanied by a strong exothermic effect. This is seen as a second stage on the TG curve (c.f. Fig. 1B).

Dicofol, which differs from p,p'-DDT by the presence of an OH group instead of a hydrogen atom in the ethane moiety, starts to decompose at a higher temperature than do the isomers of DDT and p,p'-methoxychlor (Table 2). The thermoanalytical curves indicate the complex thermolysis course of this compound. Detailed studies of the thermal decomposition of dicofol have not been undertaken. However, on the basis of the thermoanalytical curves, one can discern two principal reaction stages. The first, accompanied by a several percent weight loss of the sample, exhibits a decomposition pattern similar to that characteristic for the isomers of DDT or methoxychlor. In the second step, the remaining part of the sample volatilizes. The temperature and shape of the thermoanalytical curves corresponding to this latter stage are very close to those for p,p'-DDE. This would imply that in the first step, the molecule of dicofol loses OH and Cl to form p,p'-DDE. The latter compound is completely transferred to the gaseous phase at higher temperatures. It is worth mentioning that under certain conditions dicofol can be metabolically converted to p,p'-DDE [105].

Careful examination of the thermal analysis curves reveals that for all the compounds studied, with the exceptions of β-BHC and HCB, an additional effect was recorded before the onset of volatilization or decomposition (Table 2). These effects result from the melting of the pesticides. The temperatures of the DTA peaks corresponding to this process are always somewhat higher than the literature m.p. values, and than those determined by the standard capillary method. This feature is characteristic of dynamic thermoanalytical methods. However, the effect resulting from fusion of β-BHC and HCB is not seen in the DTA curves although the literature information predicts the existence of a melting point for these derivatives. The lack of T_m peaks for these two compounds is presumably due to the fact that the fusion begins when volatilization of the compounds is far advanced. Thus, the weak thermal effects resulting from melting are overlapped by the much stronger effects which accompany the volatilization process.

The examination of characteristic temperatures of the thermal processes provides qualitative information on the volatility and thermal stability of the compounds studied. Among hexachlorocyclohexanes, the β isomer is the less volatile one. Volatility of HCB and PCNB is comparable to that of α-BHC. DDT isomers and p,p'-methoxychlor are unstable at higher temperatures, whereas the related compounds with the ethene moiety are generally stable at volatilization temperatures. α-chloro-DDT and dicofol have a lower tendency to changes with rising temperature than does p,p'-DDT.

Thermodynamics of the thermal processes

For the compounds exhibiting simple volatilization patterns, the thermodynamics of the process can be examined assuming that the system attains equilibrium at any stage (equilibrium hypothesis). This implies that the only barrier existing for the process is a thermochemical one, i.e. ΔH_v. Moreover, experimental conditions must be such that the process is close to the equilibrium state. Thus, the analyses were performed at a moderate heating rate using as small a sample as possible. Furthermore, the compounds were analysed in a thin layer placed on a relatively large surface to enable free diffusion of gaseous molecules and to avoid side processes. If equilibrium is achieved, the experimental value of the extent of the process α at a given temperature T determines the ratio of the equilibrium vapour pressure P to the outward pressure P_o (atmospheric pressure).

The thermodynamics of the volatilization process is described by the Clausius–Clapeyron equation,

$$\left(\frac{\partial \ln P}{\partial T}\right)_{P_o} = \frac{\Delta H_v^{\ominus}}{RT^2} \tag{1}$$

where R is the gas constant and other symbols are described above. Rearranging eqn. (1) one obtains

$$\int_P^{P_o} \mathrm{d} \ln P = \frac{\Delta H_v^{\ominus}}{R} \int_T^{T_v} \frac{\mathrm{d}T}{T^2} \tag{2}$$

and after integration

$$\ln \frac{P}{P_o} = \frac{\Delta H_v^{\ominus}}{R} \frac{1}{T_v} - \frac{\Delta H_v^{\ominus}}{R} \frac{1}{T} \tag{3}$$

where T_v is the volatilization temperature at P_o (the boiling temperature in the case of liquids). The first term of the right hand side is a constant for a given substance. Thus by plotting ln α against $1/T$, one can determine both $\Delta H_v^{\ominus}$ and the constant. For compounds with a simple thermolysis course, the values of both latter quantities are listed in Table 3. To investigate the problem further, the volatilization temperatures and the temperatures of the onset and of the completion of the process on the basis of eqn. (3) were also determined. They are also shown in Table 3. It is interesting to compare the thermochemical characteristics derived in this work with those reported in the literature. The agreement is rather poor. The main reason for the observed discrepancies is that the values in the present work correspond to much higher temperatures than those determined by other authors. A more valid comparison would be of values corresponding to the ambient temperature at which all the studied compounds remain in the solid phase. This

