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THERMODYNAMICS OF SILICON COMPOUNDS
II. ETHYL- AND PHENYLCHLOROSILANES

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SUMMARY

Heats of formation, heat contents, and entropies have been evaluated for the title compounds, mainly by use of a second order additivity method.

INTRODUCTION

In experimental work on organochlorosilicon compounds, particularly those obtainable by the Direct Synthesis, there is need for reliable thermochemical data. As some data are not easily obtained by experimental means, literature studies were carried out which led to methods of estimating heats of formation, heat contents and entropies[1,2]. The estimation methods are of a first or a second order type; first order additivity for a number of silicon compounds was applied[2] on heat of formation, specific heat and entropy for 298°K. A second order additivity method for heats of formation, which takes into account the mutual influence of ligands in compounds with tetravalent central atoms (C, Si) needs more experimental data as a basis for the "curve-fitting", and it also makes use of measurements on rearrangement equilibria. For the data obtained in this way the internal consistency is better than in some of the data based on experiments only. A previous paper dealt with methyl(chloro)silanes and we now give data for ethyl- and phenylchlorosilanes.

RESULTS AND DISCUSSION

Heat of formation

Use of literature data on heats of formation of methyl- and ethylsilanes, often reveals a lack of internal consistency. In Table 1, column 2 the data which have been obtained by measurement of the heat of combustion are listed. The lack of consistency can be demonstrated by a calculation of the reaction heat of a disproportionation reaction. Such a reaction, in which the number and type of bonds in the molecules remain unchanged, is very unlikely to involve an enthalpy change more than a few kcal. However, the rearrangements equilibria, represented by reactions (1) and (2), involve an enthalpy change of +12 and +22 kcal respectively, at 25°, if the data in column 2 are correct.

TABLE 1

HEATS OF FORMATION OF METHYL- AND ETHYLSILANES (KCAL/MOLE)

Compound	ΔH_f^0 (comb.)	Ref.	ΔH_f^0	Diff. per Si–H
Me_4Si	−77 ± 9	9	*−80*[1]	
Me_3SiH	−68 ± 8	9	*−57.8*[1]	−10.2
Me_2SiH_2	−50 ± 6	9	*−35.8*[1]	− 7.1
SiH_4	−11.3	10	+ 7.6[3,4]	− 4.7
$EtSiH_3$	−29 ± 6	9	*− 8.3*	− 6.9
Et_2SiH_2	−44 ± 10	9	*−24.2*	− 9.9
Et_3SiH	−47 ± 13	9	*−40.1*	− 6.9
Et_4Si	−58.2	11	*−56*	
	−45 ± 16	9		
Si_2H_6	−35.8	10	+17.1[4]	− 8.8

$$2\,Et_2SiH_2 \rightleftarrows EtSiH_3 + Et_3SiH \qquad (1)$$

$$2\,EtSiH_3 \rightleftarrows Et_2SiH_2 + SiH_4 \qquad (2)$$

For the compounds in Table 1, only for silane and disilane is there an alternative method for the determination of the heat of formation, for because these are unstable relative to their elements the heat of decomposition could be determined[3,4]. The result for silane and disilane deviate substantially from the data obtained by combustion. Consistent data (italics) for methylsilanes were proposed earlier[1]. These data and the differences are in Table 1, column 4 and 5. The origin of the deviations and the inaccuracy of the combustion data presumably lies in the often noted incompleteness of the combustion of the silicon compounds, which leads to a heat of formation that is too negative. The deviations seem to increase with increasing number of Si–H bonds, the error per Si–H bond varying from 5 to 10 kcal per mole. If it is assumed that the experimental errors are related to the number of Si–H bonds and if such a correction is also applied to the ethylsilanes, then a consistent set of data can be obtained by assuming an additive contribution of −14 kcal/mole for each ethyl group bonded to silicon.

For methyl(chloro)silanes, refinements could be applied to take account of the mutual influence of the ligands. As there are only few data available on equilibria in mixtures of ethyl(chloro)silanes the possibility of refinement is limited. By use of the bond terms for chlorine and hydrogen [a(Si–H) = +1.9 kcal, a(Si–Cl) = −39.6 kcal][1], the heat of formations for ethyl(chloro)silanes may be calculated by means of the eqn.:

$$\Delta H_f^0(X_nSiY_{4-n}) = n\cdot a(\text{Si–X}) + (4-n)\cdot a(\text{Si–Y}) + n(4-n)\cdot i(\text{X, Y})$$

In this empirical equation, a(Si–X) and a(Si–Y) are contributions to the heat of formation from the Si–X and the Si–Y part of the molecule, respectively; i(X,Y) is a parameter to describe the mutual influence of the X- and Y-groups or -atoms. There is no information enabling evaluation of $i(H, C_2H_5)$ in this system, and the only value that can be assigned at present is zero.

