AN ADDITIVITY SCHEME FOR THE ESTIMATION OF HEATS OF FORMATION, ENTROPIES, AND HEAT CAPACITIES OF SILANES, POLYSILANES, AND THEIR ALKYL DERIVATIVES

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Summary

Heat of formation data available for silanes and alkylsilanes have been evaluated using the Benson-Luria electrostatic energy corrected bond additivity method for a priori calculations of heats of formation of hydrocarbons. It is concluded that the calculational method is applicable to silanes and alkyl-silanes, and that the recent combustion measurements employing HF and O_2 are reliable. Group additivity enthalpies based on these data are presented. Results of a large number of statistical thermodynamic calculations of entropies and heat capacities are also given, and values of the group additivities derivable from these results are presented. Internal consistencies of estimated thermodynamic properties (i.e., estimated reaction enthalpy, entropy, and heat capacity changes) are thought to be reliable to within ±1.5 kcal and ±1.0 e.u., respectively. Group additivity estimates for individual compounds could be significantly less accurate due to the limited accuracy and extent of the ΔH_f^0 data base, and to the uncertainties in assigned frequencies and internal rotational barriers employed in calculating entropies and heat capacities.

Introduction

Thermochemistry can be a powerful tool in understanding and predicting the behaviours of chemical systems [1]. Thus the standard free energy changes of reaction define reaction and the magnitude of driving potentials, while thermochemical kinetic considerations permit estimations of reaction rates and evaluations of reaction mechanisms. Applications of thermochemical analyses to chemical systems have become increasingly more common. This is due in large part to the development of a number of additivity schemes [2—5] by which the accurate estimation of the thermochemical properties of most organic compounds can be made quite easily. Unfortunately, the great power

of thermodynamics has not as yet been applied to the analysis of silicon compound reactions. The reason is that the thermochemical data base for these compounds is just too sparse, and, relative to the heats of formation, the data are also of questionable accuracy. Since the development of an additivity scheme for silicon compounds is highly desirable, to derive and provide such a scheme are the objectives of this paper.

In an earlier paper [6] we attempted to derive bond additivity values for the estimation of entropies and heats of formation for silicon compounds. Enormous inconsistencies in the heat of formation data were apparent. Thus our 'best' set of bond additivity enthalpies produced estimated heats of formation which differed from the reported values by an average of about 16 kcal/mole. Since an error of 1.4 kcal in a reaction enthalpy produces a power of ten variation in the corresponding equilibrium constant at room temperature, to have any thermochemical predictive value an additivity scheme must be able to generate heat of formation estimates which are similarly reliable (i.e., ±1.5 kcal/mole). Thus a fairly accurate heat of formation data base is required.

Of all the existing addivitity schemes, the Benson group additivity scheme [5] is the most extensive (covering fairly completely compounds of H, C, O, N, S, P and the halogens, the most accurate (to ±1.5 e.u./mole in entropies and heat capacities, and ±0.5 kcal/mole in heats of formation), and perhaps the easiest to use. Unfortunately, group additivities can only be obtained from a quite extensive data base. Thus there is a two-fold problem in deriving a group additivity scheme encompassing silicon compounds: 1) a wide data base is needed, and 2) an accurate data base is needed. This is not really a problem relative to entropy and heat capacities. These properties can be estimated with reasonable reliability using standard statistical thermodynamic methods. One needs only to estimate with fair accuracy the frequencies of the pertinent normal mode vibrations of the various bond or group motions. The real problem comes in evaluating or generating a sufficiently accurate number of heat of formation values.

Heats of formation

Benson and Luria [7—10] have recently presented a new method for the a priori estimation of heats of formation which requires a very modest data base. In applications to hydrocarbons (alkanes, alkenes, alkynes and aromatics) and their free radical counterparts, the Benson-Luria method (which is really an electrostatic energy corrected-bond additivity scheme subsequently referred to here as EECBA) has been extraordinarily successful. Thus heats of formation for these types of compounds can be calculated to accuracies exceeding those obtained by group additivity methods without having to make the additional "next to nearest neighbor" corrections. Heats of formation are calculated from eq. 1,

$$\overline{\Delta H_f^0} = \sum_i m_i \Delta H_f^0(i, \text{ bond}) + 1/2 \sum_{i=1}^n \sum_{j=i+1}^n q_i q_j / r_{ij} \tag{1}$$

