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THEORETICAL PREDICTION OF ENTHALPIES AND TEMPERATURES OF SUBLIMATION OF ORGANOCHLORINE COMPOUNDS INCLUDING PESTICIDES

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Abstract

Crystal lattice energies of several organochlorine compounds – including pesticides, of known crystal structures, were calculated on the basis of a model which takes into account electrostatic, dispersive and repulsive interactions – using three different sets of empirical parameters. These characteristics compare reasonably with experimental heats of volatilization, and it was subsequently shown how statistical and classical thermodynamics can be employed to evaluate dependencies of function of states of gaseous and solid compounds on temperature and how enthalpies and temperatures of sublimation at standard pressure, as well as vapour pressure *vs.* temperature dependencies can be predicted.

Keywords: lattice energy, organochlorine pesticides, thermodynamics of volatilization

Introduction

The first pesticides used on a large scale included organochlorine compounds [1]. Owing to their high stability and lack of ability to undergo thermal [2] and photochemical [3] degradation they will remain unchanged in the environment for hundreds of years. Moreover, due to their relatively high volatility they can be transported through the atmosphere from sites in which they are used to even very remote sites on the earth [4]. Knowledge of the properties of these compounds is therefore crucial for understanding their fates in the environment.

In this paper we present the theoretical approach to determination of basic thermodynamic characteristics of several organochlorine compounds and their volatilization ability. This includes calculations of the energies of intermolecular interactions in the solid phase (crystal lattice energies), which combined with classical and statistical thermodynamics, afford basic characteristics for the volatilization process, i.e. enthalpies and temperatures of sublimation and thus dependencies of vapour pressures on temperature.

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Theoretical method

Lattice (potential) energy (E_c) of molecular crystals combines three contributions [5–7]: electrostatic (E_{el}), dispersive (E_d) and repulsive (E_r), as well as the term zero point energy (E_0). If each of these contributions is expressed in terms of potentials (V) multiplied by relevant parameters then the equation for E_c admits the form

$$E_c = \frac{1}{2} N\sum_{i=1}^{k} [(V_{el})_i\, q_i + (V_d)_i\, d_i + (V_r)_i r_i] + E_0 \tag{1}$$

where N is the Avogadro number, q, d, r represent charge, and dispersive and repulsive parameters for the chosen site (atom) i, while $(V_{el})_i$, $(V_d)_i$ and $(V_r)_i$- electrostatic, dispersive and repulsive potentials created by all surrounding atoms (j) except those forming a given molecule (k is the number of atoms in the molecule), while the factor 1/2 eliminates the duplication of interactions. Potentials in Eq. (1) are generally defined as

$$V_i = \alpha \sum_{j \neq i} \frac{P_j}{D_{ij}^{n}} \tag{2}$$

($P=q$, d or r, D denotes distance between sites i and j, $\alpha = 1/(4\pi\varepsilon_0)$ (ε_0 is the permittivity of free space) for electrostatic or $\alpha=1$ for other interactions, and $n=1$ for electrostatic, 6 – for dispersive and 12 – for repulsive interactions, respectively) although for repulsive interactions exponential dependency is often assumed [5–7]

$$V_i = \alpha \sum_{j \neq i} A_j \exp(-P_j D_{ij}) \tag{3}$$

(A is a parameter ascribed to an atom).

The zero point energy in Eq. (1) is represented by [6]

$$E_0 = \frac{1}{2} \sum_{l} Nhc(\bar{\nu}_L)_l \tag{4}$$

where h and c denote the Planck constant and velocity of light, while $\bar{\nu}_L$ – wavenumbers of lattice vibrations (summation extends over all (l) such vibrations). Calculations of the crystal lattice energies were carried out employing the PCK83 (Crystal Molecular Packing Analysis) program [8] developed by Williams [9], in which repulsive interactions are expressed by Eq. (3). Three types of parameters developed by Reynolds, Kjems and White (RKW) [10], Bates and Busing (BB) [6], and Mirsky and Cohen (MC) [11] were used (these parameters are specific for given pairs of atoms). Net atomic charges were obtained by the AM1 method [12] incorporated in MOPAC93 program [13].

