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THERMOCHEMICAL STUDIES OF ORGANOMETALLIC COMPOUNDS
II. THERMOCHEMISTRY OF METHYLCHLOROSILANES

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SUMMARY

This paper presents the results of the experimental determination of the heats of formation of trimethylchlorosilane and methyltrichlorosilane and the calculation for the heat of formation for a sixth compound in this series—gaseous monomethylmonochlorosilane has been estimated. In addition, the thermodynamic properties of the methylchlorosilanes have been listed. These were calculated on the basis of our enthalpies of formation and the entropies of these compounds cited in the literature.

INTRODUCTION

In an earlier paper[1] we discussed a new method for the combustion of liquid organochlorosilanes in a calorimetric bomb, and the determination of the enthalpies of formation of liquid $(CH_3)_2HSiCl$, CH_3HSiCl_2 and $(CH_3)_2SiCl_2$. These were found to be -79.8 ± 0.6, -105.9 ± 0.8 and -118.4 ± 0.5 kcal·mole^{-1}, respectively.

EXPERIMENTAL

The parameters of these compounds, which were purified by using a highly efficient rectification column of a special design, are summarized in Table 1.

Under the conditions described previously[1], methyltrichlorosilane burned with either a weak explosion or no explosion, thus resulting in incomplete combustion. To ensure a sufficiently strong explosion with methyltrichlorosilane, glass spheres[1] of a larger diameter (44 mm) were used and the distance of the heater from the igniter was maintained in the range 28–30 mm.

In other respects the experimental procedure, operating conditions, calorimeter parameters, and measuring circuit data were similar to those described in our previous paper[1].

RESULTS

The results of the calorimetric experiments are presented in Tables 2 and 3.

In these Tables:
$E_{(\text{cont.})}$ = 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.

Intrinsic energy change and combustion enthalpy hold for the reaction:

$$(CH_3)_nSiCl_{4-n}(\text{liq}) + 2n\ O_2\ (\text{gas}) + (2402-602\ n)H_2O\ (\text{liq}) \rightarrow$$
$$SiO_2\ (\text{amorph., hydrat.}) + n\ CO_2\ (\text{gas}) + (4-n)[HCl \cdot 600\ H_2O]\ (\text{liq})$$

TABLE 1

PARAMETERS FOR PURE METHYLCHLOROSILANES

Compound	B.p. (°C)		d_4^{20}	n_D^{20}	Chlorine content of compound (%)		Composition[b] (%)	
	Actual (mm Hg)	Recalcd. for 760 mm[a]			Found	Calcd.		
$(CH_3)_3SiCl$	57.6_7(759)	57.7_1	0.8590	1.3890	32.7	32.63	Basic compd.	99.76
							$SiCl_4$	0.17
							CH_3SiCl_3	0.07
CH_3SiCl_3	66.4_4(768)	66.1_2	1.2761	1.4123	71.1	71.15	Basic compd.	99.80
							$(CH_3)_3SiCl$	0.20

[a] Recalculation for 760 mm was carried out according to ref. 2. [b] Determined by gas chromatography (see ref. 1).

DISCUSSION

In order to calculate the heat of combustion of the methylchlorosilanes under study, it was assumed[3] that:

$$\Delta H_f^0\ CO_2\ (g) = -94.052 \pm 0.008\ \text{kcal} \cdot \text{mole}^{-1}$$

$$\Delta H_f^0\ H_2O\ (l) = -68.315 \pm 0.009\ \text{kcal} \cdot \text{mole}^{-1}$$

$$\Delta H_f^0\ [HCl\ \text{in}\ 600\ H_2O]\ (l) = -39.823 \pm 0.01\ \text{kcal} \cdot \text{mole}^{-1}.$$

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* See ref. 1.