For knowledge of $i(Cl, C_2H_5)$, an accurate heat of formation of at least one ethylchlorosilane or data on disproportionation equilibria is needed in addition to the data for tetrachlorosilane and tetraethylsilane. Two values for $EtSiCl_3$ are known from the literature, *i.e.*, −160 kcal/mole[5] and −124 ± 6 kcal/mole[6]. The first of these values was obtained by electron impact, a method which does not seem to yield accurate results on heats of formation[7]. On disproportionation equilibria, only one quantitative result is available[8]. In Table 2 the composition of a mixture of ethylchlorosilanes before and after equilibration with 2 mol. % of $AlCl_3$ at 85° and atmospheric pressure is given. Gaseous $EtSiH_3$ was formed during the conversion. The equilibration may well be co-catalyzed by the presence of compounds which contain Si–H, because under the mild conditions of these experiments no change of composition was observed in the absence of such compounds. For this reason it is not certain that reactions between ethylchlorosilanes proceed as schematized in reaction (3) so there is no proof that the final composition of the liquid mixture really represents an equilibrium. The figures of Table 2 allow the calculation of a free enthalpy change of −0.4 (±0.7) kcal, for the equilibrium represented by reaction (3).

TABLE 2

PRODUCT COMPOSITION (IN MOL %) OF CATALYTIC REARRANGEMENT OF A MIXTURE OF ETHYLCHLOROSILANES WITH 2 MOL % $AlCl_3$ (TEMP. 85°)

Compound	Exp. 1		Exp. 2	
	Start	End	Start	End
$SiHCl_3$	22.5	19.0	23.1	15.6
$EtSiHCl_2$	26.2	4.8	25.7	7.2
Et_2SiHCl	17.9	< 0.1	16.4	< 0.1
Et_3SiH	27.2	< 0.1	28.9	< 0.1
$EtSiCl_3$	< 0.1	7.6	< 0.1	12.4
Et_2SiCl_2	< 0.1	19.9	< 0.1	12.4
Et_3SiCl	< 0.1	43.6	< 0.1	36.2
unknown	6.3	5.1	6.0	16.3

$$2\,Et_2SiCl_2 \rightleftarrows Et_3SiCl + EtSiCl_3 \qquad (3)$$

The free enthalpy change calculated only from entropy differences (−0.2 kcal) lies well within the range of this result, an indication that the influence term $[i(Cl, C_2H_5)]$ is close to zero. The results show that for ethylchlorosilanes at least, there is a first order bond additivity for the heats of formation[2]. Only with more accurate experimental data can more accurate values for heats of formation of ethyl(chloro)silanes be evaluated.

In Table 3 the present "best values" for the ethylchlorosilanes are given with an estimated accuracy of about 2 kcal per ethyl group. The possible error is based upon two literature results for tetraethylsilane.

For phenylchlorosilanes the available data (Table 3) suggest a value of +23 kcal for the Si–Ph bond term and a value of −4.7 kcal for the phenyl/chlorine influence factor $[i(Ph, Cl)]$. From these values the heat of formation of Ph_3SiCl and $PhSiCl_3$ may be calculated with reasonable accuracy. The results are presented in Table 3, together with data for the other phenylchlorosilanes, based upon a tentative value for $i(Ph, H)$ of zero. Only for the apparently strong deviation from bond additivity in the compounds Ph_nSiCl_{4-n} has the proposed second order additivity method

TABLE 3

HEATS OF FORMATION OF GASEOUS ETHYL- AND PHENYL(CHLORO)SILANES (KCAL/MOLE)