TABLE 3

Thermochemical and kinetic characteristics for chloro-organic pesticides and related compounds exhibiting a simple volatilization pattern

Substance	Thermochemical characteristics [b]								Kinetic constants [d]	
No. (see Table 2)	Constant		$\Delta H_v^{\ominus}$ [c]	(kJ mol^{-1})	$T_{0.01}$ (K)	$T_{0.99}$ (K)	T_v (K)	$\Delta H_v^{\ominus} + \Delta H_{fn}^{\ominus}$ (kJ mol^{-1})	Z (s^{-1})	E_a (kJ mol^{-1})
	This work	From literature	This work	From literature (refs. in square brackets)						
1	18.4	12.5 [28]	77.8	56.5 (293–333) [28]	407	508	509		5.9×10^3	73.8
		20.9 [29]	(454–505)	92.9 (324–344) [29]						
		22.9 [32]		98.0 (313–343) [32]						
2	22.4	28.3 [28]	103.7	97.3 (293–333) [28]	462	557	557		3.1×10^5	99.3
		20.5 [29]	(506–551)	102.9 (368–390) [29]						
		23.4 [32]		110.6 (313–343) [32]						
3	17.7	13.0 [28]	76.3	56.3 (293–333) [28]	411	518	518	91.5	3.2×10^3	72.3
		29.1 [29]	(457–514)	115.3 (333–365) [29]						
		20.5 [32]		89.7 (313–343) [32]						
		24.6 [33]		101.3 (293–313) [33]						
4	20.0	19.6 [30]	85.5	91.8 (369–397) [30]	418	514	514		3.1×10^4	81.5
			(461–506)	75.3 [36]						
		23.2 [37]		101.1 (288–318) [37]						
		13.1 [106]		63.7 (388–583) [106]						
5	16.7		70.7		399	509	509	89.1	1.2×10^3	66.8
			(448–507)							
6 [a]	16.6	26.0 [29]	77.5	117.9 (339–373) [29]	440	561	562	106.1	9.2×10^4	73.1
		25.1 [31]	(493–559)	115.1 (323–363) [31]						
8 [a]	19.0		89.4		456	566	566		1.1×10^6	85.0
			(503–558)							
11	16.4		74.2		425	544	544		8.1×10^2	70.0
			(476–536)							
12	16.9		79.2		443	563	564		1.3×10^3	74.8
			(495–557)							

[a] Possibility of the occurrence of chemical processes upon volatilization.

[b] Values derived from eqn. (3) or corresponding to this equation.

[c] The temperature range in which the thermochemical quantities were evaluated is indicated in parentheses.

[d] Values evaluated from the logarithmic form of eqn. (6) for the Polanyi–Wigner kinetic model (zero kinetic order model) for the volatilization process: $g(1-\alpha) = \alpha$.

would require a modification of the values of $\Delta H_{\mathrm{v}}^{\ominus}$ derived from eqn. (3) according to the equation

$$\Delta H_{\mathrm{v},298}^{\ominus} = \Delta H_{\mathrm{v}}^{\ominus} + \Delta H_{\mathrm{fn}}^{\ominus} + \int_{298}^{T_{0.01}} C_p^{\ominus} \mathrm{d}T \qquad (4)$$

where $\Delta H_{\mathrm{v},298}^{\ominus}$ is the enthalpy of volatilization at ambient temperature, $\Delta H_{\mathrm{fn}}^{\ominus}$ denotes the enthalpy of fusion while the term $\int_{298}^{T_{0.01}} C_p^{\ominus} \mathrm{d}T$ accounts for the changes in enthalpy resulting from changes in the heat capacity of the condensed phase. Values of the enthalpies of fusion are reported for only a few of the compounds studied: γ-BHC, 15.2 [82]; HCB, 23.9 [106]; PCNB, 18.4 [62]; *p,p′*-DDT, 28.6 [107]; and dicofol, 23.9 [62] (values of $\Delta H_{\mathrm{fn}}^{\ominus}$ in kJ mol^{-1}). An attempt was made to estimate the values of $\Delta H_{\mathrm{fn}}^{\ominus}$ for the remaining compounds on the basis of the empirical relationship relating to the entropy of fusion: $\Delta S_{\mathrm{fn}}^{\ominus} = \Delta H_{\mathrm{fn}}^{\ominus}/T_{\mathrm{m}} = \mathrm{const}$, assuming that $\Delta S_{\mathrm{fn}}^{\ominus}$ has the same value for any of the compounds examined in this work. Unfortunately, this was not successful because the above dependency does not apply to these derivatives. The estimated values of the entropy of fusion, on the basis of the above-mentioned heats of fusion, differ from each other by more than 100% and do not show any correlation with the structure of the molecules.

