

## HEATS OF FORMATION OF SILICON TETRACHLORIDE, DIMETHYLDICHLOROSILANE AND DIPHENYLDICHLOROSILANE

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## INTRODUCTION

Heats of formation of the majority of organosilicon compounds are unknown. The organochlorosilanes may be included in this category. Even the heat of formation of silicon tetrachloride is not well resolved. Since extensive combustion studies have been made on the polydimethyl and the polydiphenylsiloxanes, which are the condensed hydrolysis products of dimethyl and diphenyldichlorosilane, the heats of formation of the corresponding chlorosilanes may be determined from additional data on their heats of hydrolysis.

In this paper we describe the determination of the heats of hydrolysis of several chlorosilanes and discuss the enthalpy bond additivity relationships in these compounds.

## EXPERIMENTAL

The compounds studied were obtained from the Matheson, Coleman, and Bell Company. Each compound was vacuum distilled to remove dissolved hydrogen chloride. Hydrolyzed samples of each compound were analyzed for chloride ion, and the following sample purities were obtained: Silicon tetrachloride ( $99.58 \pm 0.08\%$ ), dimethyldichlorosilane ( $97.60 \pm 0.15\%$ ), trimethylchlorosilane ( $98.08 \pm 0.08\%$ ), phenyltrichlorosilane ( $99.70 \pm 0.06\%$ ) and diphenyldichlorosilane ( $99.81 \pm 0.02\%$ ). The analyses showed that the hydrolysis reactions did go to completion. Proton nuclear magnetic resonance spectra were obtained for dimethyl and diphenyl dichlorosilane, trimethylchlorosilane and phenyltrichlorosilane. The spectra showed that the samples were free from reciprocal contamination. Dimethyldichlorosilane and trimethylchlorosilane were treated with lithium aluminum hydride in di-*n*-butyl ether. No silane was formed indicating that silicon tetrachloride, a possible contaminant, was not present.

The calorimeter used was similar in design and operation to one described by Stern and Passchier<sup>1</sup>.

## RESULTS

The heats of hydrolysis are listed in Table I. Corrections for sample purity were made on the assumption that the impurity did not hydrolyze.

TABLE I  
CALORIMETRIC RESULTS

Compound	Moles $\times 10^{-3}$	$\Delta T$ ( $^{\circ}K$ )	$C_p$ (system) (cal/ $^{\circ}K$ )	$-\Delta H_{Hyd.}$ (kcal/mole)	Mean $\Delta H_{Hyd.}$ (kcal/mole)
SiCl <sub>4</sub>	3.04	1.457	162.05	79.35	$-79.75 \pm 0.14$
	2.94	1.399	167.84	79.86	
	3.22	1.477	173.10	79.43	
	2.56	1.215	168.68	80.08	
	2.36	1.180	174.36	79.75	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	2.87	1.339	171.58	80.03	$-31.64 \pm 0.46$
	4.38	0.824	175.62	33.04	
	5.36	1.007	166.30	31.23	
	6.05	1.156	159.96	30.55	
C <sub>6</sub> H <sub>5</sub> SiCl <sub>3</sub>	6.26	1.138	174.58	31.73	$-55.07 \pm 0.17$
	5.77	1.046	174.67	31.66	
	3.64	1.267	158.72	55.20	
	2.79	0.962	159.77	55.15	
	2.73	0.933	158.67	54.23	
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	5.62	1.991	154.93	55.48	$-32.09 \pm 0.03$
	2.93	1.038	155.58	55.22	
	3.65	1.264	159.36	55.19	
(CH <sub>3</sub> ) <sub>3</sub> SiCl	14.26	1.817	246.08	32.12	$-12.42 \pm 0.19$
	14.69	2.035	225.85	32.06	
	19.31	1.036	232.30	12.70	
	16.06	1.099	170.99	11.94	
	18.21	1.283	180.79	13.00	
	17.63	1.187	178.00	12.22	
	16.07	1.088	173.72	12.00	
	19.76	1.350	168.94	11.77	
	19.72	1.492	164.52	13.10	
	17.71	1.265	175.58	12.60	