TABLE 2

EXPERIMENTAL RESULTS IN THE DETERMINATION OF THE FORMATION ENTHALPY OF $(CH_3)_3SiCl$ (LIQUID)

m (substance) (g)	$\Delta T_{corr.}$ (deg.)	$E_{cont.}$ (cal·deg.$^{-1}$)	$(E_{cal}+E_{cont.})\cdot\Delta T_{corr.}$	n_1 (g-mole)	n_2 (g-mole)	q_1 (cal)	q_2 (cal)	q_3 (cal)	q_4 (cal)	q_5 (cal)	q_6 (cal)	q_7 (cal)	q_8 (cal)	$-\Delta u_c$ (cal·g^{-1})
0.40417	1.1484	−9.0	−2894.86	0.000474	0.00010	63.50	−0.35	118.63	37.37	0.78	−0.97	3.47	1.99	6610.59
0.44836	1.3874	−9.0	−3497.25	0.000930	0.000255	124.50	−0.90	362.16	37.33	0.86	−1.27	3.43	2.21	6624.73
0.32824	0.9689	−9.0	−2442.36	0.000523	0.000225	70.03	−0.79	158.57	37.35	0.65	−0.69	1.37	1.62	6628.00
0.33993	1.0753	−8.7	−2710.09	0.000830	0.00020	111.95	−0.70	313.39	37.34	0.67	−0.82	1.49	1.67	6608.48
0.42756	1.2106	−9.0	−3051.65	0.000622	0.00014	83.33	−0.49	96.44	37.35	0.83	−1.03	2.76	2.10	6628.95

$-\Delta u_c^0(\text{mean}) = 6618.95 \pm 7.80$ cal·g^{-1}
$-\Delta U_c^0 = 719.1 \pm 0.8$ kcal·mole^{-1}
$-\Delta H_c^0 = 720.9 \pm 0.8$ kcal·mole^{-1}
$-\Delta H_f^0 = 91.8 \pm 0.9$ kcal·mole^{-1}.

TABLE 3

EXPERIMENTAL RESULTS IN THE DETERMINATION OF THE FORMATION ENTHALPY OF CH_3SiCl_3 (LIQUID)

m (substance) (g)	$\Delta T_{corr.}$ (deg.)	$E_{cont.}$ (cal·deg.$^{-1}$)	$(E_{cal}+E_{cont.})\cdot\Delta T_{corr.}$	n_1 (g-mole)	n_2 (g-mole)	q_1 (cal)	q_2 (cal)	q_3 (cal)	q_4 (cal)	q_5 (cal)	q_6 (cal)	q_7 (cal)	q_8 (cal)	$-\Delta u_c$ (cal·g^{-1})
0.64442	0.7362	−8.7	−1855.53	0.000925	0.00012	123.90	−0.42	462.78	37.35	0.34	−3.50	2.76	8.55	1901.08
0.63507	0.8454	−9.0	−2130.99	0.000863	0.00020	115.65	−0.70	771.54	37.35	0.34	−3.07	1.93	8.42	1890.90
0.62022	0.8122	−8.8	−2047.17	0.001010	0.00023	135.21	−0.81	690.15	37.37	0.33	−3.87	3.31	8.23	1900.26
0.63647	0.6915	−8.8	−1742.93	0.000724	0.00009	97.10	−0.32	397.13	37.34	0.34	−2.37	2.48	8.44	1891.87
0.71071	0.7807	−9.0	−1967.92	0.000885	0.00017	118.60	−0.60	463.18	37.35	0.37	−3.43	2.62	9.43	1887.89

$-\Delta u_c^0(\text{mean}) = 1894.40 \pm 5.30$ cal·g^{-1}
$-\Delta U_c^0 = 283.2 \pm 0.8$ kcal·mole^{-1}
$-\Delta H_c^0 = 283.8 \pm 0.8$ kcal·mole^{-1}
$-\Delta H_f^0 = 147.2 \pm 0.9$ kcal·mole^{-1}.

The selection of the enthalpy of formation for the amorphous, finely dispersed hydrated silica which is formed when burning organosilicon compounds, is difficult. Although this value is fundamental for thermochemistry of organosilicon compounds, its selection has not yet been thoroughly analysed. Therefore, we think it necessary to give, on the basis of a survey of literature data, our own considerations about the selection of this value.

The enthalpy of formation for α-quartz reported by Hubbard and co-workers[4] as -217.72 ± 0.34 kcal·mole^{-1} is now universally accepted. This value is also confirmed by the results of Good[5] (-217.5 ± 0.5 kcal·mole^{-1}) obtained by another independent method. Later, Hubbard and co-workers[6] in another paper made a reliable determination of the enthalpy of amorphous glassy silica formation as -215.94 ± 0.31 kcal·mole^{-1}.

