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THERMOCHEMICAL STUDIES OF ORGANOMETALLIC COMPOUNDS
I. HEATS OF FORMATION OF DIMETHYLCHLOROSILANE, METHYLDICHLOROSILANE AND DIMETHYLDICHLOROSILANE

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INTRODUCTION

Thermochemical studies of organosilicon compounds began in 1950, and the first article on thermochemical studies of their chlorine derivatives was published in 1953 by Andrianov and Pavlov[1], who determined the heats of hydrolysis of a number of alkyl- and aryl-chlorosilanes.

Later, other investigators[2] used the hydrolysis method to determine the heats of formation of these compounds, but, the results were reported as unsatisfactory because of the difficulties in determining the composition of the hydrolysis products. Also, other authors[3,4] have suggested that the composition of the hydrolysis products of alkyl- and aryl-chlorosilanes depends not only on the nature of the substance, but also on the reaction conditions (and therefore any accurate determination is impossible, except in those cases when trialkyl(aryl)-monochlorosilanes are subjected to hydrolysis). It seemed of interest, therefore, to develop a method for determining the heats of formation of these compounds by their direct combustion in a calorimetric bomb.

Recently, two new works[5,6], on the determination of the heats of formation of organochlorosilanes based on the hydrolysis method, have been published. This approach is quite justifiable as it seemed to be impossible to use the method of direct combustion of the substance as will be seen below.

As a rule, the combustion of organosilicon compounds in a calorimetric bomb is incomplete[7,8] for the following reason[9]. As combustion starts, the silica which is formed covers the surface of the compound under investigation and interferes with the access to oxygen; when burning is over, the unburned part of the compound is pyrolyzed to form a mixture of silica and the products of decomposition and incomplete combustion. The results obtained when this mixture is analysed to assess the conversion level, are unreliable and frequently erroneous. Therefore, the assumption that all the unburned residue consists of carbon is probably not more erroneous. This assumption was probably[10,11] based on the dark, grey-to-black, colour of the residue (and on the insufficient amount of CO_2 formed). Thus the attainment of complete combustion should be considered as the principle criterion of reliability of results obtained when burning organosilicon compounds in a calorimetric bomb.

In case of organochlorosilicon compounds, the problem is more complicated, mainly because the combustion of such compounds is even less complete. Also it is necessary to reduce Cl_2, evolved on burning, to HCl in order to attain a certain thermodynamic state of the final products as well as to protect the walls and fittings of the bomb from chemical attack of highly corrosive combustion products.

Since 1961, we have carried out systematic thermochemical studies of organometal compounds. Some of the results will be published in this series of articles. A description is given below of the calorimetric method of combustion of liquid organochlorosilanes and results for the formation enthalpies for three methylchlorosilanes are presented.

EXPERIMENTAL

As a result of experimental studies carried out over a long period of time we[9] have achieved complete combustion of liquid organosilicon compounds with boiling points below 120° (including those containing up to 70% chlorine) by the method of explosive combustion in a calorimetric bomb. This was the first, though essential step in this direction. Later, other problems were also solved, *i.e.*, converting Cl_2 evolved during combustion, to HCl by reduction with hydrazine dihydrochloride