The heats of formation of gaseous silicon tetrachloride, dimethyldichlorosilane and diphenyldichlorosilane (Table 2) were obtained from the appropriate combinations of the following reactions:

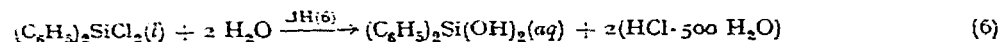
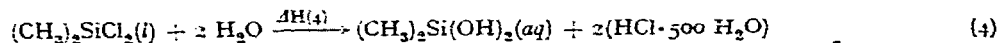
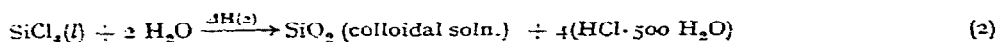


TABLE 2

HEATS OF HYDROLYSIS IN AQUEOUS SOLUTION

Compound	$\Delta H_{\text{Hyd.}}$ (kcal/mole)	$\Delta H^{\circ}_f(g)$ (kcal/mole)	Ref.
SiCl <sub>4</sub>	-79.8	-153.7	a
	-76.6	-156.9	b
	-70.1	-163.4	c
CH <sub>3</sub> SiCl <sub>3</sub>	-51.5	b	S
C <sub>2</sub> H <sub>5</sub> SiCl <sub>2</sub>	-52.1	b	S
C <sub>6</sub> H <sub>5</sub> SiCl <sub>2</sub>	-55.1	b	a
	-48.6	b	S
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	-32.5	-108.0	S
	-32.1	-108.4	a
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	-31.6	-52.2	a
(CH <sub>3</sub> ) <sub>3</sub> SiCl	-16.1	b	S
	-12.4	b	a

<sup>a</sup> This paper. <sup>b</sup> No combustion data available.

The following heats were used:

$\Delta H(1) = -7.0$ kcal/mole (ref. 2)	$\Delta H^{\circ}_f[\text{H}_2\text{O}(l)] = -68.32$ kcal/mole (ref. 2)
$\Delta H(2) = -79.8$ kcal/mole (this paper)	$\Delta H^{\circ}_f(\text{HCl} \cdot 500 \text{ H}_2\text{O}) = -39.87$ kcal/mole (ref. 2)
$\Delta H(3) = -7.6$ kcal/mole*	$\Delta H^{\circ}_f[\text{SiO}_2(\text{colloidal soln.})] = -217.6$ kcal/mole (ref. 4)
$\Delta H(4) = -32.1$ kcal/mole (this paper)	$\Delta H^{\circ}_f[(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2(aq)] = -155$ kcal/mole (ref. 5)
$\Delta H(5) = -14.3$ kcal/mole (ref. 3)	$\Delta H^{\circ}_f[(\text{CH}_3)_2\text{Si}(\text{OH})_2(aq)] = -205$ kcal/mole (ref. 5)
$\Delta H(6) = -31.6$ kcal/mole (this paper)	

## DISCUSSION

The final products of the hydrolysis reactions are written as silanols which are known to polymerize. However, the polymerizations of silanols are reactions in which  $n(\text{Si}-\text{OH})$  and  $n(\text{SiO}-\text{H})$  bonds are broken and  $n(\text{H}-\text{OH})$  and  $n(\text{SiO}-\text{Si})$  bonds are formed. Written in terms of the bonds, the polymerization reactions are disproportionations and therefore, assuming that bond additivity relationships hold<sup>6</sup>, should have zero enthalpies. Therefore, the actual final product should not effect the heat of formation calculations.

One other fact can also be considered. The hydrolysis reactions are very rapid while some polymerization reactions are not. The rate of polymerization of silanols decreases with increasing methyl substitution and greatly decreases with increasing phenyl substitution<sup>7</sup>. Also, each successive condensation product is more stable than its precursor<sup>7</sup>. Therefore, at least for diphenylsilanediol, little polymerization should occur during our heat of hydrolysis measurements.

