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THERMAL BEHAVIOUR OF ORGANOCHLORINE PESTICIDES IN THE PRESENCE OF ALKALINE SUBSTANCES

L. Gruzdiewa, P. Dokurno, J. Rak and J. Błażejowski

Department of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland

Abstract

Selected organochlorine pesticides, namely lindane, PCNB, *p,p*'-DDT and *p,p*'-methoxychlor, and some related compounds (*p,p*'-DDE and *p,p*'-DMDE) were heated in the presence of powdered KOH, Na_2CO_3, CaO and $CaCO_3$ in order to check whether degradation of the compounds is feasible in moderate conditions and temperatures. Thermal analyses, as well as investigations concerning the search for the reaction products revealed that processes occurring at atmospheric pressure are either simple volatilization of organic molecules, observed upon heating of mixtures containing lindane, PCNB, *p,p*'-DDE and *p,p*'-DMDE, or volatilization accompanied with decomposition towards HCl and *p,p*'-DDE and *p,p*'-DMDE, noted when heating mixtures of *p,p*'-DDT and *p,p*'-methoxychlor with alkaline substances, respectively. Complementary theoretical calculations enabled insight into the mechanism of HCl elimination from *p,p*'-DDT and *p,p*'-methoxychlor.

Keywords: decomposition in the presence of alkalies, organochlorine pesticides, theory of HCl elimination, thermal analyses

Introduction

Organochlorine pesticides have been widely used in the last few decades [1–3]. Gradual cumulation of the compounds in the environment (natural waters and soil), and also plant, animal and human tissues [4–10], due to their relatively high stability and specific physicochemical properties, as well as their toxic (also carcinogenic) features [11–17] resulted in their having been withdrawn from use in many countries. However, considerable amounts of some of the compounds are still stored in warehouses, therefore, the problem of their utilization becomes very important.

Most of the investigations carried out in the past concerned thermal degradation [18–27] and incineration or mineralization [9, 28–32] of the compounds. Only sporadically have efforts been undertaken to use these derivatives for other purposes [33, 34].

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Various aspects regarding thermal properties, reactivity and thermochemistry as well as behaviour upon UV-irradiation of several organochlorine pesticides, have been the subject of our previous papers [35, 36]. The present work is devoted to thermoanalytical and thermochemical studies the aim of which is to check whether degradation or incineration of the compounds may take place in the presence of active additives, at moderate temperatures and atmospheric pressure. Several earlier investigations seemed to indicate that organochlorine pesticides may decompose in such conditions [19–23, 25, 27].

Materials and methods

γ-BHC, *p,p*'-DDT and *p,p*'-methoxychlor, all from P.O.Ch. (Poland), were of analytical grade (GC analytical standards) and were used as received. PCNB of pure grade, from Aldrich, was subjected to vacuum sublimation before use. *p,p*'-DDE and *p,p*'-DMDE were synthesized by the methods described in the literature [37, 38]. KOH powder, purchased from Merck, was used as received. Na_2CO_3, CaO and $CaCO_3$, all from P.O.Ch. (Poland), were dried at 373 K and subsequently ground in agate mortar.

The dynamic thermal analyses were carried out on an OD-103 derivatograph (MOM) with α-Al_2O_3 as a reference in a dynamic atmosphere of nitrogen. The sample holder was a typical platinum crucible [39]. The samples analyzed weighted from 130 to 200 mg and were mixtures of an organic substance and an additive with a weight ratio of 1:9. Other operating conditions were: the heating rate, approx. 5 $deg \cdot min^{-1}$, and the sensitivity of TG was 50 mg.

In order to check whether organochlorine compounds undergo degradation upon heating, the complementary experiments were carried out in a manner described previously [40]. Thus, the heating of samples was performed in a quartz reactor with a cold finger inside it. The reactor, with a mixture of organic and alkaline substances at the bottom, was plunged into a bath with Wood's alloy kept at chosen constant temperature, such as to assure volatilization of an organic material. The process was realized in a continuous stream of an inert gas. The gaseous phase was checked for the presence of Cl_2 and HCl. The remainder at the bottom was then subjected to benzene extraction. The extract, as well as the deposit condensing on the cold finger were analyzed by IR and NMR spectroscopy and employing the GC method. The instruments used and the conditions of measurements have been indicated earlier [35].