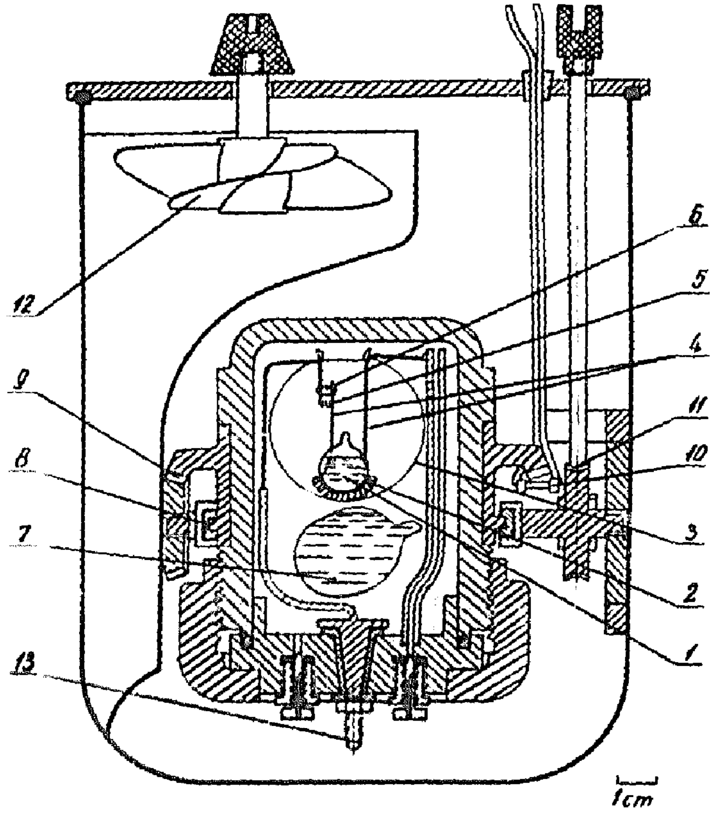

Fig. 1. (1). Ampoule with substance; (2). heater; (3). glass sphere; (4). platinum leads; (5). platinum igniter; (6). glass holder; (7). ampoule with hydrazine dihydrochloride soln.; (8). Teflon-metallic bearing; (9). gearing for rotating bomb around longitudinal axis; (10). thermistor; (11). worm gear drive for rotating bomb around lateral axis; (12). stirrer for circulating water; (13). isolated bomb lead-in.

in a rotating bomb[12] and ensuring complete inertness of the bomb material to the products of combustion by using a tantalum bomb. In addition, the method for obtaining an explosion in the bomb was also improved; this made it possible to remove some sources of errors and at the same time to simplify the experimental technique.

We shall describe only the latest version of the method. However, the necessary data on the calorimeter and measuring technique will first be briefly summarised.

The experiments have been carried out using a calorimeter with an isothermal shell[13] which was modelled on the Coops' calorimeter[14]. Inserted into the vessel of this calorimeter (Fig. 1) is a removable mechanism to rotate the bomb and constructed mainly according to a design already described[15]. The bomb and its inner fittings are made of tantalum of purity 97.75%; the main impurity is 2.10% of niobium. In the calibration burning (using benzoic acid) and in the control tests with *p*-chlorobenzoic acid (using the conventional procedure) both the cup and the igniter wire are of platinum (the bomb contents when using the explosion-combustion method are described below). A detailed description of the calorimetric system of this unit and the results of calibration and of the control experiments are given in another article[16].

The calorimeter temperature was measured by a battery of thermistors[17]. The circuit sensitivity was $2 \cdot 10^{-4}$ deg.; the ΔT measuring accuracy was $\pm 5 \cdot 10^{-4}$ deg.

The shell temperature was maintained constant at $25 \pm 0.002°$ using a special mercury contact thermometer.

All the values were based on 1961 atomic weights. It is assumed that:

$0°C = 273.15°K$; $1\ cal = 4.1840\ J$;
ΔH°_f (HNO_3) liq $= -14.1$ kcal/mole;
ΔU°_c (carbon) $= -7890$ kcal/g (ref. 18, p. 57)
ΔU°_c (fuse) $= -4000$ kcal/g

The error has been assumed as:

$$S = \pm\sqrt{\Sigma V_i^2/n(n-1)}$$

In the calorimetric experiments, the initial period consisted of 20, the main period of 50, and the final period of 40 readings. The initial oxygen pressure in the bomb was 30 atm in all experiments. The energy equivalent of the calorimeter as determined with standard benzoic acid K-1 in seven experiments is 2511.7 ± 0.3 cal/deg. at 25°. The heat of combustion of benzoic acid under standard conditions is equal to 6317.9 cal/g.