The leading term is a sum over bond values (m_i is the number of bonds of type

i and $\Delta H_f^0(i)$ is the additivity value for bond i), and the final term corrects for all pairwise bond dipole charge—charge interactions in the molecule (r_{ij} is the distance between atoms i and j bearing charges q_i and q_j and n is the number of atoms in the molecule). To apply the Benson-Luria EECBA scheme to polysilanes, only three parameters (hence three accurate heats of formation) are needed. These are the two bond additivity terms Si—H and Si—Si, and the fixed dipole charge w for the Si—H bond. Polarity in the Si—H bond is $\overset{+w}{\text{Si}}$—$\overset{-w}{\text{H}}$. To extend the method to all saturated alkylsilanes and polysilanes requires, besides the three hydrocarbon parameters already known (i.e., (C—H) = —1.13 kcal/mol, C—C = 0.24 kcal/mole, and the charge of the $\overset{-x}{\text{C}}$—$\overset{+x}{\text{H}}$ dipole, x = 0.28 × 10^{-10} esu) only two additional parameters. These are the Si—C bond additivity, and the ($\overset{+z}{\text{Si}}$—$\overset{-z}{\text{C}}$) dipole charge, z. Thus two accurate alkylsilane heats of formation are needed, and would be sufficient to establish these two parameters.

Davidson [11] has recently applied the EECBA method to some alkylsilanes, namely the four methylsilanes and hexamethyldisilane, in order to evaluate the reliability of two existing and mutually exclusive data sets: a set recommended in the CATCH tables [12] (generated from recent individual combustion calorimetric methods) and a set recommended by Potzinger, Ritter and Krause [13] (based on a least squares treatment of appearance potential measurements, several calorimetrically determined heats of formation, and a modified version of the Allen [3] additivity scheme). Since none of the heat of formation data for silicon compounds were known to be accurate (i.e., the five needed parameters could not be established), Davidson avoided the problem by adopting values of w = 0.68 × 10^{-10} esu and y = 0.31 × 10^{-10} esu which were consistent with the experimental 0.73 D dipole moment of CH_3SiH_3 *. He then calculated the electrostatic energy correction terms for silane, disilane, and the five methylated silanes and examined differences between members in the series. He concluded that the PRK set was the more internally consistent of the two. This conclusion was confirmed through several kinetic data tests of the heat of formation data, which we latter repeat. Davidson also found that changing his values for the dipole charges w and z did not significantly change the electrostatic energy differences between series members, hence this conclusion reagrding the two data sets seemed safe. Perhaps the most important contribution of Davidson's paper is the demonstration of the fact that the Benson EECBA method of estimating heats of formation is applicable to silicon compounds.

We have also used Benson's EECBA method to assess the available heat of formation data on silicon compounds, but unlike Davidson we have used all the recently available calorimetric data in an attempt to evaluate that data and to evaluate the five calculational parameters. While the older combustion data was clearly poor, there is a good chance that the more recent data, generated largely by Pedley and coworkers [12], is more reliable. Thus these recent studies have employed HF along with O_2 in the combustion. The HF converts the silicon dioxide product quantitatively to H_2SiF_6, and avoids the problems

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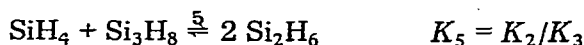* This moment is considered to be composed of dipoles H → C (+0.32 D), Si → H (+1.0 D), and C → Si (—0.60 D).

of incomplete combustion and indeterminate nature of the SiO_2 product which have plagued earlier calorimetric studies.

As previously noted, just three reliable heats of formation are needed to establish the three parameters needed to calculate all polysilane heats of formation. We begin our analysis by showing that the Gunn and Green [14] values for silane, disilane, and trisilane (recently updated in the CATCH tables) are internally consistent. Since they are derived from independent experimental studies, we conclude that they are also accurate.