Quantum chemistry calculations were carried out on a Hewlett-Packard 735 Apollo workstation.

Results and discussion

The result of thermoanalytical examinations *p,p*'-methoxychlor mixed with Na_2CO_3, CaO and $CaCO_3$ (the systems chosen as examples) are presented in

Fig. 1, while Table 1 contains information collected from the examination of thermoanalytical curves of all the systems studied.

All TG curves demonstrate the smooth shape typical for one step thermal processes. DTA curves, however, together with peaks which accompany the mass loss of the samples, also exhibit those resulting from fusion of organic components.

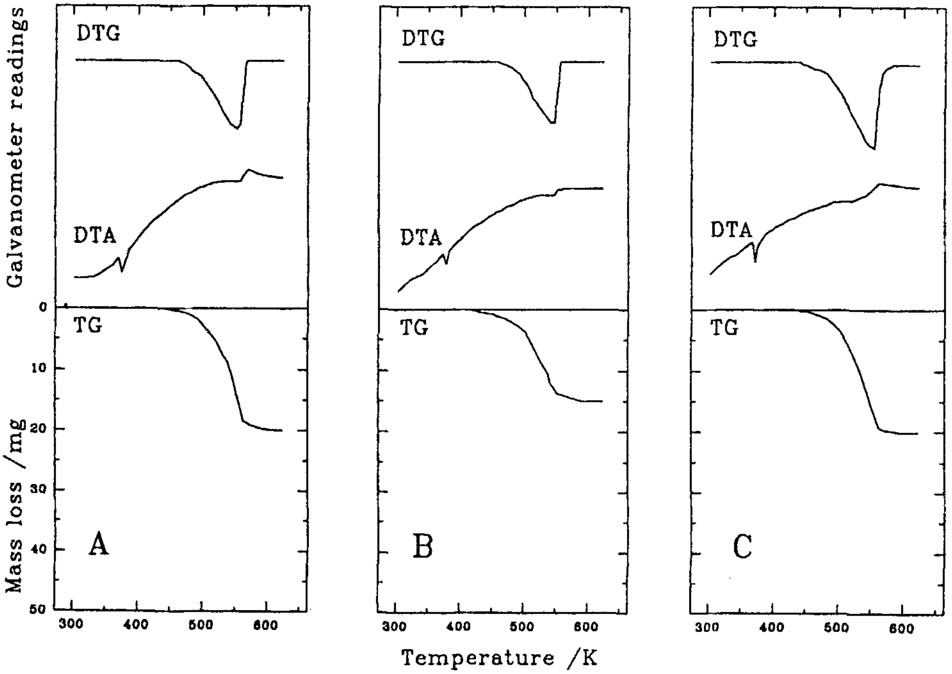

Fig. 1 Dynamic thermal analyses of 1:9 (weight ratio) mixtures of *p,p'*-methoxychlor and: A) Na_2CO_3 (200 mg); B) CaO (150 mg); and C) $CaCO_3$ (200 mg)

The comparison of temperatures characterizing thermal behaviour of neat organochlorine pesticides [35] with those derived in this work for mixtures of these compounds with alkaline substances, is given in Table 1. Only insignificantly does the presence of additives affect the temperatures of melting of organochlorine compounds. On the other hand, the temperatures of DTG and DTA peaks and the onset of weight loss ($T_{0.01}$) are generally lower for the mixtures than for neat organochlorine substances. In many cases, however, these differences are insignificant and contained within the uncertainties of the method applied. This preliminary comparison of thermoanalytical data suggests that the presence of alkaline substances may have a minor effect on the thermal behaviour of organochlorine pesticides.