p-Chlorobenzoic acid purified by double recrystallization from high purity benzene and vacuum-sublimated at 10^{-2} mm Hg was burned as reference substance. The purity, determined on the chlorine content[18], was 99.9%. The measured value for the heat of combustion of *p*-chlorobenzoic acid, $\Delta U^\circ_c = -4678.4 \pm 2.4$ cal/g, is in good agreement with the data of Smith *et al.*[19]: $\Delta U^\circ_{c\ 293} = -4680.8 \pm 2.3$ cal/g.

The heat of reaction while burning *p*-chlorobenzoic acid and the methylchlorosilanes:

$$N_2H_4 \cdot 2\ HCl\ (aq.) + O_2\ (g.) = N_2\ (g.) + 2\ H_2O\ (liq.) + 2\ HCl\ (aq.) \quad (1)$$

for each experiment was estimated allowing for the actual concentration of HCl in water[20].

The heat of reaction

$$\tfrac{1}{2}\,[N_2H_4 \cdot 2\,HCl]\,(aq.) + \tfrac{1}{2}\,H_2O\,(liq.) = NH_4Cl\,(aq.) + \tfrac{1}{4}\,O_2\,(g.) \qquad (2)$$

for NH_4Cl concentration in water equal to $NH_4Cl \cdot 12{,}000\ H_2O$ was assumed equal to 3.51 kcal and constant in all experiments because of the small amount of NH_4Cl.

The quantity of electric energy was measured by a reference meter calibrated by blank tests on the calorimeter. The constant of this meter was 45.8 ± 0.1 cal/rev.

When calculating corrections reduced to standard state, the bomb liquid was assumed to be pure water.

Methylchlorosilanes, synthesized by the method of direct reaction of CH_3Cl with silicon after pretreatment, were distilled on a laboratory column of average efficiency (18 theoretical plates). Narrow cuts of every compound obtained in the range 0.2–0.3° were transferred directly from the receiver of this column to the still of another specially designed column[21] of high efficiency (112 theoretical plates at reflux ratio = ∞).

During rectification on the column of high efficiency fractions were drawn off over the range 0.05–0.1°. The parameters for pure methylchlorosilanes are given in Table 1.

TABLE 1

PARAMETERS FOR PURE METHYLCHLOROSILANES

No.	*Compound*	*B.p. (°C)*		d_4^{20}	n_D^{20}	*Chlorine content*[a] *of compound (%)*	
		Actual (mm Hg)	*Recalcd. for 760 mm*[b]			*Found*	*Calcd.*
1	$(CH_3)_2SiHCl$	35.9_8(765)	35.7_0	0.8625	1.3832	37.6	37.47
2	CH_3SiHCl_2	41.3_8(764)	41.2_3	1.1069	1.3992	61.5	61.64
3	$(CH_3)_2SiCl_2$	70.2_8(761)	70.2_4	1.0666	1.4003	55.1	54.94

[a] Chlorine content of methylchlorosilanes was found by the difference between the total content in the bomb liquid (determined by the Volhard method) and the amount in the hydrazine dihydrochloride taken for the expt. [b] Recalculation for normal pressure, 760 mm, was done according to ref. 22.

TABLE 2

DEGREE OF PURITY OF THE SUBSTANCES (DETERMINED BY CHROMATOGRAPHY)

No.	*Substance and impurities*	*Amount (%)*	*Purity of sample (%)*
1	$(CH_3)_2HSiCl$	99.52	99.52
	CH_3HSiCl_2	0.48	
2	CH_3HSiCl_2	99.60	99.60
	$(CH_3)_2HSiCl$	0.40	
3	$(CH_3)_2SiCl_2$	99.50	99.50
	CH_3SiCl_3	0.43	
	$(CH_3)_3SiCl$	0.07	

The degree of purity of the substances was determined by chromatography[23] using a heat conductivity detector*. The results are presented in Table 2.