Crystal lattice energy calculated by Eq. (1) is related to the enthalpy of sublimation ($\Delta H_{sub(T)}$) through the equation

$$\Delta H_{sub(T)} = -E_c + \int_0^T \Delta C_{p(T)}\, dT \tag{5}$$

in which the second term on the right hand side accounts for the heat capacity changes upon transfer of molecules from solid ($(C_p)_{s(T)}$) to gaseous ($(C_p)_{g(T)}$) phases ($\Delta C_{p(T)} = (C_p)_{g(T)} - (C_p)_{s(T)}$). On the basis of the above equation, enthalpy of volatilization at any temperature and standard pressure ($P_0 = 1$ atm) can be predicted.

Vapour pressure (P) *vs.* temperature (T) dependency is included in Clausius-Clapeyron relationship, which is given below in a form suitable for the purpose of this work

$$\ln\frac{P}{P_0} = -\frac{E_c}{R}\left(\frac{1}{T_{sub}} - \frac{1}{T}\right) + \frac{1}{R}\int_{T_{sub}}^{T}\int_0^{T} \Delta\frac{C_{p(T)}}{T^2}\, \mathrm{d}T\mathrm{d}T \tag{6}$$

(R is the gas constant and T_{sub} – the sublimation temperature, i.e. temperature at which P attains P_0). Sublimation temperature reflects the equilibrium state between solid and gaseous phase at standard pressure, i.e. corresponds to the situation when free enthalpies (G) of both phases become equal. This fact creates a premise for determing values of this quantity.

Further considerations necessitate invokement of basic relationships of the statistical thermodynamics, namely

$$H_{(T)} = C + RT^2\left(\frac{\partial \ln Q_{(T)}}{\partial T}\right)_p \tag{7}$$

$$G_{(T)} = C - RT\ln Q_{(T)} \tag{8}$$

and

$$C_{p(T)} = \left[\frac{\partial\left[RT^2\left(\frac{\partial \ln Q_{(T)}}{\partial T}\right)_p\right]}{\partial T}\right]_p \tag{9}$$

where C is the potential energy of the system at 0 K and Q – the partition function. This latter function contains three contributions: translational (Q_{tr}), rotational (Q_{rot}) and vibrational (Q_{vib}) included in the relationship

$$Q = Q_{tr}\,Q_{rot}\,Q_{vib} \quad \text{or} \quad \ln Q = \ln Q_{tr} + \ln Q_{rot} + \ln Q_{vib} \tag{10}$$

For crystalline phases $\ln Q_{tr}$ and $\ln Q_{rot}$ equals 0, while for ideal gas phases: $(\partial \ln Q_{tr}/\partial T)_p = 5/(2T)$ and

$$Q_{rot} = \frac{8\pi^2(8\pi^3 I_x I_y I_z)^{1/2}\,(RT)^{3/2}}{\delta N^{3/2}\,h^3} \tag{11}$$

(I_x, I_y and I_z denote moments of inertia of the molecule relative to x, y and z axes and δ-symmetry number).
The vibrational partition function is given by the equation

$$Q_{vib} = \prod_m \left[1 - \exp\left(-\frac{Nhc\bar{v}_m}{RT}\right)\right]^{-1} \prod_l \left[1 - \exp\left(-\frac{Nhc(\bar{v}_L)_l}{RT}\right)\right]^{-1} \tag{12}$$

(m indicates wavenumbers of internal vibrations of the molecule and l-external (lattice) vibrations) the first term of which applies to the isolated molecule (gaseous phase), whereas both terms apply to the crystalline phase. If relations (7) and (9) are combined with (5) and (6) one obtains

$$\Delta H_{sub(T)} = -E_c + RT^2\left[\left(\frac{\partial \ln Q_{g(T)}}{\partial T}\right)_p - \left(\frac{\partial \ln Q_{s(T)}}{\partial T}\right)_p\right] \tag{13}$$

and

$$\ln\frac{P}{P_0} = -\frac{E_c}{R}\left(\frac{1}{T_{sub}} - \frac{1}{T}\right) + \int_{T_{sub}}^{T}\left[\left(\frac{\partial \ln Q_{g(T)}}{\partial T}\right)_p - \left(\frac{\partial \ln Q_{s(T)}}{\partial T}\right)_p\right] dT \tag{14}$$

