ELSEVIER

Thermochimica Acta 253 (1995) 235–242

thermochimica acta

Formation enthalpies and non-bonding interactions of hexachlorocyclohexanes ☆

An Xu-Wu *, Guo Da-Jun

Chemical Thermodynamics and Thermochemistry Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080, People's Republic of China

Received 6 July 1994; accepted 7 July 1994

Abstract

The enthalpies of combustion of α-, β-, γ- and δ-1,2,3,4,5,6-hexachlorocyclohexane (HCCH) isomers and of chlorocyclohexane (CCH), and the enthalpy of vaporization of CCH have been determined by precision combustion and vaporization calorimetry; the enthalpies of formation of these compounds are derived. These results are more reliable than values reported in the literature. The non-bonding interactions in these molecules are discussed using the group scheme, the electrostatic bond energy model and force field calculations.

Keywords: Heat of formation; Hexachlorocyclohexane; Non-bonding interaction

1. Introduction

In order to study the relationship between the formation enthalpies of polar compounds and their molecular structures, a research programme of combustion calorimetry of organic chloro compounds has been undertaken for some years in our laboratory [1]. Accurate thermochemical data were obtained for organic chloro compounds and an electrostatic bond energy model for enthalpies of formation of chloroalkanes was proposed [2].

---

* Corresponding author.

☆ Presented at the International and III Sino-Japanese Symposium on Thermal Measurements, Xi'an, 4–6 June 1994.

SSDI 0040-6031(94)01968-1

Table 1
HCCH isomers [a]

Isomer	α	β	γ	δ	ε	η	θ	ι
Conformer	aaeeee eeaaaa	eeeeee aaaaaa	aaaeee	aeeeee eaaaaa	aeeaee eaaeaa	aaeaee	aeaeee eaeaaa	aeaeae

[a] a and e indicate respectively the chlorine atom at axial or equatorial position.

The chlorocyclohexanes are a new series of compounds to be studied. Among these compounds hexachlorocyclohexane (HCCH) is especially interesting. It is a non-geminal multichlorocycloalkane containing six vicinal chlorine atoms, and thus large non-bonding interaction energy in the molecule is expected. HCCH has eight separable configurational isomers, and some of them give non-equivalent conformers when they interconvert between the chair forms (see Table 1). In these isomers, the type of bond and the number of each type of bond are all the same; the difference in energy among the isomers comes only from the difference of non-bonding interactions. For these reasons HCCH isomers are of interest in the study of the molecular force field model for organic chloro compounds [3]. However, in the literature the thermochemical data for HCCH isomers are inaccurate [4,5]. In this paper the enthalpies of combustion of HCCH isomers and chlorocyclohexane (CCH), together with the enthalpy of vaporization of CCH are determined, and the enthalpies of formation of these compounds and their molecular structures are discussed.

2. Experimental

2.1. Samples

Four pure samples of α-, β-, γ- and δ-HCCH isomers, as standard pesticide materials, were provided by the National Research Center of Standard Materials. The purities of these samples and the analytical methods used [6] are listed in Table 2. These HCCH samples were directly used for combustion without further purification.

CCH (c.p.) was purified by vacuum distillation in a spinning band column of a Perkin-Elmer model 251. The purified sample was analysed by GLC (Varian 3700) with a 50 m FFAP quartz capillary column and flame ionization detector, containing 0.018% of cyclohexane and 0.041% cyclohexene (vol%, internal standard method). Water content in the sample analysed by GLC [1] was 0.033% (vol%). The sample was transferred under vacuum to a receiver containing the glass ampoules with a thin capillary for filling. After sealing and pressure testing, the ampoule was weighed and the mass of sample in the ampoule was calculated.

Table 2
Purities of the samples

	α-HCCH	β-HCCH	γ-HCCH	δ-HCCH	CCH
Purification	Recryst.	Recryst.	Recryst. & zone melting	Recryst.	Distil.
Analysis	GLC, DSC	GLC	GLC, DSC, TCSP [a]	GLC, DSC	GLC
Purity/wt%	99.9 ± 0.4	99.2 ± 0.3	99.97 ± 0.09	99.9 ± 0.2	99.92 ± 0.02
Impurities					
Organic/wt%	Isomers	Isomers	Isomers	Isomers	0.047
Water/wt%	<0.0001	<0.0001	<0.0001	<0.0001	0.033

[a] Estimated from temperature change during the solidification process.