The magnitude of the heat capacity term is also difficult to assess in the absence of $C_p^{\ominus}$ data for the compounds examined in the condensed phase. On the basis of the heat capacity data for HCB in the range 100–335 K [20], $C_p^{\ominus}$ can be approximated by the expression: $14.4 + 0.81\ T$ (in J mol^{-1} K^{-1}). Similarly, the heat capacity data from the work of Hildebrand et al. [24], corresponding to the temperature range 100–300 K, can be approximated with the equation $62.7 + 0.48\ T$ (in J mol^{-1} K^{-1}). Assuming that both the above relationships are also valid within the temperature limit 298 K–$T_{0.01}$, we estimated the values of the heat capacity term to be 33.7 and 26.0 kJ mol^{-1}, respectively. These crude estimations clearly demonstrate that the value of the heat capacity term is comparable to that of the enthalpy of fusion of HCB and cannot be ignored in eqn. (4). One can expect similar regularity in the case of other compounds studied.

The above discussion reveals that it is difficult to modify the values of $\Delta H_{\mathrm{v}}^{\ominus}$ derived in this work so as to obtain reliable values of this quantity at 298 K. It is demonstrated, however, that values of the enthalpy of volatilization at ambient temperature would be several percent higher than those derived in this work. To assess the magnitude of these modifications, Table 3 shows the values of $\Delta H_{\mathrm{v}}^{\ominus} + \Delta H_{\mathrm{fn}}^{\ominus}$ for the compounds whose heats of fusion are known. These modified values, which represent the uncorrected standard temperature enthalpies of sublimation, fit much better with those reported in the literature. Only in the case of HCB has this modification been ignored as the fusion of the compound occurs when the volatilization process is far advanced and thus the experimental TG curves actually correspond to the sublimation of this derivative.

It is interesting to compare the values of temperatures derived on the basis of eqn. (3) for the onset of the process (Table 3) with those determined from the thermoanalytical measurements (Table 2). The agreement is satisfactory with the exception of *p,p′*-DDT. The latter discrepancy is caused by the fact that this compound begins to decompose before the onset of volatilization. The values of the volatilization temperatures (Table 3), however, are generally lower than the experimentally determined temperatures of the completion of volatilization (Table 3). This results from the fact that at the end of volatilization, the process is far from equilibrium and the thermodynamic energy barrier is not the only one controlling the process.

Compounds **6**–**10** more or less undergo thermal decomposition upon heating. The thermal behaviour of these derivatives could be explained by an examination of their thermochemistry. Unfortunately, no thermochemical data are available either for the parent molecules or for the expected organic decomposition products. To elucidate this matter, an attempt was made to evaluate the heats of formation of the gaseous compounds **6**–**10** and their related derivatives at 298 K, on the basis of Benson's group additivity method [108]. For this purpose, the following values of group parameters were taken from the original work of Benson et al. [108] (in kJ mol^{-1}): C–(C)(Cl)$_3$, −86.6; C$_B$–(H), 13.8; C$_B$–(C), 23.1; C$_B$–(C$_D$), 23.8; C$_B$–(O), −7.5; C$_B$–(Cl), −15.9; C$_D$–(Cl)$_2$, −7.5; CO–(C$_B$)$_2$, −163.6; O–(C)(H), −158.5 and O–(C)(C$_B$), −94.6. The value of the parameter for the C–(H)$_3$(O) group was found to be −39.5 kJ mol^{-1} by combining the values of the heat of formation of gaseous methoxybenzene given in ref. 108 and derived from the heats of combustion and vaporization of the compound reported in ref. 106, with adequate group parameters from ref. 108. Similarly, the parameters for C–(C)(C$_B$)$_2$(H) and C$_D$–(C$_B$)$_2$ groups were evaluated to be −29.5 and 27.1 kJ mol^{-1}, respectively, on the basis of heats of formation of gaseous 1,1′-ethylidenebisbenzene and 1,1′-ethenylidenebisbenzene. The latter characteristics were taken from the literature [109] or were derived from the heats of combustion [110,111] and vaporization [112,113] of both above-mentioned compounds. Unfortunately, thermochemical characteristics for α-methyl-α-phenylbenzenemethanol and 1,1′-(1′-chloroethylidene)bisbenzene or related compounds have not, so far, been reported. Therefore, parameters for the C–(C)(C$_B$)$_2$(O) and C–(C)(C$_B$)$_2$(Cl) groups cannot be directly derived. Therefore, it was assumed that for C–(C)(C$_B$)$_2$(O), the values of group parameter are −15.4 kJ mol^{-1}. This was estimated by comparison of the values of group parameters reported in ref. 108 with those derived on the basis of known heats of combustion and vaporization of benzenemethanol and α-phenylbenzenemethanol [108]. Lastly, for the C–(C)(C$_B$)$_2$(Cl) group, the value of the group parameter was assumed to be the same as for C–(C)$_3$(Cl), i.e. −53.6 kJ mol^{-1} [108]. Using the above-mentioned values of group parameters and introducing adequate