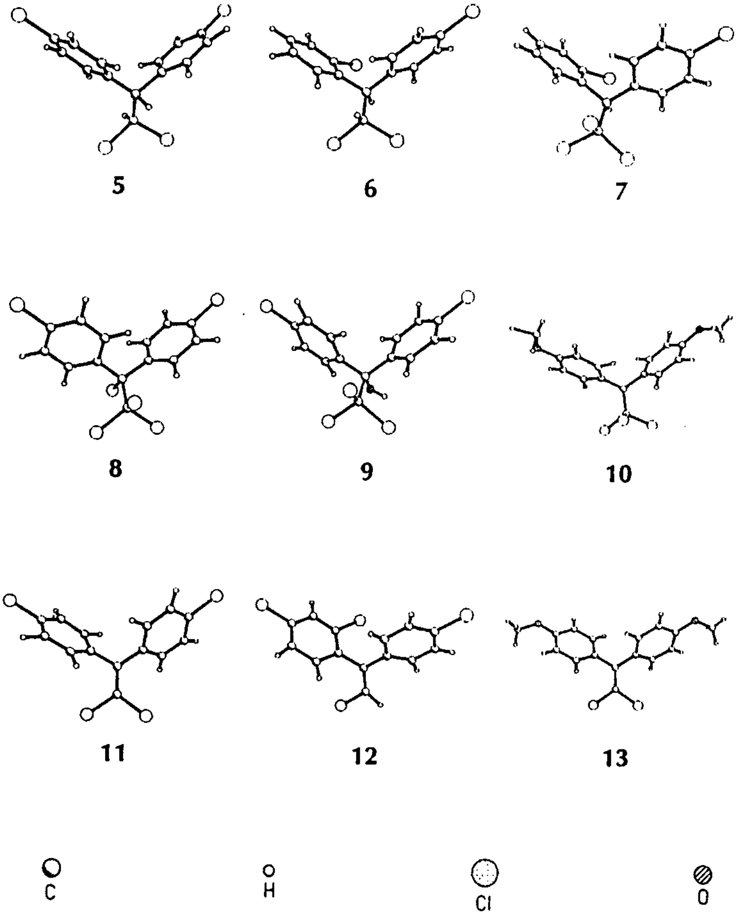
Finally, at volatilization temperature (T_{sub})

$$-RT_{sub}\ln Q_{g(T_{sub})} = E_c - RT_{sub}\ln Q_{s(T_{sub})} \tag{15}$$

Results and discussion

Crystal lattice energies were calculated for 13 compounds whose crystal structures are known, i.e. 4 chlorobenzenes and 9 organochlorine pesticides or related derivatives (crystal phase structures of the latter are shown in Fig. 1). Table 1 compiles structural information, crystal lattice energies and experimental enthalpies of sublimation of the compounds. The best conformity between calculated and experimental values is given by Bates and Busing (BB) parameters. Conformity is somewhat worse for Mirsky and Cohen (MC) parameters. Reynolds, Kjems and White (RKW) parameters give $-E_c$ values deviating most from experimental ΔH_{sub}. Concluding, crystal lattice energies predicted theoretically, particularly when using BB parameters, give reasonable estimates of the volatilization enthalpies of this group of compounds, taking into account differences in experimental values (for HCB, ΔH_{sub} reported in the literature, vary from 75 to 101 kJ·mol^{-1} – Table 1), as well as deficiencies of theoretical methods applied.