2.2. Apparatus and procedure

The combustion calorimeter and its procedures have been reported previously [1]. The oxygen pressure was 40 atm (1 atm = 101.325 kPa). Polypropylene thread was used for ignition; its heat of combustion had been determined previously to be $-46\,119.0 \pm 4.1$ J g^{-1}. The calorimeter was calibrated using benzoic acid (NBS 39i), and the standard energy equivalent was determined to be $\varepsilon_{si} = 17\,717.80 \pm 0.78$ J K^{-1}. In CCH experiments, a small quantity of squalane (designation SQ-3) was used as the auxiliary substance; its heat of combustion had been determined previously to be $-46\,765.93 \pm 1.73$ J g^{-1}. About 14 g As_2O_3 solution of 0.05366 mmol g^{-1} was placed in the bomb instead of the 1 g of water used in the calibration experiments. In HCCH experiments, a 1 g sample was burned with 0.5 g benzoic acid (NBS 39i) and a small quantity of SQ-3 as the auxiliary substance. The reduction reagent was 33 g As_2O_3 solution of 0.09305 mmol g^{-1}. The bomb was rotated 80 s after ignition, and this continued throughout the experiment. After each combustion of the chloro compound, the interior of the bomb was checked for soot. The final bomb liquid and washings were collected for the following analyses: excess As_2O_3, HNO_3, dissolved platinum and Cl^{-1}. An LKB 8721-3 vaporization calorimeter was used for the measurements of heats of vaporization of CCH. The electric heating power was 100 mW, and the heating period was set at 600 s. The experimental procedures have been described previously [1].

3. Results

The combustion experiment data were processed with the programs described previously [1]. Atomic masses of 1977 were adopted for molecular mass calculations. The values of Henry's law constant, $k(CO_2) = 0.03414$ mol dm^{-3} atm^{-1}, and for $\Delta_{soln}E(CO_2, g) = -17\,280 \pm 167$ J mol^{-1} were taken from Ref. [1]. A summary of typical combustion experiments is listed in Table 3.

Table 3
Summary of typical combustion experiments

	CCH	α-HCCH	β-HCCH	γ-HCCH	δ-HCCH
m(cpd.)/g	0.699980	0.987189	0.960199	0.982349	1.015092
m(SQ-3)/g	0.091449	0.058604	0.060741	0.045454	0.051210
m(NBS 39i)/g	0	0.500365	0.510815	0.515442	0.496553
m(Fuse)/g	0.000760	0.000830	0.000895	0.000838	0.000870
ε_i(cont)/J K^{-1}	67.56	147.21	145.76	146.60	146.31
$\Delta_{soln}E^f(CO_2)$/J	21.49	66.72	66.22	66.10	65.97
$\Delta_{dec}E^f(HNO_3)$/J	0	0	0	0	0
$\Delta_{dec}E^f(As_2O_5)$/J	42.58	550.90	524.01	564.36	563.70
$\Delta_{diln}E^f$(HCl)/J	−3.53	−15.80	−15.14	−15.72	−16.76
$\Delta_{dec}E^f(H_2PtCl_6)$/J	0.15	2.12	3.53	3.69	3.27
$\Delta_\Sigma E$/J	28.43	80.75	80.41	80.41	80.13
ΔT/K	1.48755	1.49329	1.49741	1.48151	1.48498
$\Delta_c E^\ominus$(cpd.)/kJ mol^{-1}	−3741.28	−2961.64	−2959.36	−2973.23	−2961.17

Table 4
Results of combustion and vaporization experiments (in kJ mol^{-1})

