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STUDY ON THE ELECTROSTATIC INTERACTION IN ORGANIC CHLOROCOMPOUNDS. ENTHALPIES OF COMBUSTION AND FORMATION OF 1,3- AND 1,4-DICHLOROBUTANES *

AN XU-WU, HE JUN and HU RI-HENG
Institute of Chemistry, Academia Sinica, Beijing (P.R. China)

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ABSTRACT

The enthalpies of combustion and vaporization of 1,3- and 1,4-dichlorobutanes have been measured in a tantalum-lined rotation bomb calorimeter and an LKB vaporization calorimeter and from these values the gaseous enthalpies of formation of the compounds are calculated as 194.98 ± 1.78 and 183.40 ± 1.94 kJ mol^{-1}, respectively. The electrostatic interactions in these molecules are discussed.

INTRODUCTION

In the development of the molecular mechanics method and bond energy schemes of the formation enthalpies of compounds much attention has been paid recently to the treatment of electrostatic interactions in the polar compounds [1,2]. Accurate data of these effects are of key importance. For this purpose a research project of combustion calorimetry on organic chlorocompounds is being undertaken in our laboratory. We have measured the enthalpies of combustion and vaporization or sublimation of a series of chlorobenzenes and have discussed the electrostatic interactions in these molecules by using an induced dipole model and a point-charge model [3]. A similar investigation is in progress for chloroalkanes. In this paper the results for 1,3- and 1,4-dichlorobutanes are reported and the electrostatic interactions in dichloroalkanes are discussed.

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EXPERIMENTAL

Samples

Commercially available 1,3-dichlorobutane (I) (Tokyo Kassi, E.P. grade) and 1,4-dichlorobutane (II) (Shanghai Chemical Co., C.P. grade) were used as starting materials. It was found that I originally contained about 0.4% impurities (by GLC) and II had a main impurity identified as I (by GLC–MS). After being dried with $MgClO_4$ (for I) and 5 Å molecular sieves (for II), the materials were purified by distillation in a spinning-band column of Perkin-Elmer Model 251 at a pressure of 500 Torr *.

Organic impurities in the samples were analyzed by GLC (Varian 3700) with a 50 m FFAP quartz capillary column and flame ionization detector, 1,2-dichlorobutane being selected as the internal reference material; both split and no-split techniques were used. The results are listed in Table 1.

In order to determine the water content in the samples, a GLC method similar to that of Sellers [4] was set up. Two stainless steel columns (3 mm × 2 m) packed with GDX-101 (80–100 mesh) and a backflush valve were fitted in the GLC (Varian 3700) with a thermal conductivity detector. Benzene saturated with water at 25 °C was used as the external reference material. A linear relation between the peak areas of water and the amounts of benzene injected was obtained and the straight line passed through the origin of coordinates, indicating that no interference from water adsorption on the column wall was found. The analytical results for the samples are listed in Table 1.

TABLE 1

Auxiliary data used in the calculations

Compounds	Impurities (%)		ρ ($g\ cm^{-3}$)	$(\partial V/\partial T)_p$ ($mm^3\ k^{-1}\ g^{-1}$)	C_p ($J\ K^{-1}\ g^{-1}$)
	Organic	Water			
Benzoic acid			1.32	0.43	1.21
Sq-3			0.812	0.6	2.93
I	For combustion		1.12		1.54
	0.027	0.030			
	For vaporization				
	0.10	0.039			
II	For combustion		1.14		1.54
	0.039	0.033			
	For vaporization				
	0.021	0.037			

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* 1 atm = 760 Torr = 101325 pa.

The sample for the combustion experiments was transferred under vacuum to a receiver containing the ampoules to be filled. After sealing and pressure-testing, the ampoule was weighed and the mass of sample in the ampoule was calculated.

Apparatus and procedure

The precision rotation bomb calorimeter [5] and some of its important improvements [6] have been reported previously. A tantalum-lined bomb ($V_{\text{bomb}} = 318.03$ cm^3) and a platinum crucible were used for burning the chlorocompounds to keep the As_2O_3 solution in the bomb against pre-oxidation before ignition.

The calorimeter was operated in the isoperibol mode. The oxygen pressure was 40 atm. Polypropylene thread was used for ignition; its heat of combustion was determined in a separate experiment to be equal to -46119.0 ± 4.1 J g^{-1}. One gram of benzoic acid (NBS 39i) was used in the calibration experiments, and 1 g of water was placed in the bomb. In the chlorocompound experiments, the initial bomb liquid was 40 g of 0.06 m mol g^{-1} As_2O_3 solution. Squalane (designation SQ-3) was used as the auxilliary substance, and its heat of combustion was determined as -46765.93 ± 1.73 J g^{-1}. The bomb rotation started 80 s after ignition and continued throughout the experiment. The main period in the chlorocompound experiments was prolonged to 30 min to ensure that equilibrium was established in the final state. In all other respects, the procedures of the experiment were the same as those reported previously [5,6].