To demonstrate the usefulness of theoretical methods in thermodynamics, we calculated the enthalpy of sublimation, free enthalpies for gaseous and solid phases and vapour pressure *vs.* temperature dependencies for HCB, which are shown in Figs 2A, B, C. In these calculations the E_c value was assumed to be


5 6 7

8 9 10

11 12 13

Fig. 1 Crystal phase structures of organochlorine pesticides and related compounds (for names and symbols see Table 1)

–98.3 kJ·mol^{-1} (value relevant to BB in Table 1), while wavenumbers of lattice modes were those taken from Ref. [6]. The latter characteristics, however, had to be multiplied by 1.5 to obtain reasonable values of the vibrational partition function for the solid phase. Rotational and vibrational contributions to the partition function of gaseous HCB were calculated employing routines incorporated in the MOPAC93 program [13]. The heat of sublimation of HCB decreases with the increase of temperature due to the decrease of possibilities of energy storage in vibrational degrees of freedom which are lost upon transfer

Table 1 Structural and thermodynamic characteristics of organochlorine pesticides and related compounds

Compound[a]				$-E_c^b$/kJ·mol^{-1}				ΔH_{sub}	
No.	Symbol[c]	Space group	Z^d	Lit.	RKW	BB	MC	kJ·mol^{-1}	Lit.
1	1,4-diCB(α)	$P2_1/a$	2	[10,15-17]	81.3	65.6	73.6	64.8	[22,23]
	(β)	$P1$	1	[10,17-19]	80.1	66.1	73.3		
	(γ)	$P2_1/c$	2	[10,17,20,21]	85.8	69.2	75.8		
2	1,2,4,5-tetraCB	$P2_1/n$	2	[24]	105.6	83.3	89.3		
3	pentaCB	$Pca2_1$	4	[25]	110.8	88.4	92.2		
4	HCB	$P2_1/c$	2	[26,27]	124.6	98.3	101.2	75-101	[2,6,28-30]
5	*p,p'*-DDD	$C2/c$	8	[31]	142.5	119.0	129.2		
6	*o,p'*-DDD	$P2_1/c$	4	[32]	142.6	118.3	129.8		
7	*o,p'*-DDT	$P1$	4	[33]	146.3	121.9	132.3		
		$P2_12_12_1$	4	[34]	138.9	116.2	126.3		
8	(α)-chloro-DDT	$P2_1/c$	4	[35]	152.7	123.7	140.4	89.4	[2]
9	Dicofol(Kelthane)	$P1$	4	[36]	150.5	122.6	147.9		
10	*p,p'*-Methoxychlor	$P1$	2	[37]	144.6	128.0	135.5		
11	*p,p'*-DDE	$P2_1/c$	8	[31]	141.8	118.5	125.7	74.2	[2]
12		$Pbca$	8	[38]	146.4	121.8	132.8		
13	*p,p'*-DMDE	$C2/c$	4	[39]	157.8	143.0	146.2	79.2	[2]

[a] The chemical names of the compounds: 1 = 1,4-dichlorobenzene; 2 = 1,2,4,5-tetrachlorobenzene; 3 = pentachlorobenzene; 4 = hexachlorobenzene; 5 = 1,1'-(2,2-dichloroethylidene)bis[4-chlorobenzene]; 6 = 1-chloro-2-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene; 7 = 1-chloro-2-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene; 8 = 1,1'-(tetrachloro-ethylidene)bis[4-chlorobenzene]; 9 = 4-chloro-α-(4-chlorophenyl)-α-(trichloromethyl)-benzenemethanol; 10 = 1,1'-(2,2,2-trichloroethylidene)bis[4-methoxybenzene]; 11 = 1,1'-(dichloroethylidene)bis[4-chlorobenzene]; 12 = 2,4-dichloro-1-[2-chloro-1-(4-chlorophenyl)ethenyl]benzene; 13 = 1,1'-(dichloroethenylidene)bis[4-methoxybenzene];

[b] E_C values do not include the E_0 term (Eq. (1)).

[c] For structures, see Fig. 1.