	CCH(l)		α-HCCH(c)	β-HCCH(c)	γ-HCCH(c)	δ-HCCH(c)
	$-\Delta_c E^\ominus$	$\Delta_v H^\ominus$	$-\Delta_c E^\ominus$	$-\Delta_c E^\ominus$	$-\Delta_c E^\ominus$	$-\Delta_c E^\ominus$
	3741.28	42.81	2961.64	2959.36	2973.23	2961.17
	3741.60	42.67	2961.80	2957.31	2973.21	2962.23
	3738.39	42.60	2957.23	2960.51	2974.93	2957.04
	3742.22	42.65	2959.88	2962.79	2969.66	2963.86
	3743.94	42.61	2955.31	2955.42	2977.30	2964.47
		42.60	2961.45	2962.53		
Mean	3741.49	42.66	2959.55	2959.65	2973.67	2961.75
S.d.m.	±0.90	±0.03	±1.10	±1.19	±1.25	±1.32

The results of combustion and vaporization experiments are listed in Table 4.

The standard enthalpies of combustion correspond, respectively, to the following standard state combustion reactions at 298.15 K

$$C_6H_{11}Cl(l) + 8.5O_2(g) = 6CO_2(g) + HCl(aq.\ 600H_2O) + 5H_2O(l) + \Delta_c H^\ominus(CCH,\ l)$$

$$C_6H_6Cl_6(c) + 6O_2(g) = 6CO_2(g) + 6HCl(aq.\ 600H_2O) + \Delta_c H^\ominus(HCCH,\ c)$$

The values of $\Delta_f H^\ominus(CO_2,\ g)$, $\Delta_f H^\ominus(H_2O,\ l)$ and $\Delta_f H^\ominus(HCl(600H_2O),\ soln.)$ were taken from Ref. [1]. The experimental and derived results are listed in Table 5. The uncertainty is twice the final overall standard deviation of the mean. The energy of combustion of CCH was corrected for impurities in the sample. For HCCH samples, the main impurities are their isomers, and their energies of combustion are approximately equal to each other. The correction for impurities on the energy of combustion of HCCH samples is negligible.

Table 5
Derived and literature data (in kJ mol^{-1})

	CCH(l)	α-HCCH(c)	β-HCCH(c)	γ-HCCH(c)	δ-HCCH(c)
$\Delta_c E^\ominus$(l/c)	−3741.37 ±1.88	−2959.55 ±2.34	−2959.65 ±2.52	−2973.67 ±2.64	−2961.75 ±2.78
$\Delta_c H^\ominus$(l/c)	−3747.57 ±1.88	−2959.55 ±2.23	−2959.65 ±2.52	−2973.67 ±2.64	−2961.75 ±2.78
$\Delta_f H^\ominus$(l/c)	−209.13 ±1.92	−400.75 ±2.50	−400.65 ±2.68	−386.63 ±2.80	−398.55 ±2.94
$\Delta_{v/s} H^\ominus$	40.66 ±0.08			90.82 [a] ±0.72	
$\Delta_f H^\ominus$(g)	−166.47 ±1.93	−309.93 [b] ±10	−309.83 [b] ±10	−295.81 ±2.89	−307.73 [b] ±10
Literature values					
$\Delta_f H^\ominus$(l/s)	−207.1 [c] ±1.3	−172.9 [d]	−179.9 [d]	−158.6 [d]	−171.5 [d]
$\Delta_{v/s} H^\ominus$	43.5 [c] ±3.3	92.5 [e]	102.5 [e]	115.5 [e]	97.9 [e]
$\Delta_f H^\ominus$(g)	−163.6 ±3.6	−80.4 [d,e]	−77.4 [d,e]	−43.1 [d,e]	−73.6 [d,e]

[a] Ref. [8]. [b] Calculated by assuming that $\Delta_s H^\ominus$ is equal to that of γ-HCCH. [c] Ref. [7]. [d] Ref. [4]. [e] Ref. [5].

4. Discussion

4.1. Comparison with results in the literature

The results in the literature are listed in Table 5. Kirkbride derived the enthalpy of formation of CCH(l) from the measured heat of reaction of chlorination of cyclohexane [7]. His value is compatible with our result within the uncertainty intervals.