Compound	ΔH_f^0 (est.)[a]	ΔH_f^0 (lit.)[b]	Ref.	Compound	ΔH_f^0 (est.)[a]	ΔH_f^0 (lit.)[b]	Ref.
$EtSiH_3$	-8.3	-29	9	$PhSiH_3$	$+29$		
Et_2SiH_2	-24.2	-44	9	Ph_2SiH_2	$+50$		
Et_3SiH	-40.1	-47	9	Ph_3SiH	$+71$		
Et_4Si	-56	-58.2	11	Ph_4Si	$+92$	96 ± 3	12
		-45	9			90 ± 4	15
Et_3SiCl	-81.6			Ph_3SiCl	$+15.3$		
Et_2SiCl_2	-107.2			Ph_2SiCl_2	-52	-52.2	17
$EtSiCl_3$	-132.8	-124	6	$PhSiCl_3$	-109.9		
		-160^c	5				
$EtSiHCl_2$	-92.5			$PhSiHCl_2$	-63.7		
$EtSiH_2Cl$	-51			$PhSiH_2Cl$	-1.1		
Et_2SiHCl	-66.3			Ph_2SiHCl	$+17.5$		

[a] Using: $a(\text{Si–Et}) = -14$; $a(\text{Si–H}) = +1.9$; $a(\text{Si–Cl}) = -39.6$: $a(\text{Si–Ph}) = +23$; $i(\text{Et, H})$, $i(\text{Et, Cl})$, $i(\text{Ph, H}) = 0$; $i(\text{H,Cl}) = -0.6$; $i(\text{Ph,Cl}) = -4.7$. [b] Some of the literature data have been recalculated from the heats of combustion using a newer value[16] for the heat of formation of SiO_2 (amorph): -216.1 kcal/mole. [c] Recalculated from ref. 5.

been applied. No phenyl compounds could be included in the demonstration of the value of this method for hydrocarbons[1], so the extension to phenyl groups is still questionable. Consequently the data for phenyl(chloro)silanes are expected to have an uncertainty of about 5 kcal per phenyl group.

Heat content

From results obtained by Golosova and co-workers[13], who calculated the thermodynamic functions of ethyltrichlorosilane and phenyltrichlorosilane[14] from spectroscopic data, it is possible to obtain group-contributions for the ethyl and phenyl group. The complexity of the vibrational spectra for compounds containing more than one of these organic groups, however, makes the assignment of frequencies, especially in the lower ranges, difficult and sometimes even doubtful. This complexity may cause substantial errors in the calculated thermodynamic functions. With an additivity method using group contributions and a molecular weight term, it has been possible to predict entropies for methyl(chloro)silanes with high accuracy. The definition and acceptability of the group contributions to heat content have been discussed before[1]. By using the equation:

$$[H^0_{T(1)} - H^0_{T(2)}](X_nSiY_{4-n}) = n \cdot \Phi(\text{Si–X})_{T(1),T(2)} + (4-n) \cdot \Phi(\text{Si–Y})_{T(1),T(2)} - \tfrac{3}{2}R \cdot [T(1) - T(2)] \cdot \ln M$$

in which M stands for the molecular weight of compound X_nSiY_{4-n}, the values of the heat content of phenyl- and ethyl-containing silanes can be estimated. In Table 4 are shown the available group contributions of gaseous silanes, while in Table 5 the heat contents for ethyl- and phenyl(chloro)silanes, computed from the Φ-values, are listed.

The uncertainty of the data thus estimated is 1 % or less, as revealed by comparison with some of the literature values. The reliability improves, as the compound

TABLE 4

GROUP CONTRIBUTIONS TO ADDITIVE PART OF HEAT CONTENT (KCAL/MOLE)

Bond	Group contributions for $T(1)^a$=			
	400	500	600	700
Si–H	0.553	1.165	1.820	2.443
Si–Cl	0.961	1.933	2.923	3.923
Si–Me	1.287	2.729	4.315	5.933
Si–Et	1.904	4.108	6.552	9.226
Si–Ph	3.023	6.641	10.773	15.318

[a] °K; $T(2)=298$°K.

TABLE 5

HEAT CONTENT OF GASEOUS ETHYL- AND PHENYL(CHLORO)SILANES (IN KCAL/MOLE)