TABLE 4

Enthalpies of formation and thermochemistry of the decomposition process [a]

Substance	$\Delta H^{\ominus}_{f,g}$	Thermal process [b,c]	$\Delta H^{\ominus}_{r}$
p,p'-DDT	12.0	p,p'-DDT → p,p'-DDE + HCl	45.7
o,p'-DDT	17.0	o,p'-DDT → o,p'-DDE + HCl	45.7
α-Chloro-DDT	−12.1	α-chloro-DDT → p,p'-DDE + Cl_2	162.1
Dicofol	−122.3	dicofol → p,p'-DDE + $1/2Cl_2O$ + $1/2H_2O$	189.5
		→ $(4\text{-ClPh})_2CO$ + $HCCl_3$	−58.9
p,p'-Methoxychlor	−239.4	p,p'-methoxychlor → p,p'-DMDE + HCl	45.7
p,p'-DDE	150.0		
o,p'-DDE	155.0		
p,p'-DMDE	−101.4		
$(4\text{-ClPh})_2CO$ [d]	−80.8		

[a] All enthalpy values in kJ mol^{-1}.

[b] $\Delta H^{\ominus}_{r}$ represents the enthalpy of the reaction corresponding to the process taking place with all reactants in the gaseous phase.

[c] Values used in the $\Delta H^{\ominus}_{r}$ calculations (kJ mol^{-1}) [106]: $\Delta H^{\ominus}_{f,g}$ [HCl] = −92.3; $\Delta H^{\ominus}_{f,g}$ [H_2O] = −241.9; $\Delta H^{\ominus}_{f,g}$ [Cl_2O] = 76.2; and $\Delta H^{\ominus}_{f,g}$ [$HCCl_3$] = −100.4.

[d] $(4\text{-ClPh})_2CO$ = bis(4-chlorophenyl)methanone.

next-nearest neighbour corrections on the basis of ref. 108, the standard enthalpies of formation of gaseous compounds have been evaluated and are listed in Table 4. The above data enabled the estimation of the enthalpy changes for the expected thermal processes and these characteristics are also shown in Table 4.

Despite the approximate nature of the latter estimation, some general features regarding the thermochemistry of the compounds studied are revealed. DDT and DDE isomers are characterized by positive enthalpy of formation values in the gaseous phase, and thus, in these conditions, the compounds may be expected to be thermodynamically unstable. Transfer of molecules to the solid phase would lower all the $\Delta H^{\ominus}_{f}$ values by at least $\Delta H^{\ominus}_{v} + \Delta H^{\ominus}_{fn}$. Taking into account the values of the latter quantities listed in Table 3, one can expect that all the compounds studied, with the exception of the DDE isomers, should be thermodynamically stable in the solid phase at ambient temperature.

A temperature increase may cause volatilization of the compounds or may initiate chemical changes in the system. The course of the thermal processes will, in the first approximation, be determined by their thermodynamics. Alkane-type derivatives, i.e. DDT isomers or p,p'-methoxychlor should fairly readily undergo dehydrochlorination at higher temperatures as the process is accompanied by a moderate endothermic effect. Therefore, a temperature increase will move the system towards a state of higher thermodynamic probability as a result of the general rules of chemical thermodynamics. The much higher thermochemical barrier for the dechlorination of

α-chloro-DDT implies that it should be much more stable than DDT isomers and methoxychlor; this is fully confirmed by the results of our study. Only minor changes of the system accompany the volatilization process of this compound. On the other hand, for the decomposition of dicofol, two reaction pathways can be predicted. The decomposition of the molecule to form bis(4-chlorophenyl)methanone and $HCCl_3$ is exothermic and the process should occur immediately in ambient temperatures. As this behaviour of the compound is not known, this reaction pathway must be restricted by a high kinetic barrier. The decomposition of dicofol to form p,p'-DDE accompanied by the elimination of OH and Cl requires, for thermodynamical reasons, that a high energy level be reached and thus is not very probable. Presumably, the overall process in this case is rather complicated. It is worth mentioning that processes taking place with organic reactants in condensed phases are characterized by enthalpy effects similar to those shown in Table 4, as the enthalpies of volatilization are comparable for both substrates and products.