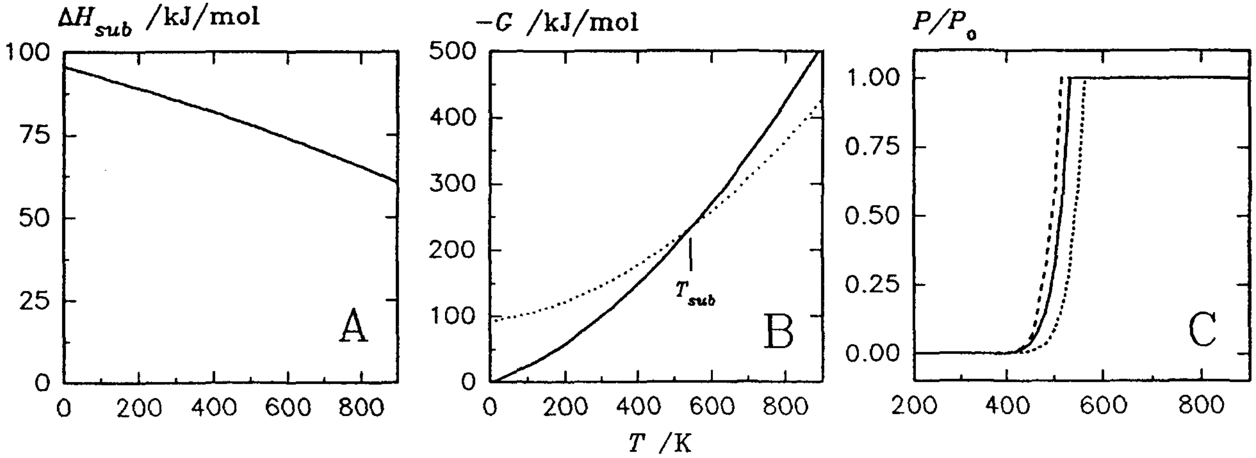


Fig. 2 (A) Enthalpy of sublimation *vs.* temperature for HCB – predicted theoretically; (B) Free enthalpy *vs.* temperature for gaseous (—) and solid (····) HCB – predicted theoretically; (C) Experimental (- - - -) [2] and (····) [28]) and theoretical (—) vapour pressure *vs.* temperature dependencies for HCB

of molecules from the solid to gaseous phase. The sublimation temperature predicted theoretically, which equals 535 K (Fig. 2B), exceeds those found experimentally, 514–563 K [2, 28, 30]. On the other hand, theoretical and experimental vapour pressure *vs.* temperature dependencies (Fig. 2C) correspond quite well, which implies that theory reasonably foresees this type of characteristics.

Concluding remarks

The combination of crystal lattice energy with statistical thermodynamics calculations enables the estimation of basic thermodynamic characteristics of crystalline solid phases. The model used contains numerous simplifications and assumptions, of which the main ones are those treating molecules and crystals as rigid and vibrations as harmonic. Lastly, values of thermodynamic quantities depend on the choice of atomic parameters (characteristic for pairs of atoms), which reflect contributions to energy of intermolecular interactions and affect predicted frequencies of lattice vibrations. If these parameters could be obtained on purely theoretical bases, it could mean real progress in this field. This problem is the subject of attention of many research groups including ours.

* * *

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Zusammenfassung — Unter Einsatz von drei verschiedenen empirischen Parametersätzen wurden auf der Grundlage eines Modelles, welches die elektrostatischen, dispersiven und repulsiven Wechselwirkungen berücksichtigt, die Kristallgitterenergien einiger Organochlorverbindungen – einschließlich Pestiziden – bekannter Kristallstruktur berechnet. Diese Merkmale lassen sich gut mit den experimentellen Verdampfungswärmen vergleichen und es wird weiterhin gezeigt, wie statistische und klassische Thermodynamik zur Bewertung der Temperaturabhängigkeit von Zustandsfunktionen gasförmiger und fester Verbindungen eingesetzt werden kann und wie die Sublimationsenthalpien und Sublimationstemperaturen bei Standarddruck als auch der Dampfdruck als Funktion der Temperatur vorausgesagt werden können.