Compound	$H^0_{T(1)}-H^0_{T(2)}$ for $T(1)^a$=				Ref.
	400	500	600	700	
Et_4Si	6.10	13.44	21.73	30.95	
Et_3SiH	4.82	10.63	17.20	24.42	
Et_2SiH_2	3.55	7.85	12.71	17.97	
$EtSiH_3$	2.32	5.14	8.33	11.65	
Et_3SiCl	5.15	11.24	18.06	25.59	
Et_2SiCl_2	4.19	9.04	14.40	20.24	
$EtSiCl_3$	3.24	6.84	10.73	14.89	13
Et_2SiHCl	3.86	8.42	13.52	19.06	
$EtSiHCl_2$	2.90	6.21	9.84	13.69	
$EtSiH_2Cl$	2.59	5.63	9.02	12.58	
Ph_4Si	10.32	23.06	37.85	54.30	
Ph_3SiH	7.93	17.74	29.13	41.73	
Ph_2SiH_2	5.57	12.47	20.49	29.27	
$PhSiH_3$	3.26	7.32	12.02	17.04	
Ph_3SiCl	8.30	18.43	30.12	43.06	
Ph_2SiCl_2	6.29	13.82	22.41	31.85	
$PhSiCl_3$	4.28	9.22	14.72	20.67	14
Ph_2SiHCl	5.92	13.14	21.44	30.55	
$PhSiHCl_2$	3.92	8.55	13.78	19.40	
$PhSiH_2Cl$	3.58	7.92	12.87	18.18	

[a] °K; $T(2)=298$°K.

in question more closely resembles a compound used in the evaluation of the group contributions. The accuracy of the heat-content for Me_2SiCl_2, for instance, can be about 0.1%; the possible error for Ph_4Si, for which no satisfactory model molecules are available, is probably much larger.

Entropy

For entropy of compounds with a tetravalent central atom a general semi-empirical eqn. has been proposed[1] containing additional terms for the four individual

TABLE 6

GROUP CONTRIBUTIONS TO ENTROPY OF SILICON COMPOUNDS (IN E.U.)

Bond	Group contributions to entropy for T^a=				
	298	400	500	600	700
Si–H	10.872	11.672	12.410	13.09	13.72
Si–Cl	17.175	18.789	20.135	21.24	22.19
Si–Me	19.265	21.767	24.473	26.705	28.78
Si–Et	27.075	31.613	35.565	39.340	42.87
Si–Ph	33.095	40.543	47.495	54.21	60.51

[a] °K.

TABLE 7

ENTROPY OF GASEOUS ETHYL- AND PHENYL(CHLORO)SILANES IN E.U.

Compound	S^0_{298}	S^0_{400}	S^0_{500}	S^0_{600}	S^0_{700}	Ref.
Et_4Si	118.18	136.33	152.14	167.24	181.36	
Et_3SiH	104.08	118.50	131.09	143.10	154.32	
Et_2SiH_2	87.86	98.54	107.92	116.83	125.15	
$EtSiH_3$	71.89	78.83	85.00	90.81	96.23	
Et_3SiCl	111.16	126.39	139.59	152.02	163.56	
Et_2SiCl_2	102.19	114.50	125.09	134.85	143.81	
$EtSiCl_3$	93.79	103.17	111.16	118.25	124.63	13
Et_2SiHCl	96.53	108.02	118.01	127.34	135.98	
$EtSiHCl_2$	86.78	95.35	102.73	109.40	115.46	
$EtSiH_2Cl$	79.55	87.30	94.08	100.32	106.06	
Ph_4Si	144.78	174.57	202.38	229.24	254.44	
Ph_3SiH	124.55	147.69	169.29	190.11	209.64	
Ph_2SiH_2	102.10	118.60	133.98	148.77	162.63	
$PhSiH_3$	79.67	89.51	98.68	107.44	115.63	
Ph_3SiCl	131.22	155.18	177.38	198.63	218.48	
Ph_2SiCl_2	115.66	133.78	150.38	166.02	180.52	
$PhSiCl_3$	100.58	112.87	123.86	133.89	143.04	14
Ph_2SiHCl	110.29	127.60	143.59	158.81	172.99	
$PhSiHCl_2$	93.75	105.22	115.60	125.21	134.04	
$PhSiH_2Cl$	86.80	97.46	107.23	116.41	124.92	

groups, a term with the molecular weight and a term for the contribution of the molecular symmetry:

$$S^0_T(X_nAY_{4-n}) = n\cdot\Phi'(A\text{–}X)_T + (4-n)\cdot\Phi'(A\text{–}Y)_T + \tfrac{3}{2}\,R\cdot\ln M - R\cdot\ln\sigma$$

Ethyl[13] and phenyl[14] group contributions can be derived from recent literature results, and the full set of available data for silicon compounds is given in Table 6. For ethyl- and phenyl(chloro)silanes the entropy-values have been calculated from the data in Table 6, and the results are listed in Table 7. For compounds of the type $RSiX_3$ ($R = C_2H_5$, C_6H_5 and $X = H$, Cl), the symmetry constant has been taken to be unity because of the absence of symmetry of these molecules.

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