Kinetics of volatilization

The compounds listed in Table 3 undergo volatilization with heating and, thus, an attempt was made to examine the kinetics of this process. According to the classical approach, the kinetics of processes in non-isothermal conditions can be approximated with the Arrhenius-type equation [114]

$$g(1-\alpha) = Z(T/\Phi)\,\mathrm{e}^{-E_a/(RT)} \qquad (5)$$

where $g(1-\alpha)$ is the function describing the kinetic model for the process, Φ denotes the heating rate, and E_a and Z are the Arrhenius constants, and E_a can be identified with the kinetic activation barrier for the process. Values of both constants depend on the choice of the $g(1-\alpha)$ function. In this work we considered several such functions [71]. Rearranging eqn. (5) to the form

$$\ln[g(1-\alpha)/T] = \ln Z/\Phi - (E_a/R)(1/T) \qquad (6)$$

the standard least-squares procedure to evaluate both constants was used. Considering the linear correlation coefficient as a factor determining the measure of the fit, it was found, however, that several kinetic models fit quite well with the experimental α versus T dependencies. In Table 3, values of both constants for the Polanyi–Wigner model (zero kinetic order mechanism) are shown which, on the basis of chemical intuition, seem to most adequately describe the kinetics of the evaporation processes. If the process actually proceeds according to this model, it would not be required to overcome any additional barrier over that resulting from the thermodynamic requirements. Another model which could be considered is that describing the processes taking place on the surface of a condensed phase (R2 mechanism). Using this model, the values of E_a obtained were always around 10% higher than the appropriate ΔH_v values. For the R2 mechanism, this would mean that the process would have to overcome some activation barrier over ΔH_v. Thus, it can be concluded that the R1 mechanism best represents the kinetics of the volatilization process in this simple approach.

Equations (5) and (6) well describe the kinetics of the process in the first fast stage (Fig. 1A). This approach, however, is no longer valid at the end of the volatilization when the rate considerably slows down. One of the theories accounting qualitatively for this effect is that outlined by Jacobs and Russell-Jones [115]. The main premise of this approach is that the migration of molecules over the surface of a condensed phase is the crucial step in the volatilization process. According to the authors, the rate of volatilization can be expressed with the equation which, with linearly increasing temperature conditions, has the form [115,116]

$$\left(X_2 T - \frac{\Delta}{a_o}\right)\left[1 - (1-\alpha)^{\frac{1}{3}}\right] + \tfrac{1}{2}\left[1 - (1-\alpha)^{\frac{2}{3}}\right] - \left(\frac{\Delta}{a_o}\right)^2 \ln\left[\frac{(1-\alpha)^{\frac{1}{3}} + \Delta/a_o}{1 + \Delta/a_o}\right] = \frac{1}{3}\frac{X_1}{\Phi} T^{\frac{3}{2}} \exp[-E_a/(RT)] \qquad (7)$$

where X_1 and X_2 are constants, a_o represents the initial radius of particles from which the volatilization process occurs, Δ denotes the distance between collisions (i.e. the distance which a molecule travels after leaving the condensed phase before a collision occurs), and the meaning of the other symbols is as given above. According to this approach, the rate of the process slows down when the mean free path for the molecules increases in comparison with the geometric surface area of the drops or crystals, i.e. when Δ approaches a_o in magnitude. This would take place at the beginning and end of the process. Presumably this phenomenon causes the effect seen as a "tail" on the TG curves (see e.g. Fig. 1A).

In this work, some aspects of the thermochemistry and the thermal properties of several important, from the practical point of view, chloroorganic pesticides have been examined, reviewed and discussed. Our studies have proved that the compounds are characterized by a relatively high thermal stability. It is thus not very probable that they will decompose in the environment along thermal pathways. On the other hand, in natural conditions many substances can act catalytically, substantially lowering activation barriers for numerous thermal processes. This fact indicates the direction of further investigations in this area.