The variations apparent in Table 2 for the heats of hydrolysis of the chlorosilanes studied are much larger than one would expect for such elementary reaction calorimetry techniques. The most probable source of these errors is sample purity, since these compounds are not readily obtainable in a high degree of purity. As described in the experimental section, we carefully examined our samples for cross-contamination

\* Calculated from a Trouton's constant of 22 eu/mole and a boiling point of 343.3° K.

and chloride content. Similar precautions, if any, exercised by other workers have not been described. It is our opinion that chloride analysis alone is not a sufficient indication of sample purity. It should also be noted that the most probable errors in sample purity would lead to less exothermic heats of hydrolysis for silicon tetrachloride and phenyltrichlorosilanes and a more exothermic heat of hydrolysis for trimethylchlorosilane.

The data suggest that the heats of hydrolysis for chlorosilanes containing the same number of silicon-chloride bonds are rather insensitive to the nature of the organic group bonded to silicon. In addition, all data show a consistent decrease in the hydrolysis heat per silicon-chloride bond in going from the tetrachloride to the monochloride. Although the heats of hydrolysis may be interpreted in terms of many separate heat terms such as heats of solution or heats of vaporization, such a variation in the hydrolysis heats could be interpreted as an indication of silicon-chloride bond strengthening with increasing degree of chlorine substitution.

Examination of Table 3 shows that prior to the hydrolysis studies reported here, four separate determinations of the heat of formation of silicon tetrachloride had been made using three different standard reactions. The results of these earlier studies<sup>8-11</sup>

TABLE 3  
HEATS OF FORMATION OF SILICON TETRACHLORIDE

$\Delta H_f^0(g)$ (kcal/mole)	Method	$\Delta H_{hyd}^0(l)$ (aq. soln.) (kcal/mole)	Ref.
-153.7	aq. hydrolysis	-79.8	This paper
-156.9	aq. hydrolysis	-76.6	8
-156.9	SiCl <sub>4</sub> + AgF in HF		10
-163.2	hydrolysis in HF		11
-163.4	aq. hydrolysis	-70.1	9

centered on the two values of  $\Delta H_f^0 = -156.9$  and  $-163.3$  kcal/mole. Our hydrolysis result supports the more positive value. It should be mentioned that in all of these determinations, the most probable experimental errors (sample purity and loss of sample by evaporation during the reaction) would lead to more negative heats of formation of silicon tetrachloride. Thus, we feel that a  $\Delta H_f^0[\text{SiCl}_4(g)] = -155.8$  kcal/mole obtained as the average of the three more positive results represents a "best value" at this time.

It is interesting to examine the enthalpy bond additivity relations in the chlorosilanes as a function of the degree of chlorination. Silicon-methyl (Si-Me) and silicon-phenyl (Si-Ph) enthalpy bond additivities are  $-18.0$  and  $+10.5$  kcal/mole-bond respectively<sup>5</sup>. With these values and the determined heats of formation of dimethyldichlorosilane and diphenyldichlorosilane we obtain Si-Cl bond additivities of  $-36.2$  and  $-36.6$  kcal/mole-bond in these disubstituted chlorosilanes. The Si-Cl bond additivity in silicon tetrachloride using  $\Delta H_f^0[\text{SiCl}_4(g)] = -155.8$  kcal/mole is  $-38.9$  kcal/mole-bond. An examination of the heats of formation of many methyl-containing organosilicon compounds has previously shown no variation of the silicon-methyl bond strength with degree of methyl substitution<sup>5</sup>. Thus, there appears to be a definite

bond strengthening of the order of 2 kcal/mole-bond per Si-Cl bond with an increase in chlorine substitution in the chlorosilanes.

If our zero enthalpy assumptions for the condensation reactions of the silanols are incorrect and the enthalpies of the reactions are negative, the heats of formation of the organochlorosilanes would be more positive than we calculate. Therefore, even if our zero enthalpy assumptions are incorrect, the conclusion of silicon-chlorine bond strengthening with an increase in chlorine substitution is still valid.