A sample of the substance burned in the ampoule, 1 (Fig. 1), made of glass of a high coefficient of expansion was placed on a heater, 2, which in turn was inside the glass sphere, 3 (a mass of ~8 g). A heater made of 30-cm nichrome wire (0.2-mm diam. and 13-Ω resistance) in the form of a spiral is inserted into a glass tube (inner diam. 2.5 mm) and hermetically sealed. Platinum leads, 4, (0.5 mm diam.) were taken from this tube. In the sphere, 3, above the heater is placed an igniter, 5, (a spiral with 3–4 turns made of platinum wire, 0.1-mm diam. and 25 mm length) which is connected in series to the lead near the glass holder, 6. Under the sphere, 3, on the bottom of the bomb, there is a glass ampoule, 7, containing 8 ml of a 2.5% solution of hydrazine dihydrochloride. After the bomb had been filled with dry oxygen, an experiment was started. At the beginning of the main period of the experiment, a 1.2-A electric current was fed to the heater, 2, the heating causes the ampoule, 1, to break. After the liquid has poured onto the heater, it begins to evaporate. Vapours mixed with oxygen reach the platinum igniter, 5, and catch fire with an explosion. As a result, the sphere is smashed into fine pieces and a complete combustion of the substance occurs**. The ampoule, 7, is also broken and the hydrazine dihydrochloride solution from it spreads over the bomb bottom. After the explosion, the current was switched off and the bomb rotation was started (10 min). The heat effect of rotation was calculated from the number of revolutions, identical in all the experiments.

It should be noted that an explosive force of a certain strength is required, as combustion may be incomplete if the explosion is weak or does not occur at all, while a powerful explosion may cause a bomb deformation. Under similar conditions, the explosive force decreases with increase of chlorine content and this force should therefore be controlled. The explosion can be made more powerful by increasing the amount of the substance vaporized. This is achieved by extending the diameter of the sphere, 3 (from 37 to 41 mm) and by increasing the distance between the heater and the igniter (from 23 to 30 mm).

After completion of the experiment, the gaseous products were checked for Cl_2 (by iodine–starch solution) and for CO (using $PdCl_2$) and analysed for CO_2 content. The presence of Cl_2 was not observed. CO was found only in cases of incomplete combustion, when the experiments were rejected. In all other experiments, the values found for CO_2 were in good agreement with the calculated values. The bomb contents were then washed off with hot, distilled water and the amounts of unconverted $N_2H_4 \cdot 2\,HCl$[24], and NH_4Cl[25] and HNO_3[25] formed, were determined. SiO_2 formed in the combustion of organochlorosilanes by this method is snow-white in colour. According to X-ray analysis data, it consists of an amorphous phase.

To calculate the values of heat of formation the following indices were accepted (in kcal/mole): ΔH_f° CO_2 (g.) = −94.05; ΔH_f° H_2O (liq.) = −68.315; ΔH_f° $N_2H_4 \cdot 2\,HCl$ (aq.) = −81.8; ΔH_f° ($HCl \cdot 600\,H_2O$) = −39.823[20]; ΔH_f° SiO_2 (colloidal soln.) = −217.44[26].

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** The completeness of combustion was controlled by quantitative analysis of CO_2 formed in the bomb as well as visually[8–11].

RESULTS

The results of the experiments on the determination of the formation enthalpy of $(CH_3)_2SiHCl$, CH_3SiHCl_2 and $(CH_3)_2SiCl_2$ are summarised in Tables 3, 4 and 5, respectively.