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REFERENCES

1 R. White-Stevens, Pesticides in the Environment, Vol. 1, Marcel Dekker, New York, 1971; Polish translation, PWRiL, Warsaw, 1977.
2 S. Byrdy, K. Górecki and E. Łaszcz, Pesticides, PWRiL, Warsaw, 1976.
3 Environmental Health Criteria, No. 9: DDT and Its Derivatives, World Health Organization (WHO), Geneva, Switzerland, 1979.
4 T.H. Jukes, Int. J. Environ. Stud., 1 (1970) 43.
5 M.D. Reuber, EHP, Environ. Health Perspect., 36 (1980) 205.
6 M.D. Reuber, J. Environ. Pathol. Toxicol., 4 (1982) 355.
7 M. Spindler, Residue Rev., 90 (1983) 1.
8 T.J. Haley, Dangerous Prop. Int. Mater. Rep., 5 (1985) 11.
9 G. Renner, H.H. Otto and P.T. Nguyen, Toxicol. Environ. Chem., 10 (1985) 119.
10 A. Jori, Ann. Inst. Super. Sanita, 23 (1987) 147.
11 H. Choudhury, J. Coleman, F.L. Mink, C.T. DeRosa and J.F. Stara, Toxicol. Ind. Health, 3 (1987) 5.
12 J. Ashby and R.W. Tennant, Mutat. Res., 204 (1988) 17.
13 D.K.R. Steward and D. Chisholm, Can. J. Soil Sci., 61 (1971) 379.
14 H.V. Morley, Environ. Sci. Res., 10 (1977) 53.
15 T.S.S. Dikshith, J. Sci. Ind. Res., 37 (1978) 316.
16 P. Michel and A. Abarnou, Bull. Acad. Natl. Med. (Paris), 167 (1983) 491.
17 S.J. Yosim, K.M. Barclay and L.F. Grantham, ASC Symp. Ser., 1978, 73 (Disposal Decontam. Pestic.) (1978) 118; Chem. Abstr., 89 (1978) 101531s.
18 C. Borket-Verhage, C. Cheng, L. De Galan and E.W.B. De Leer, Contam. Soil, Int. TNO Conf., (1985) 883; Chem. Abstr., 104 (1986) 124839r.
19 R.A. Carnes and B. Dellinger, Toxicol. Environ. Chem., 14 (1987) 307.
20 D.H. Andrews and E. Haworth, J. Am. Chem. Soc., 50 (1928) 2988.
21 I.E. Balaban and F.K. Sutcliffe, Nature, 155 (1945) 755.
22 K. Schwabe, Chem. Tech., 5 (1953) 392.
23 K. Schwabe, Z. Elektrochem., 60 (1956) 151.
24 D.L. Hildebrand, W.R. Kramer and D.R. Stull, J. Phys. Chem., 62 (1958) 958.
25 I.B. Johns, E.A. McElhill and J.O. Smith, J. Chem. Eng. Data, 7 (1962) 277.
26 J.B. Butler and J. Lielmezs, J. Chem. Eng. Data, 14 (1969) 335.
27 V.A. Platonov and Yu.N. Simulin, Zh. Fiz. Khim., 57 (1983) 1387.
28 R.E. Slade, Chem. Ind., (1945) 314.
29 E.W. Balson, Trans. Faraday Soc., 43 (1947) 54.
30 G.W. Sears and E.R. Hopke, J. Am. Chem. Soc., 71 (1949) 1632.
31 W. Dickinson, Trans. Faraday Soc., 52 (1956) 31.
32 K. Schwabe and C. Legler, Z. Elektrochem., 64 (1960) 902.