Table 1 Dynamic thermal analysis data for mixtures of organochlorine pesticides and related compounds with alkaline substances

Components		Mass of the sample/mg	Temperature of peaks /K			$T_{0.01}$	$T_{0.99}$
Pesticide[a]	Additive		DTG	DTA			
			T_p	T_m	T_p		
γ-BHC		50[b]	516[b]	394[b]	516[b]	400[b]	535[b]
	Na_2CO_3	200	490	403	492	401	503
	CaO	150	477	400	479		485
	$CaCO_3$	200	483	400	488	398	507
PCNB		50[b]	505[b]	424[b]	505[b]	415[b]	535[b]
	Na_2CO_3	200	483	427		408	493
	CaO	150	473	429		393	483
	$CaCO_3$	200	484	423		402	501
p,p'-DDT		50[b]	557[b]	391b	559[b]	436[b]	595[b]
	Na_2CO_3	200	543	391	546	431	550
	CaO	150	515	391	517	426	521
	$CaCO_3$	200	532	394	533	427	542
p,p'-methoxy-chlor		50[b]	557[b]	375[b]	578[b]	430[b]	
	Na_2CO_3[c]	200	556	375	558	446	563
	CaO[c]	150	545	376	545		553
	$CaCO_3$[c]	200	546	372		436	553

[a] For chemical names of the compounds see Ref. [35], Table 2.

[b] Values from Ref. [35].

[c] For complete results of thermoanalytical investigations see Fig. 1.

Table 1 Continued

Components		Mass of the	Temperature of peaks /K			$T_{0.01}$	$T_{0.99}$
Pesticide[a]	Additive	sample/mg	DTG	DTA			
			T_p	T_m	T_p		
p,p'-DDE		50^b	535^b	373^b	537^b	425^b	655^b
	Na_2CO_3	200	530	376	533	424	533
	CaO	150	522	376	524	418	529
	$CaCO_3$	200	526	379	528	419	531
p,p'-DMDE		50^b	555^b	396^b	556^b	460^b	630^b
	Na_2CO_3	200	555	401	555	453	561
	CaO	130	535	395	537		
	$CaCO_3$	200	544	396	546	441	550

[a] For chemical names of the compounds see Ref. [35], Table 2.

[b] Values from Ref. [35].

[c] For complete results of thermoanalytical investigations see Fig. 1.

Table 2 Conditions and results of thermal decompositions in a quartz reactor

Substance	Additive	Temperature of reaction/ K	Extent of HCl elimination[a]
p,p'-DDT	KOH	390–400	1.00
	Na_2CO_3	480	0.20
	CaO	480	0.75
	$CaCO_3$	480	0.00
p,p'-methoxychlor	KOH	390–400	1.00
	Na_2CO_3	480	0.60
	CaO	480	0.90
	$CaCO_3$	480	0.05

[a] Ratio of the number of moles of products of dehydrochlorination (*p,p'*-DDE or *p,p'*-DMDE) to initial number of moles of substances (*p,p'*-DDT or *p,p'*-methoxychlor, respectively).

Further insight into reactivity of organochlorine compounds enables analysis of the results of experiments carried out in a quartz reactor. γ-BHC, PCNB, *p,p'*-DDE and *p,p'*-DMDE do not change their chemical constitution in the presence of KOH, Na_2CO_3, CaO and $CaCO_3$, upon heating. *p,p'*-DDT and *p,p'*-methoxychlor undergo more or less advanced dehydrochlorination in the above-mentioned conditions, leading to *p,p'*-DDE and *p,p'*-DMDE, respectively (Table 2). Both organochlorine pesticides remain either completely (*p,p'*-DDT) or almost completely (*p,p'*-methoxychlor) unchanged when heated in the presence of $CaCO_3$. Dehydrochlorination is, in both cases, completed in the presence of KOH. With Na_2CO_3 and CaO as additives, only partial dehydrochlorination takes place, although the process is more advanced in the case of *p,p'*-methoxychlor. Generally, the stronger the alkalies used, the more advanced the dehydrochlorination of organochlorine molecules. It should be noted, that in the presence of KOH, the strongest alkalies of those used, the dehydrochlorination is completed in temperatures ca. 100 K lower than for other additives.