The heats of formation of other SiO_2 modifications are calculated from the data on the heats of quartz transformation into these modifications, obtained by measuring the heats of dissolution of the latter in HF[7-14]. The published results though not in good agreement, make it possible to suggest that the heat of quartz transformation into a certain amorphous modification will rise (in terms of absolute value) from 1.0 to 3.0 kcal·mole^{-1} with increase in the degree of dispersion of amorphous SiO_2 (in ref. 10 $\Delta H^0[SiO_2(\text{quartz}) \rightarrow SiO_2(\text{amorph., finely dispersed})] = 3.3$ kcal·mole^{-1}, but in view of the findings of other workers[11-13] this value may be considered to be somewhat overestimated).

Even less clearly understood are the solubility in water and hydration heat of various amorphous forms of SiO_2 in water. The value $\Delta H_{\text{hydrat.}}\ SiO_2 = +1.5$ kcal·mole^{-1}, reported by Mulert[7], is obsolete and erroneous. It is surprising that it has been used by the authors of fundamental reference work[3,15]. Thiessen and Koerner[16] have reported that the values for the heat of decomposition of hydrates, $SiO_2 \cdot 2H_2O$, $2SiO_2 \cdot 3H_2O$ and $SiO_2 \cdot H_2O$ are in the range +1.2 to +1.5 kcal per mole SiO_2, *i.e.*, this value is opposite in sign to that of Mulert. Some otjer works[17-19] dealing with the silica hydration process also indicate that this process is exothermal. It can be readily concluded therefore that increased specific surface of the material results in increase of the hydration heat in terms of absolute value, *i.e.*, it is expected to be greatest in finely dispersed SiO_2. It has been shown[19] that with increased specific surface of the compound, the hydration heat varies from -0.2 to -2.2 kcal mole^{-1}.

A consideration of the above work[7-14,16-19] shows that the heats of formation of amorphous hydrated silica are independent of the type of amorphous silica, *i.e.*, that

$$\Delta H_f^0\ SiO_2\ (\text{amorph., any type, hydrated}) = \Delta H_f^0\ SiO_2\ (\text{quartz}) +$$
$$+ \Delta H^0[SiO_2(\text{quartz}) \rightarrow SiO_2(\text{amorph.})] + \Delta H^0_{\text{hydrat.}}\ SiO_2(\text{amorph.}) \approx \text{const.}$$

Moreover, this value is close to the heat of quartz formation, since the heat of quartz transformation into a certain amorphous silica and the hydration heat for an amorphous SiO_2 of the same type are approximately equal in magnitude but opposite in sign. Therefore, we decided to use the data of the particular SiO_2 type for which the two values, ΔH_f^0 and $\Delta H^0_{\text{hydrat.}}$, had been accurately determined. As mentioned above, ΔH_f^0 has been reliably determined for amorphous glassy silica only ($\Delta H_f^0\ SiO_2$ (amorph., glassy) $= -215.94 \pm 0.31$ kcal·mole^{-1} [6]). The heat of hydration indicated for this type of silica[16-18] is -1.5 ± 0.5 kcal·mole^{-1}. For these reasons, we have selected the value $\Delta H_f^0\ SiO_2$ (amorph., hydrat.) $= -217.4 \pm 0.5$ kcal·mole^{-1}. It should be noted that although this value is reasonable at the present time, it is far from being indisputably and conclusively established. A wholly reliable ΔH_f^0 SiO_2(amorph., hydrat.) value can only be determined using special precision measurements which are planned for future studies.

The experimental heat-of-formation values for five methylchlorosilanes, can be used to calculate the enthalpy of formation of the sixth compound in this series, gaseous CH_3SiH_2Cl.

A simple and rather accurate calculation method is that applied by Bernstein[20] to methane derivatives. The bond and interaction contributions (Table 4) necessary for this procedure were found from eqn. (1) (on the basis of the experimental values) using the least-squares method. The heats of evaporation of the methylchlorosilanes were taken from the literature[21-22]. The enthalpy of formation of gaseous CH_3-SiH_2Cl was found to be -60.2 kcal·mole^{-1}.