After each experiment the bomb gas was tested for CO and the interior of the bomb was checked for soot. In the calibration experiments the total bomb liquid was titrated with 0.1 N NaOH solution for HNO_3 analysis. In the experiments of chlorocompounds, the final bomb solution and washings (about 180 g) was divided into parts for the following analyses: (a) excess As_2O_3 by potentiometric titration with standard potassium permanganate solution; (b) HNO_3 by the Kjeldahl procedure [7]; (c) dissolved platinum by colorimetry using an iodate method [8]; (d) Cl^- by potentiometric titration with $AgNO_3$ solution.

An LKB 8721-3 vaporization calorimeter was used for the heat of vaporization measurements. All electric instruments used in the calorimeter were re-calibrated. The heating power was set at 100 mW (for I) or 50 mW (for II), and the heating time was set at 900 s. The experimental procedures were the same as those in the calorimeter manual.

RESULTS

The combustion experiment data were processed with a program obtained by courtesy of Lund University, Sweden (with some modifications by us).

TABLE 2

Summary of typical combustion experiments

		I	II
m(Compd)	(g)	0.880378	0.892940
m(oil)	(g)	0.185013	0.163062
m(Fuse)	(g)	0.000859	0.000713
ϵ_i(Cont)	($J\ K^{-1}$)	131.73	179.85
ΔT	(K)	1.48033	1.43955
$\Delta E^f_{soln}(CO_2)$	(J)	46.02	60.76
$\Delta E^f_{diln}(HCl)$	(J)	−8.88	−6.70
$\Delta E^f_{dec}(HNO_3)$	(J)	0.33	0.63
$\Delta E^f_{dec}(H_2PtCl_6)$	(J)	3.15	0.85
$\Delta E^f_{dec}(As_2O_5)$	(J)	199.14	222.08
ΔE_Σ	(J)	49.87	63.13
ΔE_c°(Compd)	($J\ g^{-1}$)	−19868.50	−19938.66

Atomic masses of 1977 were adopted for molecular mass calculations. The values for Henry's Law constant, $k(CO_2) = 0.03414$ mol dm^{-3} atm^{-1}, and for $\Delta E_{soln}(CO_2,g) = -17280 \pm 167$ J mol^{-1} were taken from ref. 9.

The auxiliary data used in the calculations are listed in Table 1. Five calibration experiments gave a mean value with s.d.m. of ϵ_i^0(calorimeter) = 17700.97 ± 1.04 J K^{-1}, which was used for calculating the results for II. Before burning I, the internal parts of the bomb had been changed, so a second calibration was taken with a result of ϵ_i^0(calorimeter) = 17720.43 ± 0.42 J K^{-1}. Results from a typical combustion experiment are shown in Table 2. The results of combustion and vaporization experiments are given in Table 3. The stardard enthalpies of combustion of both I and II refer to the following standard state combustion reaction at 298.15 K.

$$C_4H_8Cl_2(l) + 5.5\ O_2(g) = 4\ CO_2(g) + 3\ H_2O(l) + 2\ HCl(600\ H_2O)(soln.)$$

The derived gaseous enthalpies of formation are listed in Table 4. The values

TABLE 3

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

	I		II	
	$-\Delta E_c^\circ(l)$	ΔH_v°	$-\Delta E_c^\circ(l)$	ΔH_v°
	2523.56	42.34	2532.47	46.49
	2525.84	42.24	2530.02	46.85
	2522.89	42.30	2527.72	46.36
	2521.55	42.25	2529.29	46.39
	2520.82	42.37	2532.43	46.67
Mean	2522.93	42.30	2530.39	46.55
s.d.m.	±0.87	±0.02	±0.92	±0.09

TABLE 4

Results and derived quantities (kJ mol^{-1})

The uncertainties given are twice the final overall s.d.m. Corrections for the water content of the combustion samples have been made.