Data reported by Purnell and Walsh [15] on the kinetic study of the thermal decomposition of silane along with the CATCH heats of formation of silane and disilane [12] and our calculated entropies and heat capacities (see later) can be used to obtain an independent experimental measure of the heat of formation of trisilane. The early stages of the silane decomposition (0—20%) are known [16] to be well characterized by the reactions:

$$SiH_4 + (M) \rightarrow SiH_2 + (M) + H_2 \tag{1}$$

$$SiH_2 + SiH_4 \rightleftharpoons Si_2H_6 \tag{2}$$

$$SiH_2 + Si_2H_6 \rightleftharpoons Si_3H_8 \tag{3}$$

$$xSiH_2 \rightarrow products \tag{4}$$

After about 5—10% decomposition, reactions 2 and 3 are essentially at equilibrium. Purnell and Walsh reported that at their peak concentrations (i.e., here interpreted as equilibrium concentrations) $\frac{[Si_2H_6]_{Max}}{[SiH_4]_0} = 0.0274 \pm 0.0011$ and $\frac{[Si_3H_8]_{Max}}{[SiH_4]_0} = 0.00474 \pm 0.00023$, independent of temperature and initial silane pressure. These data, then, provide a measure of the equilibrium constant at mean reaction temperatures for reaction 5.

$$SiH_4 + Si_3H_8 \overset{5}{\rightleftharpoons} 2\,Si_2H_6 \qquad K_5 = K_2/K_3$$

$$K_5(T\,673\,K) = \left(\frac{[Si_2H_6]_{Max}}{[SiH_4]_0}\right)^2 \times \frac{[SiH_4]_0}{[SiH_4]} \times \frac{[SiH_4]_0}{[Si_3H_8]}$$

The maximum for Si_2H_6/SiH_4 occurred at about 15% reaction, therefore $\frac{[SiH_4]_0}{[SiH_4]} \simeq 1.15$ at time $= t_{max}$. This gives K_{eq} (673 K) $\simeq 0.186$, which, along with the CATCH heats of formation of silane (8.2 kcal/mol), disilane (19.1 kcal/mol), the entropy of silane (49.0 e.u./mol) [1], disilane (64.6 e.u./mol), trisilane (81.7 e.u./mol), and the appropriate reaction heat capacity corrections gives: ΔS_5^0 (673 K) = —1.16 e.u., ΔH_5^0 (673 K) = 1.47 kcal, ΔH_f^0 (298 K) = 1.39 kcal, and finally $\overline{\Delta H_f^0}$ (Si_3H_8) = 28.6 kcal/mol. Thus the equilibrium based calculated heat of formation of trisilane is in exceptionally good agreement with the CATCH table's revised Gunn and Greene value of 28.9 kcal/mol. The heats of formation of silane, disilane, and trisilane, then, should be able to be used to obtain the three EECBA calculation parameters. On this basis, we have obtained an (Si—H) charge dipole term of $w = 0.41 \times 10^{-10}$ esu, and the bond energy terms of

TABLE 1

REPORTED AND CALCULATED [a] HEATS OF FORMATION

Compound	$-E_{el}$ (kcal/mol)	$\overline{\Delta H_f^0}$ (kcal/mol)			
		CATCH (Exp)	Calculated [a]	PRK	Calculated [a]
Si_2H_6	22.18	19.1	19.1	17.1	
Si_3H_8	26.99	28.9	28.6 [b]		
iso-Si_4H_{10}	34.65		36.7		
neo-Si_5H_{12}	45.14		43.3		
n-Si_5H_{12}			47.4		
1,1-dimethylsilacyclobutane		−33.0			
1,1-dimethylsilacyclopentane		−43.4			
1,1,3,3-tetramethyl-1,3-disila-cyclobutane		−72.0			
CH_3SiH_3	23.04	(−8.0)	−8.1	−4.3	−4.3
$(CH_3)_2SiH_2$	26.62	(−24.3)	−24.8	(17.0), −16.8	−17.2
$(CH_3)_3SiH$	30.92	(−41.4)	−41.9	(−30.3), −29.6	−30.4
$(CH_3)_4Si$	35.93	−58.7(−58.7)	−59.1	(−44.0), −42.4	−43.9
$CH_3SiH_2SiH_3$	26.92		1.9		5.7
$(CH_3)_2SiHSiH_3$	32.39		−15.7		−8.1
$(CH_3)_3SiSiH_3$	38.57		−33.7	−22.2	−22.3
$CH_3SiH_2SiH_2CH_3$	31.56		−15.3	−9.3	−7.7
$(CH_3)_2SiHSiH_2CH_3$	36.80		−32.8	−21.8	−21.4
$(CH_3)_3SiSiH_2CH_3$	42.76		−50.6		−35.4
$(CH_3)_2SiHSiH(CH_3)_2$	41.92		−50.2	−34.8	−35.0
$(CH_3)_3SiSiH(CH_3)_2$	47.65		−67.9	−47.3	−48.9
$(CH_3)_3SiSi(CH_3)_3$	53.25	−86.8	−85.6	−60.1	−62.8
$(CH_3)_8Si_3$	71.28	−112.4	−112.4		−82.0
n-$(CH_3)_{10}Si_4$	89.30	−135.8	−139.2		−101.3
$[(CH_3)_3Si]_4Si$	106.5	−133.7	−166.7(−133.7) [b]		−121.9
$(C_2H_5)_2SiH_2$	30.96	−43.6	−30.96	−23.5	
$(C_2H_5)_3SiH$	37.48	−48.0	−51.1(48.7) [b]	−39.5	−39.7
$(C_2H_5)_4Si$	47.56	−63.4	−73.0(−63.4) [b]	−56.6	−57.8
$(SiH_3)_4C$	52.76		0.9		
$(SiH_3)_3CCH_3$	47.56		−6.5		
$(SiH_3)_2C(CH_3)_2$	41.72		−13.5		
$SiH_3C(CH_3)_3$	35.24		−20.3		
$(SiH_3)_3CH$	43.06		−2.2		
$(SiH_3)_2CH_2$	33.16		−5.2		
$(SiH_3)_2CHCH_3$	36.50		−8.9		
$(SiH_3)CH(CH_3)_2$	29.29		−15.3		
$(SiH_3)_3SiCH_3$	43.18		17.5		
$(SiH_3)_2Si(CH_3)_2$	40.98		−8.1		
$(SiH_3)_2SiHCH_3$	33.63		10.4		