TABLE 4

BOND AND INTERACTION CONTRIBUTIONS FOR CALCULATING THE THERMOCHEMICAL PROPERTIES OF METHYLCHLOROSILANES

(for gas at 25°, in kcal·mole^{-1})

Bond contributions			Interaction contributions		
Bond	for ΔH_f^0 (kcal)	for S^0 (e.u.)	Interaction	for ΔH_f^0 (kcal)	for S^0 (e.u.)
$\overline{\text{SiH}}$	1.97	12.42	$\Delta[H(CH_3)]$	0.33	0.03
$\overline{\text{Si(CH}_3)}$	14.41	21.38	$\Delta(HCl)$	-0.02	1.28
$\overline{\text{SiCl}}$	40.97	19.73	$\Delta[Cl(CH_3)]$	0.26	0.81

The mean energies of bond cleavage calculated from our experimental data using the least-squares method are:

$E(Si\text{–}CH_3) = 74.8$ kcal

$E(Si\text{–}H) = 81.8$ kcal

$E(Si\text{–}Cl) = 98.0$ kcal.

The entropies of methylchlorosilanes have been studied by many authors[23-26]. To achieve good agreement these values were also handled using Bernstein's method.

The calculations were carried out with the following formula:

$$P[SiH_n(CH_3)_mCl_{4-n-m}(\text{gas})] = n(\overline{\text{SiH}})+m\,[\overline{\text{Si(CH}_3)}]+(4-n-m)(\overline{\text{SiCl}})+ \\ +nm\Delta[H(CH_3)]+n(4-n-m)\Delta(HCl)+m(4-n-m)\Delta[(CH_3)Cl]\,, \quad (1)$$

where P is calculated property of the molecule (in this instance the enthalpy of formation or entropy), the superior lines denote different bond contributions to the magnitude of this property and Δ denotes contributions of interactions between atoms two at time.

Table 5 gives our recommended values of enthalpy of formation (ΔH_f^0), entropies (S^0), entropies of formation (ΔS_f^0) and isobaric potentials of formation (ΔG_f^0) for the methylchlorosilanes in the gaseous state.

TABLE 5

THERMOCHEMICAL PROPERTIES OF METHYLCHLOROSILANES

(for gas at 25°)

Compound	ΔH_f^0 (kcal·mole^{-1})	S^0 (e.u.)	ΔS_f^0 (e.u.)	ΔG_f^0 (kcal·mole^{-1})
$SiCH_3Cl_3$	−139.8	83.0	−49.6	−125.0
$Si(CH_3)_2Cl_2$	−110.9	85.5	−68.7	−90.4
$Si(CH_3)_3Cl$	−84.6	86.3	−89.3	−58.0
$SiHCH_3Cl_2$	−99.0	77.5	−44.1	−85.9
$SiH(CH_3)_2Cl$	−73.0	77.9	−65.2	−53.6
SiH_2CH_3Cl	−60.2	69.4	−41.1	−47.9

CONCLUSIONS

1. The enthalpies of combustion of trimethylchlorosilane and methyltrichlorosilane were measured using explosive combustion in oxygen in a rotating tantalum bomb; the following values were obtained:

$\Delta H_c^0 (CH_3)_3SiCl\,(liq) = -720.9 \pm 0.8$ kcal·mole^{-1}

$\Delta H_c^0\ CH_3SiCl_3\,(liq) = -283.8 \pm 0.8$ kcal·mole^{-1}.

2. The enthalpies of formation of the compounds under study were calculated:

$\Delta H_f^0\ (CH_3)_3SiCl\,(liq) = -91.8 \pm 0.9$ kcal·mole^{-1}

$\Delta H_f^0\ CH_3SiCl_3\,(liq) = -147.2 \pm 0.9$ kcal·mole^{-1}.

The value of the enthalpy of formation of trimethylchlorosilane obtained by Beezer and Mortimer[27] using the hydrolysis method is $\Delta H_f^0 (CH_3)_3SiCl\,(liq) = -91.9 \pm 0.8$ kcal·mole^{-1}. It is the only value given in the literature and is in a very good agreement with our data.

3. The enthalpy of formation of monomethylmonochlorosilane was calculated on the basis of our experimental data using Bernstein's method as $\Delta H_f^0\ CH_3SiH_2Cl$ (gas) = −60.2 kcal·mole^{-1}.

4. The thermochemical parameters of methylchlorosilanes (ΔH_f^0, S^0, ΔS_f^0, and ΔG_f^0) were computed and tabulated.

5. The selection of the value $\Delta H_f^0\ SiO_2$ (amorph., hydrat.) = -217.4 ± 0.5 kcal·mole^{-1} was substantiated by a literature analysis.

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