Schwabe [4] measured the enthalpies of combustion of α-, β-, γ- and δ-HCCH using a static aneroid bomb calorimeter and a reducing agent of hydrazine hydrochloride solution supported on quartz wool. The derived enthalpies of formatioin are very different (about 200 kJ mol^{-1}) from our results. Schwabe's values are questionable due to the older method which he employed.

The enthalpies of sublimation derived by Schwabe and Legler [5] from vapour pressure measurements near room temperature are also inaccurate due to very low vapour pressures; for example, the enthalpy of sublimation of γ-HCCH from vapour pressure measurements is 25 kJ mol^{-1} more than that from direct calorimetry [8].

4.2. Group scheme calculation

The group scheme for enthalpy of formation is sound for hydrocarbons and their mono-substituted compounds [7]. However, for polar multi-substituted compounds,

Table 6
Calculated results

	CCH	α-HCCH	β-HCCH	γ-HCCH	δ-HCCH
Experimental					
μ/debye [a]	2.2–2.4	2.20–2.34	0	2.8–3.0	2.2–2.32
$\Delta_f H^\ominus(g)/(kJ\ mol^{-1})$	-166.47 ± 1.93	(-309.93) ± 10	(-309.83) ± 10	-295.81 ± 2.89	(-307.73) ± 10
Calculated					
Group scheme					
$\Delta_f H^\ominus(g)/(kJ\ mol^{-1})$	(-166.47)	-382.8	-382.8	-382.8	-382.8
Electrostatic model					
μ/debye	2.404	2.23	0	3.086	2.287
$\Delta_f H^\ominus(g)/(kJ\ mol^{-1})$	-169.40	-307.77	-295.31	-309.00	-299.18

[a] Ref. [3].

(multichloroalkanes for example) electrostatic interaction of Cl $\cdots$ Cl plays a more important role [1]. It has been indicated [1] that the bond energy term of $\Delta_f E^\ominus[C-C_2HCl, g]$ listed in Ref. [7] is erroneous. We obtained it from the equation

$$\Delta_f H^\ominus(C-C_2HCl,\ g) = \Delta_f H^\ominus(CCH,\ g) - (5/6)\Delta_f H^\ominus(C_6H_{12},\ g)$$
$$= -63.76\ kJ\ mol^{-1}$$

where $\Delta_f H^\ominus(CCH,\ g)$ was taken from this work, and $\Delta_f H^\ominus(C_6H_{12},\ g)$ from Ref. [7].

According to the group scheme, $\Delta_f H^\ominus(HCCH,\ g) = 6 \times \Delta_f H^\ominus(C-C_2HCl,\ g) = -382.5\ kJ\ mol^{-1}$ (see Table 6). This value is about 80 kJ mol^{-1} more than those listed in Table 5.

The HCCH molecule contains six pairs of vicinal, three pairs of 1,3 substituted and two pairs of 1,4 substituted atoms of chlorine; the interaction energies were estimated to be 10.5, small and 0 kJ mol^{-1} per pair respectively [1]. Then the total interaction energy in HCCH is estimated to be $> 6 \times 10.5 = 63$ kJ mol^{-1}, close to the value estimated above of 80 kJ mol^{-1}.

4.3. Electrostatic bond energy model calculation

For the electrostatic bond energy model developed in our laboratory, the molecular skeleton is assumed to be composed of "standard" bond lengths, bond angles and torsion angles. The charge distributions were calculated by an electrostatic approach similar to the "MSE" method [9], and the enthalpy of formation of a molecule was the sum of the covalent bond energy terms plus the total electrostatic energy between the charges on all atoms. Seven parameters in the model were determined using a least-squares procedure, i.e. two original formal charges on atoms of H or Cl, three longitudinal polarization tensors of bonds C–H, C–C and C–Cl and three covalent bond energy terms of C–H, C–C and C–Cl. The calculated dipole moments of all the alkanes were zero, and those of mono- and multichloroalkanes coincide reasonably well with the determined values. The differences between the calculated and experimental enthalpies of formation of 13 non-geminal chloroalkanes were small, with maxima of 2.8 kJ mol^{-1} and a mean of 1.0 kJ mol^{-1}.