33 W.F. Spencer and M.M. Cliath, J. Agr. Food Chem., 18 (1970) 529.
34 W.F. Spencer and M.M. Cliath, J. Agr. Food Chem., 20 (1972) 645.
35 T. Kawahara, Noyaku Kensasho Hokoku, (1972) 46, 49; Chem. Abstr., 81 (1974) 34512f and 34513g.
36 H. Steinwandter, Chemosphere, 6 (1977) 59.
37 W.J. Farmer, M.S. Yang, J. Letey and W.F. Spencer, Soil Sci. Soc. Am. J., 44 (1980) 676.
38 W.D. Guenzi and W.E. Beard, Soil Sci. Soc. Am. Proc., 34 (1970) 443.
39 N. Khan, S. Ferhat, M.M.H. Biag and K.A. Lord, Pak. J. Sci. Ind. Res., 15 (1972) 227.
40 R. Siddaramappa and N. Sethunathan, J. Environ. Sci., B11 (1976) 119.
41 A.L. Flenner, J. Am. Chem. Soc., 68 (1946) 2399.
42 F.A. Gunther, J. Econ. Entomol., 40 (1947) 874.
43 Z. Eckstein, Z. Mazankowa and J. Orlowski, Przem. Chem., 41 (1962) 649, 705.
44 N.M. Chopra, J.J. Domanski and N.B. Osborne, Beitr. Tabakforsch., 5 (1970) 167.
45 M.V. Kennedy, B.J. Stojanovic and F.L. Shuman, J. Agr. Food Chem., 20 (1972) 341.
46 H. Nagayoshi, R. Kaneko and K. Suzuki, Noyaku Kensasho Hokoku, (1980) 23; Chem. Abstr., 95 (1981) 92338d.
47 B. Dellinger, J.L. Torres, W.A. Rubey, D.L. Hall, J.L. Grahan and R.A. Carnes, Hazard. Waste, 1 (1984) 137.
48 N.M. Chopra and N.B. Osborne, Anal. Chem., 43 (1971) 849.
49 R.R. Whetstone, F.C. Davis and S.A. Ballard, J. Am. Chem. Soc., 75 (1953) 1768.
50 H. Elias, K.H. Lieser and H.W. Kohlschutler, Chem. Ber., 93 (1960) 2128.
51 M. Suwanai and S. Moriya, Noyaku Seisan Gijutsu, 16 (1967) 9; Chem. Abstr., 67 (1967) 21469h.
52 T. Kawahara and M. Moku, Noyaku Kansasho Hokoku, (1972) 35; Chem. Abstr., 81 (1974) 34166w.
53 H. Steinwandter and H. Schlueter, Bull. Environ. Contam. Toxicol., 20 (1978) 174.
54 E.E. Fleck and H.L. Haller, J. Am. Chem. Soc., 68 (1946) 142.
55 P.G. Scholefield, S.T. Bowden and W.J. Jones, J. Soc. Chem. Ind., 65 (1946) 354.
56 K.S. Birrell, New Zealand J. Sci., 6 (1963) 169.
57 R. Zinburg and K. Ballschmiter, Chemosphere, 10 (1981) 957
58 R.D. Baker and H.G. Applegate, Agron. J., 62 (1970) 509.
59 M.M. Cliath and W.F. Spencer, Environ. Sci. Technol., 6 (1972) 910.
60 T. Chekareva, R.V. Galiczkin, N.D. Anavieva, N.V. Perfilova, B.P. Strekozov, M.S. Sokolov, A.R. Aliev and G.A. Aliev, Khim. Sel'sk. Khoz., (1981) 29.
61 A. Kofler, Chem. Ber., 84 (1951) 376.
62 C. Plato, Anal. Chem., 44 (1972) 1531.
63 J.S. Venugopal, B.V. Hirannaiah and S.K. Majumder, J. Therm. Anal., 18 (1980) 15.
64 H.G. Wiedemann and G. Bayer, Thermochim. Acta, 92 (1985) 399.
65 O. Grummitt, A. Buck and A. Jenkins, J. Am. Chem. Soc., 67 (1945) 155.
66 E.V. Sergeev, V.N. Egorova, N.M. Zakharov and N.G. Kashirina, USSR 166, 552 (Cl. A01n), Nov. 19, 1964; Appl. Sept. 16, 1963; Chem. Abstr., 62 (1965) 11736h.
67 E.E. Haris and G.B. Frankforter, J. Am. Chem. Soc., 48 (1926) 3144.
68 G. Liptay (Ed.), Atlas of Thermoanalytical Curves, Akadémiai Kiadó, Budapest, 1973.
69 J. Paulik and F. Paulik, Comprehensive Analytical Chemistry, Vol. 12, Part A, Elsevier, Amsterdam, 1981.
70 J. Błażejowski and J. Szychlinski, Thermochim. Acta, 35 (1980) 211.
71 J. Błażejowski, J. Szychlinski and K. Windorpska, Thermochim. Acta, 46 (1981) 147.
72 R.C. Mackenzie, J. Therm. Anal., 21 (1981) 173.
73 F.A. Gunther, Chem. Ind., (1946) 399.
74 S.J. Cristol, J. Am. Chem. Soc., 69 (1947) 388.
75 J. Bolle, Mem. Services Chim. Etat (Paris), 34 (1948) 333; Chem. Abstr., 44 (1950) 6394i.