[a] Calculated using eq. 1 and dipole charges of 0.28×10^{-10} esu (for C—H), 0.48×10^{-10} esu (for Si—H), and 0.098×10^{-10} esu for (C—Si). [b] $(C_2H_5)_3SiH$ has 2 H ↔ H interactions at 2.36 Å; 1.2 kcal/H—H gives −51.1 → −48.7 $(C_2H_5)_4Si$ has 8 H ↔ H interactions at 2.36 Å; 1.2 kcal/H—H gives −73.0 → −63.4 tetrakis trimethylsilane has 12 H—H at 1.64 Å; 2.75 kcal/H—H gives −166.7 → 133.7.

(Si—Si) = 2.76 kcal/mol of bonds and Si—H = 4.57 kcal/mol of bonds. The corresponding electrostatic energies and heats of formation of these and other polysilanes are shown in Table 1. It should be noted that Davidson's charge value for w, along with the CATCH heats of formation of silane and disilane predicts for trisilane, $\overline{\Delta H_f^0}$ (Si_3H_8) = 26.1 kcal/mol, a value which is in rather poor agreement with the calorimetric and equilibria based values. When extended

to the more highly branched polysilanes, the values calculated using Davidson's w gives for isotetrasilane and neopentasilane, heats of formation of 29.1 and 28.1 kcal/mol, respectively. These values deviate so excessively from bond additivity that they clearly must be in error. It is interesting to note, however, that our w value also produces heats of formation which suggest a small but not insignificant increase in stability with branching in polysilanes. Thus neopentasilane is predicted to be 5.2 kcal/mol more stable than n-pentasilane. If this trend is real, and we believe that it is, one must conclude that uncorrected bond additivity schemes would not be very reliable in predicting heats of formation for polysilanes. There is experimental evidence for this predicted increase in stability with increased branching in silicon compounds. Thus in the disproportionation of Si_2Cl_6 catalyzed by trace quantities of $N(CH_3)_3$, the Si_5Cl_{12} [17] and Si_6Cl_{14} [18] products produced were found by IR spectra to be predominantly the neopentyl and neohexyl isomers [19].

To extend the Benson EECBA scheme to organosilanes it is necessary to evaluate the two additional parameters z and (Si—C). This requires two accurate heats of formation, which in turn requires an evaluation (like Davidson's) of the CATCH and PRK data sets. The data evaluated here, and which comprise these two sets, are shown in columns 3 (CATCH) and 5 (PRK) of Table 1. The heat of formation values for the methylsilanes (in parenthesis, Table 1) should be quite accurate in a relative sense, since they have been derived from disproportionation equilibrium data reported by Russell [20] *.