Using the model, the calculated dipole moments of CCH and HCCH isomers and the formation enthalpy of CCH are in agreement with the experimental values, and the errors of calculated formation enthalpies of α-, β- and δ-HCCH isomers are also reduced to about 10 kJ mol^{-1} which is near the estimated error for $\Delta_s H^\ominus$ of these isomers. This shows that our electrostatic model is satisfactory for non-geminal multi-substituted chloroalkanes.

4.4. *Formation enthalpy and molecular structure of γ-HCCH*

The formation enthalpy of γ-HCCH in the solid state is about 13 kJ mol^{-1} higher than those of other three isomers, and experimental gaseous formation enthalpy of γ-HCCH is 13 kJ mol^{-1} higher than that calculated from our electrostatic model. Usually these differences can be considered as resulting from the strong interaction between 1,3-aa substitution of chlorine atoms in the γ-HCCH molecule with its "standard" configuration. X-ray results [3] indicate that in the real configuration most of the strain caused by the interaction between 1,3-aa substitution of chlorine atoms is reduced as a result of increasing their distance from 2.515 to 3.32 Å (1 Å = 10^{-8} cm) by rotating the C–C bonds and by deforming the molecular skeleton, despite simultaneous small increases in other strains (bond stretching, angle bending, torsion and so on).

Some calculations using the molecular force field method have been done to facilitate understanding of the details in energy change. The potential functions and the force constants in Ref. [10] used were

$$E_v = k[2.25(r^*/r)^6 + 8.28 \times 10^5 \exp(-r/0.0736r^*)]$$

$$E_b = 0.021914k_b(\theta - \theta_0)^2[1 - 2(1 - 0.006(\theta - \theta_0)]$$

$$E_s = 71.94k_s(l - l_0)^2[1 - 2(l - l_0)]$$

$$E_{tor} = (1/2)[V_1(1 + \cos W) + V_2(1 - \cos 2W) + V_3(1 + \cos 3W).$$

Because the locations of hydrogen atoms determined by the X-ray method were not accurate, the calculation of energy terms involving hydrogen atoms was ignored. The calculated results are listed in Table 7.

Table 7
Calculated results [a] (in kJ mol^{-1}) of γ-HCCH by molecular force field method

	$E(1)$	$E(2)$	$E(3)$	$E(4)$	$E(5)$	E(es)	E(s)	E(b)	E(tor)
Standard skeleton	79.70	6.65	2.79	2.74	−0.89	−24.79	0	0	8.91
Real skeleton	0.95	0.90	2.5	2.5	−0.90	−21.68	1.60	5.50	13.86
Difference	−78.75	−5.75				3.21	1.60	5.50	4.77

[a] Non-bonded interaction energy: $E(1)$ for 1,3-aa Cl · · · Cl, $E(2)$ for 1,3-aa Cl · · · H, $E(3)$ for vicinal-ae Cl · · · Cl, $E(4)$ for vicinal-ee Cl · · · Cl, $E(5)$ for vicinal-aa Cl · · · Cl; E(es), electrostatic energy; E(s), energy of bond stretching; E(b), energy of angle bending; E(tor), energy of torsion.

Acknowledgement

This research programme was supported by the National Natural Science Foundation of China.

References

[1] An Xu-Wu, He Jun and Hu Ri-Heng, Thermochim. Acta, 169 (1990) 331.

[2] He Jun, An Xu-Wu and Hu Ri-Heng, Sci. China, Ser. B, 36 (1993) 1036.

[3] P.D. de la More, D. Hall and N. Pavitt, J. Comput. Chem., 4 (1983) 114.

[4] K. Schwabe, Z. Electrochem., 60 (1956) 151.

[5] K. Schwabe and C. Legler, Z. Electrochem., 64 (1960) 902.

[6] Ma Ya-Ping, Wu Fang-Di et al., Research Report of HCCH as the Standard Materials of Pesticide, National Research Center of Standard Materials, China.

[7] J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.

[8] R. Sabbah et Xu-Wu An, Thermochim. Acta, 178 (1991) 339.

[9] N.L. Allinger and T. Wuesthoff, Tetrahedron, 33 (1977) 3.

[10] A.Y. Meyer, J. Mol. Struct., 40 (1977) 127.