76 M. Hamada, I. Sasakawa and M. Ohno, Bochu-Kagaku, 10 (1948) 17; Chem. Abstr., 43 (1949) 5894f.
77 D.J. Whittingham and D.L. Garmaise, Can. J. Res., 27B (1949) 415.
78 C.J. Arceneaux, Anal. Chem., 23 (1951) 906.
79 R. Riemschneider and G. Man, Chem. Ber., 90 (1957) 2713.
80 T. Shishido, Nippon Nogei Kagaku Kaishi, 36 (1962) 222; Chem. Abstr., 61 (1964) 7638a,b.
81 J. Hine, R.D. Weimar, P.B. Langford and O.B. Ramsay, J. Am. Chem. Soc., 88 (1966) 5522.
82 M. Nakajima and T. Matsuura, Botyu-Koyaku, 19 (1954) 19; Chem. Abstr., 48 (1954) 11709e.
83 P. Clechet and J.C. Guillot, Bull. Soc. Chim. Fr., (1963) 2481.
84 I. Hrabovecky, J. Paulen and B. Neubauer, Chem. Prumysl., 14 (1964) 342.
85 M.N. Dvornikoff, D.G. Sheets and F.B. Zienty, J. Am. Chem. Soc., 68 (1946) 142.
86 A. Roedig and K. Kiepert, Justus Liebig's Ann. Chem., 593 (1955) 71.
87 D.E. Pearson, H.W. Pope, W.W. Hargrove and V.E. Stamper, J. Org. Chem., 23 (1958) 1412.
88 Anon, Analyst, 87 (1962) 304.
89 W. Qvist and A. Salo, Acta Acad. Aboensis Math. Phys., 8 (1934) No. 4; Chem. Abstr., 29 (1935) 6884^4.
90 A. Roedig and K. Kiepert, Justus Liebig's Ann. Chem., 593 (1955) 55.
91 E.A. Lojewski, U.S. 3,026,358, Mar. 20, 1962, Appl. Nov. 1, 1961; Chem. Abstr., 57 (1962) 7170g.
92 M. Hamada, T. Sasakawa and M. Ohno, Bochu-Kagaku, 10 (1948) 9; Chem. Abstr., 43 (1949) 5894d.
93 M. Hamada and M. Ohno, Bochu-Kagaku, 13 (1949) 19; Chem. Abstr., 44 (1950) 2960i.
94 S.J. Cristol, N.L. Hause, A.J. Quant, H.W. Miller, K.R. Eilar and J.S. Meek, J. Am. Chem. Soc., 74 (1952) 3333.
95 R. Riemschneider, J. Am. Chem. Soc., 75 (1953) 4853.
96 W. Awe and I. Reinecke, Arch. Pharm., 283 (1950) 162.
97 R. Reimschneider, Monatsh. Chem., 84 (1953) 1228.
98 Y.-L. Chen, H-M. Cheng and S.-C. Tsai, Chung Kuo Nung Yeh Hua Hsueh Hui Chih, Spec. Issue, (1965) 1; Chem. Abstr., 65 (1965) 20039b.
99 C.M. Welch and H.A. Smith, J. Am. Chem. Soc., 75 (1953) 1412.
100W. Tadros, A.B. Sakla, A.A.A. Helmg and M.K. Khalil, J. Chem. Soc., (1965) 3994.
101 S.B. Mahato, N.B. Manfal, A.K. Pal and S.K. Maitra, J. Org. Chem., 49 (1984) 718.
102 G.W. Ware, W.P. Cahill and B.J. Estesen, Bull. Environ. Contam. Toxicol., 14 (1975) 88.
103 R.G. Zepp, N.L. Wolfe, L.V. Azarraga, C.H. Cox and C.W. Pape, Arch. Environ. Contam. Toxicol., 6 (1977) 305.
104 N.L. Wolfe, R.G. Zepp, D.F. Paris, G.L. Baughman and R.C. Hollis, Environ. Sci. Technol., 11 (1977) 1077.
105 R.W. Risenbrough, W.M. Jarman, A.M. Springer, W. Walker and W.G. Hunt, Environ. Toxicol. Chem., 5 (1986) 13.
106 CRS Handbook of Chemistry and Physics, 67th edn., 1986–1987, Boca Raton, Florida.
107 A. Van Tets and H.G. Wiedemann, Therm. Anal., Proc. Int. Conf., 2nd, 1 (1968) 121; Chem. Abstr., 72 (1970) 33583g.
108 S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, Chem. Rev., 69 (1969) 279.
109 J. Kao and N.L. Allinger, J. Am. Chem. Soc., 99 (1977) 975.
110 J. Coops, D. Mulder, J.W. Dienske and J. Smittenberg, Recl. Trav. Chim. Pays-Bas, 72 (1953) 785.

111 J. Coops and G.J. Hoijtink, Recl. Trav. Chim. Pays-Bas, 69 (1950) 358.
112 J.H. Beynon and G.R. Nicholson, J. Sci. Instr., 33 (1956) 376.
113 W.S. Holmes and E. Tyrrall, Chem. Ind., (1956) 662.
114 J. Błażejowski, Thermochim. Acta, 76 (1984) 359.
115 P.W.M. Jacobs and A. Russell-Jones, J. Phys. Chem., 72 (1968) 202.
116 J. Błażejowski, Thermochim. Acta, 68 (1983) 233.