	$-\Delta E_c^\circ(l)$	$-\Delta H_c^\circ(l)$	$-\Delta H_f^\circ(l)$	ΔH_v°	$-\Delta H_f^\circ(g)$
I	2523.61 ± 1.76	2527.33 ± 1.76	237.28 ± 1.78	42.30 ± 0.05	194.98 ± 1.78
II	2531.12 ± 1.92	2534.84 ± 1.92	229.77 ± 1.94	46.37 ± 0.02	183.40 ± 1.94

of $\Delta H_f^\circ(CO_2, g)$, $\Delta H_f^\circ(H_2O, l)$ and ΔH_f°(HCl (600 H_2O), soln.) were taken from refs. 10 and 11.

DISCUSSION

For ΔH_v°(II), direct calorimetric results by Wadso [12], (46.36 ± 0.02 kJ mol^{-1} and those from a measurement previously undertaken in our laboratory [13] (46.36 ± 0.03 kJ mol^{-1}) were compatible with the result of this work within the uncertainty intervals. A selected value was taken as 46.37 ± 0.02 kJ mol^{-1}. No calorimetric data for ΔH_v°(I) were found in the literature. For comparison, Varushchenko's results derived from vapour pressure measurements [14] were 42.13 ± 0.59 kJ mol^{-1} for I and 46.32 ± 0.71 kJ mol^{-1} for II.

Rozhnov et al. [15] reported the enthalpies of formation of dichlorobutanes from the equilibrium constant measurements, $\Delta H_f^\circ(I, l) = -236.4$ kJ mol^{-1} and $\Delta H_f^\circ(II, l) = -228.4$ kJ mol^{-1}, respectively. These data are in agreement with our results, though our direct calorimetric data are more reliable.

In order to compare the electrostatic interactions in the dichloroalkane molecules, we consider the following redistribution reaction a,b-$C_nH_{2n}Cl_2(g) + C_nH_{2n+2}(g) = a$-$C_nH_{2n+1}Cl(g) + b$-$C_nH_{2n+1}Cl(g) + \Delta H_r^\circ$ where a and b are used to indicate the substitution sites of Cl atoms. On both sides of the reaction, the number and kind of the chemical bonds, the carbon skeletons of the molecules and the sites of chlorine substitution are the same. If there is no excess electrostatic interaction between the two Cl atoms in the dichloroalkane, ΔH_r° of this reaction can be expected to be zero. In other words, the $-\Delta H_r^\circ$ of these reactions, if any, can be identified as the electrostatic interactions between the chlorine atoms in the dichloroalkanes. The calculated results from our data and that in the literature are listed in Table 5. From the enthalpy of formation of 2-chlorobutane listed in ref. 17 (−161.2 ± 8.4 kJ mol^{-1}), the calculated ΔH_r° for 1,3-dichlorobutane is a positive value with a large uncertainty of +5.51 ± 8.4 kJ mol^{-1}. The above value for 2-chlorobutane was obtained originally from combustion

TABLE 5

Calculated results of $\Delta H_r°$(g) of the redistribution reactions [1] of some dichloroalkanes (in kJ mol^{-1})

Compound	N_c	$-\Delta H_f°$(g, expt)	$-\Delta H_r°$(g) [c]
1,1-$C_2H_4Cl_2$	1	127.8 ±1.1 [a]	12.4±1.3
2,2-$C_3H_6Cl_2$	1	173.2 ±8.5 [a]	12.3±8.5
1,2-$C_2H_4Cl_2$	2	129.7 ±1.7 [a]	10.5±1.9
1,2-$C_3H_6Cl_2$	2	162.6 ±1.2 [a]	10.3±1.5
1,3-$C_3H_6Cl_2$	3	159.5 ±8.4 [a]	0.8±8.4
1,3-$C_4H_8Cl_2$	3	194.98±1.78 [b]	−0.1 [d]
1,4-$C_4H_8Cl_2$	4	183.40±1.94 [b]	−0.4±2.7

[a] From ref. 17.

[b] This work.

[c] The data of $\Delta H_f°$(g) (kJ mol^{-1}) used in the calculations are: C_2H_6, −84.0±0.2 [17]; C_3H_8, −104.5±0.3 [17]; n-C_4H_{10}, −126.39±0.77 [17]; C_2H_5Cl, −112.1±0.5 [17]; 1-C_3H_7Cl, −132.4±0.6 [17]; 2-C_3H_7Cl, −145.0±0.6 [17]; 1-C_4H_9Cl, −154.66±1.25 [16]; 2-C_4H_9Cl, −166.6 (see text).