In these Tables:

$E_{(cont.)}$—energy equivalent of the bomb contents
n_1—number of moles of hydrazine dihydrochloride in reaction (1)
n_2—number of moles of NH_4Cl in reaction (2)
q_1—heat evolved according to reaction (1)
q_2—heat evolved according to reaction (2)
q_3—heat due to electric heating
q_4—heat due to the bomb rotation
q_5—heat of dissolution of CO_2 in water
q_6—correction for reduction to $HCl \cdot 600\ H_2O$
q_7—heat evolved on HNO_3 formation
q_8—correction for admixtures.

Correction for the heat of evaporation of water in the bomb is 1.33 cal for every experiment.

There is only one literature report[5] dealing with $(CH_3)_2SiCl_2$(gas), $\Delta H_f^\circ = -108.4$ kcal/mole.

TABLE 3

RESULTS OF THE EXPERIMENTS ON THE DETERMINATION OF THE FORMATION ENTHALPY OF $(CH_3)_2SiHCl$ (LIQUID)

m (substance) (g)	0.35283	0.31316	0.51657	0.29736	0.35326
ΔT_{corr} (deg.)	1.0599	0.8905	1.3560	0.8322	1.0377
E_{cont} (cal/deg.)	−11.1	−10.9	−11.3	−11.1	−11.1
$(E_{cal}+E_{cont})\Delta T_{corr}$	−2673.80	−2246.54	−3421.19	−2099.47	−2617.91
n_1 (g-mole)	0.000293	0.000394	0.000711	0.000372	0.000363
n_2 (g-mole)	0.00020	0.000150	0.000113	0.000120	0.000140
q_1 (cal)	39.24	52.84	95.32	49.93	48.68
q_2 (cal)	−0.70	−0.53	−0.40	−0.42	−0.49
q_3 (cal)	471.87	266.87	178.70	221.15	398.88
q_4 (cal)	37.37	37.35	37.37	37.37	37.35
q_5 (cal)	0.55	0.49	0.77	0.47	0.55
q_6 (cal)	−0.62	−0.62	−1.32	−0.44	−0.75
q_7 (cal)	1.52	1.38	2.07	1.46	2.76
q_8 (cal)	5.22	4.63	7.64	4.40	5.22
$-\Delta u_c$ (cal/g)	6010.50	6019.16	6005.71	6009.15	6021.18

$-\Delta u_c$ (mean) $= 6013.14 \pm 5.98$ cal/g

$-\Delta U_c^\circ = 569.0 \pm 0.6$ kcal/mole

$-\Delta H_c^\circ = 570.5 \pm 0.6$ kcal/mole

$-\Delta H_f = 79.8 \pm 0.6$ kcal/mole

TABLE 4

RESULTS OF THE EXPERIMENTS ON THE DETERMINATION OF THE FORMATION ENTHALPY OF CH_3SiHCl_2 (LIQUID)

m (substance) (g)	0.42197	0.52653	0.46091	0.56024	0.53847
$\Delta T_{corr.}$ (deg.)	0.6951	0.7798	0.7645	0.8598	0.8312
$E_{cont.}$ (cal/deg.)	−11.1	−11.1	−11.2	−11.2	−11.2
$(E_{cal}+E_{cont.})\cdot\Delta T_{corr.}$	−1753.69	−1967.30	−1928.67	−2167.92	−2096.93
n_1 (g-mole)	0.000915	0.000883	0.000891	0.000654	0.000877
n_2 (g-mole)	0.000110	0.000130	0.000210	0.000090	0.000125
q_1 (cal)	122.03	118.28	119.40	87.71	117.53
q_2 (cal)	−0.39	−0.46	−0.74	−0.32	−0.44
q_3 (cal)	292.30	185.21	343.32	310.16	282.44
q_4 (cal)	37.35	37.37	37.35	37.35	37.35
q_5 (cal)	0.30	0.36	0.32	0.38	0.37
q_6 (cal)	−2.06	−2.38	−1.93	−1.76	−2.44
q_7 (cal)	2.76	3.24	3.14	2.82	2.76
q_8 (cal)	10.17	12.69	11.11	13.50	12.98
$-\Delta u_c$ (cal/g)	3063.05	3065.96	3076.78	3069.06	3056.30