Like Davidson, we have appealed to the dipole moment of CH_3SiH_3 to obtain an initial value for the Si—C charge, z. Thus, from our $w = 0.41 \times 10^{-10}$ esu and Benson's $x = 0.28 \times 10^{-10}$ esu (which give dipoles of 0.607 D (Si—H), and 0.306 D (C—H)) we obtain 0.18 D for C—Si and $z = 0.098 \times 10^{-10}$ esu. Calculations of the electrostatic energies using these charge values gave the results shown in column 2 of Table 1. The column 4 heats of formation (to be compared to the CATCH data set) were obtained using C—H, Si—H and Si—Si bond enthalpies of −1.13, +4.57, and 2.76 kcal/mol, respectively and a C—Si bond additivity of −6.90 kcal/mol. The latter is a best fit value for all the CATCH enthalpies. The column 6 heats of formation (to be compared to the PRK data set) were obtained using a C—Si bond additivity of −3.1 kcal/mol. This is a value consistent with $\overline{\Delta H_f^0}(CH_3SiH_3) = -4.3$ kcal/mol, which is the base compound of the PRK enthalpies. Quite good agreement between calculated and recommended heats of formation is apparent for both data sets (i.e., both CATCH and PRK enthalpies are internally consistent!). This conclusion is not dependent on our choice of charge values. Any set of charges which produces good agreements between

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* Russell's data can be used to calculate the equilibrium constants of the following three disproportionation reactions.

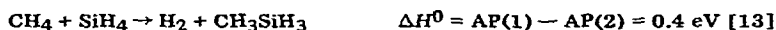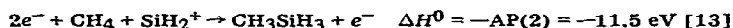| Reactions	K	$\Delta S°$ (e.u.)	$\Delta H°$ (kcal)
$2\ Me_3SiH \rightleftharpoons Me_2SiH_2 + Me_4Si$	0.39	−3.5	−0.43
$2\ Me_2SiH_2 \rightleftharpoons MeSiH_3 + Me_3SiH$	0.77	−2.5	−0.62
$2\ MeSiH_3 \rightleftharpoons SiH_4 + Me_2SiH_2$	0.98	−0.1	−0.27

The reaction entropy changes have been calculated using the entropy data of Table 4 and $V_0 = 1.7$ kcal/Me rotor. The reference enthalpies used were $\Delta H_f^0(SiH_4) = 8.2$ kcal/mol, and $\Delta H_f^0(Me_4Si) = -58.7$ kcal/mol (CATCH), and $\Delta H_f^0(MeSiH_3) = -4.3$ kcal/mol (PRK).

the calculated and recommended heats of formation for one set, produces comparably good agreements for the other. Thus we have also performed the calculations with two other charge assignments, one similar to Davidson's values (Set A: $w = 0.685 \times 10^{-10}$ esu, $z = 0.316 \times 10^{-10}$ esu, and $x = 0.279 \times 10^{-10}$ esu), and another designed to be consistent with $\overline{\Delta H_f^0}(Si_3H_8) = 27.6$ kcal/mol and 0.73 D for CH_3SiH_3 (Set B: $w = 0.53 \times 10^{-10}$ esu, $z = 0.20 \times 10^{-10}$ esu, and $x = 0.28 \times 10^{-10}$ esu). The calculated heats of formation with these charges for methylsilane, tetramethylsilane, and hexamethylsilane are, respectively: Set A: PRK (−4.3, −44.0, −63.4 kcal/mol), CATCH (−7.8, −58.7, −90.0 kcal/mol); Set B: PRK (−4.3, −44.1, −65.0 kcal/mol), CATCH (−7.8, −58.1, −86.0 kcal/mol), where both sets have been standardized to their methylsilane heat of formation values.

The acceptably good internal consistency of both data sets is, we feel, significant relative to the CATCH heats of formation, but not so significant relative to the PRK values. Thus, as previously stated, the PRK enthalpies were obtained by a least squares analysis of a number of equations relating heats of formation to appearance potential measurements *, plus a few calorimetric heats of formation (specifically SiH_4 (8.2), Si_2H_6 (17.1), $(C_2H_5)_4Si$, and six methyl chlorosilanes). Reactants and products were then written in terms of the Allen scheme bond energy and bond energy interaction terms. A "best set" for the Allen additivity parameters were then derived by a least squares method and these in turn were used to calculate the PRK recommended enthalpies. The PRK enthalpies, then, have been additivity smoothed via the Allen scheme. Hence their internal consistency is in fact expected, and should not be interpreted as an indication of accuracy **. By contrast, the CATCH enthalpies are the result of independent experimental measurements. As such, some scatter relative to the calculated values, is natural. That the CATCH enthalpies agree as well as they do with the Benson EECBA calculated heats of formation, we feel, can attest as much to their accuracy as it does to their internal consistency. We therefore favor the CATCH-calorimetric heats of formation, and believe that Pedley's recent combustion studies with HF are providing reliable heat of formation data for alkylsilanes and alkylpolysilanes.