This apparent change in the silicon-chlorine bond strength which suggests that bond additivity relationships do not hold in the organochlorosilanes appears to cast doubt on the validity of our zero enthalpy assumption for the silanol condensations. However, during the condensation reactions, the silicon atoms are always bonded to the same number and kind of atoms and therefore the bond additivity relationships should hold very well for the silicon compounds involved. With the formation of water an O-Si bond is broken and an O-H bond is formed. Since the electronegativity of hydrogen and silicon are not too different, bond additivity relationships should also be valid for this part of the reaction system.

The observed bond strengthening can be rationalized on the basis of an increase in "s" character in the hybridized silicon orbitals bonded to chlorine with increasing degree of chlorination<sup>12</sup>. The observed decrease in silicon-halogen bond length with an increasing degree of halogenation in the halo-silanes support this hypothesis<sup>13</sup>. Thus, the bond length and bond additivity variations would be expected to occur when the electronegativity of the ligands are appreciably different from each other.

It would be of interest to obtain accurate heats of formations for some mono- and trichlorosilanes and for compounds of the other halosilane series.

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#### SUMMARY

Heats of hydrolysis in aqueous solutions have been obtained for the following chlorosilanes:  $\text{SiCl}_4$  ( $-79.75 \pm 0.14$  kcal/mole),  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$  ( $-31.64 \pm 0.46$  kcal/mole),  $\text{C}_6\text{H}_5\text{SiCl}_3$  ( $-55.07 \pm 0.17$  kcal/mole),  $(\text{CH}_3)_2\text{SiCl}_2$  ( $-32.09 \pm 0.03$  kcal/mole) and  $(\text{CH}_3)_3\text{SiCl}$  ( $-12.42 \pm 0.19$  kcal/mole). From these data we have calculated heats of formation for the following gaseous chlorosilanes:  $\text{SiCl}_4$  ( $-153.7$  kcal/mole),  $(\text{CH}_3)_2\text{SiCl}_2$  ( $-108.4$  kcal/mole) and  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$  ( $-52.2$  kcal/mole).

A change in silicon-chlorine bond strength with degree of chlorination is discussed.

#### REFERENCES

- 1 J. H. STERN AND A. PASSCHIER, *J. Chem. Eng. Data*, 7 (1962) 73.
- 2 *Natl. Bur. Std. Circ.*, No. 500, Wash., D.C., (1952).
- 3 D. R. STULL, *Ind. Eng. Chem.*, 39 (1947) 517.
- 4 S. W. WISE, J. L. MARGRAVE, H. M. FEDER AND W. N. HUBBARD, *J. Phys. Chem.*, 66 (1962) 381; W. D. GOOD, *J. Phys. Chem.*, 66 (1962) 380.
- 5 H. E. O'NEAL AND M. A. RING, to be published.

- 6 S. W. BENSON AND J. H. BUSS, *J. Chem. Phys.*, 29 (1958) 546.
- 7 C. EABORN, *Organosilicon Compounds*, Academic Press, New York, 1960, p. 246-250.
- 8 K. A. ANDRIANOV AND S. A. PAVLOV, *Dokl. Akad. Nauk SSSR*, 88 (1953) 811.
- 9 W. A. ROTH AND O. SCHWARTZ, *Z. Phys. Chem.*, 134 (1928) 456.
- 10 H. SCHAEFER AND H. HEINE, *Z. Anorg. Allgem. Chem.*, 332 (1964) 25.
- 11 A. E. BEEZER AND C. T. MORTIMER, *J. Chem. Soc.*, (1964) 2727.
- 12 H. A. BENT, *J. Chem. Educ.*, 37 (1960) 616; also, *Chem. Rev.*, 61 (1961) 275.
- 13 E. A. V. EBSWORTH, *Volatile Silicon Compounds*, MacMillan, New York, 1963, p. 56.

*J. Organometal. Chem.*, 5 (1966) 124-129