As elimination of HCl takes place upon heating *p,p'*-DDT and *p,p'*-methoxychlor in the presence of additives, one would expect it in a stream of gas leaving the quartz reactor. Actually, neither HCl nor Cl_2 were detected. This means that primarily released HCl reacts instantaneously with alkaline substances present in considerable excess in the reaction zone. In consequence, HCl is kept in a condensed phase and the elimination process is not reflected on the thermogravimetric curves (Fig. 1) (thermoanalytical investigations on neat *p,p'*-DDT revealed that dehydrochlorination precedes volatilization of *p,p'*-DDE [35]).

Upon heating of *p,p'*-DDT and *p,p'*-methoxychlor with alkaline additives chemical processes are most probably initiated by primary elimination of HCl from substrate molecules. To gain an insight as to how such elimination can proceed by employing the AM1 semi-empirical quantum chemistry method [41] (incorporated in the SPARTAN 3.1 programme [42]), we determined structures of substrates (*p,p*'-DDT and *p,p*'-methoxychlor) and products (*p,p*'-DDE and *p,p*'-DMDE, respectively) molecules, as well as transition state structures for the dehydrochlorination process. These structures are shown in Fig. 2, while information on their thermochemical and physicochemical characteristics – in Table 3. Data from this table reveal that kinetic barriers for the dehydrochlorination of *p,p*'-DDT and *p,p*'-methoxychlor, respectively, are (in kJ·mol^{-1}): 214.8 or 214.9 – on the enthalpy level, and 212.7 or 212.5 – on the free enthalpy level (at 298 K). These barriers are relatively high, if the process is

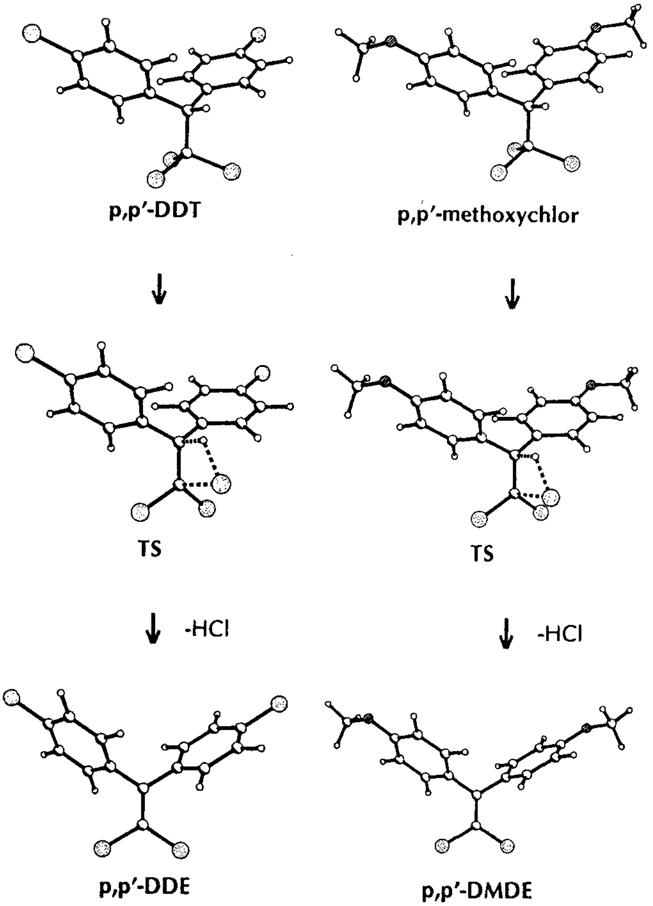

Fig. 2 Theoretically optimized structures of *p,p*'-DDT and *p,p*'-methoxychlor, transition states (*TS*) for dehydrochlorination and products of this reaction (*p,p*'-DDE and *p,p*'-DMDE, respectively)