[d] See text.

calorimetry with a "quartz wool" technique and a platinum-lined bomb. The sample in the glass ampoule was covered with a layer of paraffin oil which could not prevent the liquid sample from evaporating. The $\Delta H_f°$(g) of 1-chlorobutane obtained by the same technique was −148.1 kJ mol^{-1}, in significant disagreement with the result of Stridh and Sunner [16] obtained using a rotation bomb calorimeter. So it seems that the data for 2-chlorobutane is unreliable, and a redetermination project is in progress in our laboratory. Here an estimated value of this is approached. (1) The differences of $\Delta H_f°$(g) between alkanes and the corresponding chloroalkanes with its chlorine substituted on secondary carbon were calculated, from the data listed in ref. 17, as 40.5 ± 0.7 kJ mol^{-1} for propane and 2-chloropropane, 38.8 ± 1.8 kJ mol^{-1} for hexane and 2-chlorohexane and 40.3 ± 3.8 kJ mol^{-1} of cyclohexane and chlorocyclohexane, respectively. A weighting mean of 40.1 kJ mol^{-1} and $\Delta H_f°$(butane, g) = −126.4 ± 0.8 kJ mol^{-1} were used to derive the $\Delta H_f°$(2-chlorobutane, g) = −166.5 kJ mol^{-1}. (2) The differences of $\Delta H_f°$(g) between 1-chloroalkanes and their isomeric 2-chloroalkanes were calculated from the data found in ref. 17 as −12.6 ± 0.8 kJ mol^{-1} for chloropropanes and −9.9 ± 3.5 kJ mol^{-1} for chlorohexanes. A weighting mean of −12.1 kJ mol^{-1} was selected and the $\Delta H_f°$(g) of 2-chlorobutane was derived as −166.8 kJ mol^{-1}. Finally, the mean value of $\Delta H_f°$(g) of 2-chlorobutane was taken as −166.6 kJ mol^{-1} to calculate the $\Delta H_r°$ of 1,3-dichlorobutane listed in Table 5.

From Table 5, it can be found that the Cl · · · Cl electrostatic interaction (i.e. $-\Delta H_r°$ here) in dichloroalkanes decreases with the intervening number of carbons, N_c, between the Cl atoms. They are, respectively, 12.4 (for $N_c = 1$), 10.5 (for $N_c = 2$), small (for $N_c = 3$) and ~ 0 (for $N_c \geq 4$) kJ mol^{-1}.

It is known that two polar substituents in a molecule could act on each other either through the space, the so-called "field effect", or through the bond system, the "induction effect". There are reasons to believe that the induction effect reduces exponentially and approaches zero after a few bonds. Our results in Table 5 show that the induction effect plays an important role in the intramolecular electrostatic interaction in chloroalkanes. A further treatment of the electrostatic energies and dipole moments in chloroalkanes is in progress.

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REFERENCES

1 L-G. Hammarstrom, T. Liljefors nd J. Gasteiger, J. Comput. Chem., 9 (1988) 424.
2 G.S. Buckley and A.S. Rodgers, J. Phys. Chem., 87 (1983) 126.
3 An Xuwu and Hu Riheng, Sino-Japanese Joint Symposium on Calorimetry and thermal Analysis Abstracts, 1986, Hangzhow, China, p. 97.
4 P. Sellers, Acta Chem. Scand., 25 (1971) 2295.
5 An Xuwu, Yan Haike and Hu Riheng, Chim. Acta Sin., 40 (1982) 713.
6 An Xuwu, Zhu Huiping and Hu Riheng, Thermochim. Acta, 121 (1987) 713.
7 A.I. Vogel, A Text-Book of Quantitative Inorganic Analysis, Longmans, London, 1961, p. 255.
8 E.B. Sandell, Anal. Chem., 20 (1948) 253.
9 R.L. Berg and C.E. Vanderzee, J. Chem. Thermodyn., 10 (1978) 1113.
10 CODATA recommended key values for thermodynamics, J. Chem. Thermodyn., 7 (1975) 1.
11 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, Natl. Bur. Stand. (U.S.) Tech. Note, 270-3 (1968), 270-4 (1969).
12 I. Wadso, Acta Chem. Scand., 22 (1968) 2438.
13 An Xuwu and Hu Hui, Acta Physicochim. Sin., 5 (1989) 565.
14 R.M. Varushchenko, V.V. Pisarev and T.A. Kotel'nikova, Zh. Fiz. Khim., 54 (1980) 2666.
15 A.M. Rozhnov and T.N. Nesterova, Zh. Fiz. Khim., 52 (1978) 1834.
16 G. Stridh and S. Sunner, J. Chem. Thermodyn., 7 (1975) 161.
17 J.B. Pedley and J. Rylance, Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds, University of Sussex, Brighton, Gt. Britain, 1977.