$-\Delta u_c^{\circ}$ (over) $= 3066.23 \pm 6.75$ cal/g

$-\Delta U_c^{\circ} = 352.7 \pm 0.8$ kcal/mole

$-\Delta H_c^{\circ} = 353.6 \pm 0.8$ kcal/mole

$-\Delta H_f^{\circ} = 105.9 \pm 0.8$ kcal/mole

TABLE 5

RESULTS OF THE EXPERIMENTS ON THE DETERMINATION OF THE FORMATION ENTHALPY OF $(CH_3)_2SiCl_2$ (LIQUID)

m (substance) (g)	0.31972	0.50516	0.35407	0.40085	0.49455
$\Delta T_{corr.}$ (deg.)	0.8412	0.9416	1.2559	0.8509	0.9625
$E_{cont.}$ (cal/deg.)	−8.8	−8.8	−8.8	−9.0	−9.0
$(E_{cal}+E_{cont.})\cdot\Delta T_{corr.}$	−2120.12	−2369.47	−3164.56	−2144.80	−2426.28
n_1 (g-mole)	0.000483	0.001000	0.000672	0.000626	0.000519
n_2 (g-mole)	0.000175	0.000200	0.000290	0.000180	0.000190
q_1 (cal)	64.57	133.93	89.94	83.99	69.59
q_2 (cal)	−0.61	−0.70	−1.02	−0.63	−0.67
q_3 (cal)	769.38	229.16	1657.97	457.68	391.46
q_4 (cal)	37.35	37.37	37.35	37.34	37.35
q_5 (cal)	0.39	0.57	0.42	0.47	0.56
q_6 (cal)	−1.66	−2.21	−1.68	−1.00	−1.54
q_7 (cal)	1.52	1.48	2.14	2.76	1.82
q_8 (cal)	4.06	6.41	4.49	5.09	6.28
$-\Delta u_c$ (cal/g)	3898.52	3889.42	3887.05	3892.80	3887.89

$-\Delta u_c^{\circ}$ (over) $= 3891.13 \pm 4.18$ cal/g

$-\Delta U_c^{\circ} = 502.2 \pm 0.5$ kcal/mole

$-\Delta H_c^{\circ} = 503.4 \pm 0.5$ kcal/mole

$-\Delta H_f^{\circ} = 118.4 \pm 0.5$ kcal/mole

SUMMARY

1. A method of combustion for organosilicon compounds including those containing up to 70% of chlorine has been developed, which allows complete combustion to be achieved with an explosion in a calorimetric bomb.

2. Combustion enthalpies for three methylchlorosilanes have been evaluated in a rotating tantalum bomb, and the values: $\Delta H^\circ_{c,\,298}\,((CH_3)_2HSiCl)_{liq.} = -570.5 \pm 0.6$; $\Delta H^\circ_{c,\,298}\,(CH_3HSiCl_2)_{liq.} = -353.6 \pm 0.8$, and $\Delta H^\circ_{c,\,298}\,((CH_3)_2SiCl_2)_{liq.} = -503.4 \pm 0.5$ kcal/mole have been obtained.

3. The formation enthalpies of compounds have been calculated, and the values: $\Delta H^\circ_{f,\,298}\,((CH_3)_2HSiCl)_{liq.} = -79.8 \pm 0.6$; $\Delta H^\circ_{f,\,298}\,(CH_3HSiCl_2)_{liq.} = -105.9 \pm 0.8$, and $\Delta H^\circ_{f,\,298}\,((CH_3)_2SiCl_2)_{liq.} = -118.4 \pm 0.5$ kcal/mole, have been obtained.

There is only one indirectly determined value in the literature[5], $\Delta H^\circ_f\,((CH_3)_2SiCl_2)_{liq.} = -116.0$ kcal/mole, that is near our data.

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