Table 3 Theoretically determined thermochemical and physicochemical data for *p,p*'-DDT and *p,p*'-methoxychlor, as well as for transition states and products of their dehydrochlorination

Compound/Transition	Thermochemical data[a]			Physicochemical data[b]		
state (TS)	$\Delta_{f,298}H^{o}$	${}_{298}S^{o}$	${}_{298}C_{p}^{o}$	DM	Energy	
(Fig. 2)					HOMO	LUMO
p,p'-DDT	76.7	582.7	268.9	1.075	–9.586	–0.518
p,p'-methoxychlor	–183.5	638.6	312.9	1.499	–8.979	–0.221
p,p'-DDE	167.3	566.6	247.6	0.081	–9.244	–0.565
p,p'-DMDE	–92.4	626.1	291.5	1.056	–8.797	–0.099
HCl	–103.0	186.8	29.1	1.384	–12.333	1.866
p,p'-DDT (TS)	291.5	589.7	271.3	2.587	–9.159	–1.761
p,p'-methoxychlor (TS)	31.4	646.5	315.2	3.754	–8.756	–1.544

[a] $\Delta_{f,298}H^{o}$ values in kJ·mol^{-1}; ${}_{298}S^{o}$ and ${}_{298}C_{p}^{o}$ values in J·mol^{-1}·K^{-1}.

[b] Dipole moment (DM) values in D; energies of Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) in eV.

carried out in the gaseous phase. Thus, in such a phase one would not expect HCl elimination (el) despite the fact that the process is thermodynamically favoured ($\Delta_{el,298}H^0$ equals −12.4 and −11.9, and $\Delta_{el,298}G^0$ equals −63.3 and −63.8 (in $kJ\cdot mol^{-1}$), for *p,p*'-DDT and *p,p*'-methoxychlor, respectively). This implies that surroundings must have considerable influence on the barrier and thus the mechanism of dehydrochlorination of organochlorine pesticides in condensed phases.

Concluding remarks

Undertaking the studies described in this work we believed that the presence of highly active, alkaline substances could initiate degradation of organochlorine pesticides. In reality, only *p,p*'-DDT and *p,p*'-methoxychlor undergo simple dehydrochlorination. The results of this work, therefore, undoubtedly supply new elements to the understanding of chemistry of organochlorine derivatives, but do not seem to be promising as regards the discovery of a convenient method for their destruction or incineration.

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Zusammenfassung — Einzelne Organochlorpestizide, namentlich Lindan, PCNB, *p,p'*-DDT und *p,p'*-Methoxychlor sowie einige verwandte Verbindungen (*p,p'*-DDE und *p,p'*-DMDE) wurden in der Gegenwart von zerpulvertem KOH, Na_2CO_3, CaO und $CaCO_3$ erhitzt, um zu prüfen, ob der Abbau der Verbindungen durch eine Änderung von Bedingungen und Temperaturen möglich ist. Thermoanalyse als auch Untersuchungen bezüglich der Suche nach den Reaktionsprodukten zeigten, daß es sich bei den bei atmosphärischem Druck ablaufenden Vorgängen entweder eine einfache Verdampfung organischer Moleküle handelt, wie sie beim Erhitzen der Gemische mit Gehalt an Lindan, PCNB, *p,p'*-DDE und *p,p'*-DMDE beobachtet wird, oder aber um eine Verdampfung, begleitet von Zersetzung zu HCl und *p,p'*-DDE oder *p,p'*-DMDE, wie sie beim Erhitzen von Gemischen aus *p,p'*-DDT und *p,p'*-Methoxychlor mit alkalischen Substanzen beobachtet wird. Zusätzliche theoretische Berechnungen ermöglichten einen Einblick in den Mechanismus der Abspaltung von HCl aus *p,p'*-DDT und *p,p'*-Methoxychlor.