Sizeable differencies between some of the CATCH enthalpies and their calculated counterparts do however exist (e.g., diethylsilane, tetraethylsilane, and tetrakis(trimethylsilyl)silane). Benson [10] has noted that for some highly branched hydrocarbons, the ECCBA calculations give heats of formation which are too negative. In all such cases there were non-bonded H atoms at distances less than 2.5 Å. At this distance steric repulsions of the H atoms amount to about 1.0 kcal/mol. The tetrakis(trimethylsilyl)silane is a crowded structure

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* For example, the appearance potentials of the SiH_2^+ ion from SiH_4 and CH_3SiH_3 can be used to obtain the enthalpy of an equation relating their heats of formation.
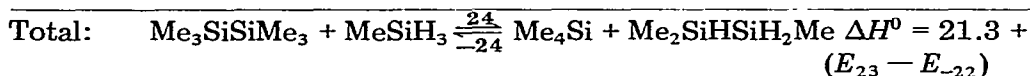
$e^- + SiH_4 \rightarrow SiH_2^+ + H_2 + 2e^-$ $\Delta H^0 = AP(1) = 11.9$ eV [13]

$2e^- + CH_4 + SiH_2^+ \rightarrow CH_3SiH_3 + e^-$ $\Delta H^0 = -AP(2) = -11.5$ eV [13]

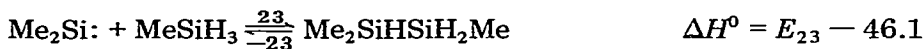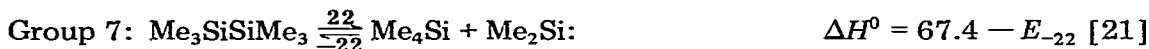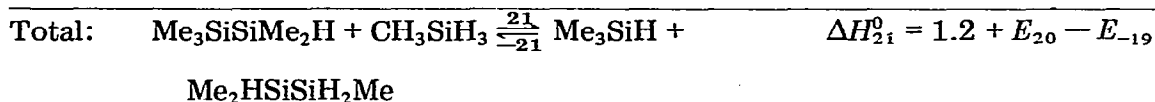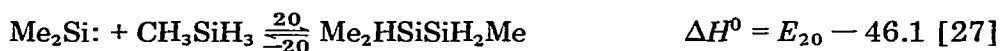$CH_4 + SiH_4 \rightarrow H_2 + CH_3SiH_3$ $\Delta H^0 = AP(1) - AP(2) = 0.4$ eV [13]

** It should be noted that PRK excluded from their analysis the calorimetrically derived heat of formation of hexamethyldisilane on the grounds that its inclusion increased the standard deviation of their least squares treatment. This was probably not a wise decision.

with 12 H—H interactions at even closer distances (i.e., 1.64 Å). Similarly, tetraethylsilane has 8 H—H interactions at 2.36 Å, and triethylsilane has 2 at the same distance. Applying the quite reasonable corrections of 1.2 kcal per H—H interaction at 2.36 Å, and 2.75 kcal per H—H interaction at 1.64 Å to the ECBA values brings calculated and observed heats of formation for these three compounds into excellent agreement. Thus the only HF—O_2 calorimetric result in large disagreement with the calculations is that for diethylsilane, and a reinvestigation of the combustion of this compound seems warranted.

As noted by Davidson, it is possible to apply some kinetic data tests to the two enthalpy data sets. Several groups of reactions which can be so utilized are shown below. The first two groups are those already considered by Davidson.

Group 1: $Me_6Si_2 \xrightarrow{6} 2\ Me_3Si\cdot$ $\Delta H_6^0 = E_6 = 80.5 \pm 1$ kcal [21]

  $2\ Me_3Si + 2\ Me\cdot \xrightarrow{7} 2\ Me_4Si$ $\Delta H_7^0 = -2E_{-7} = -2(84.8 \pm 2.4)$ kcal [22]

Total: $Me_6Si_3 + 2\ Me\cdot \xrightarrow{8} 2\ Me_4Si$ $\Delta H_8^0 = -89.1 \pm 5.8$ kcal

Group 2: $Me_3SiSiMe_3 \xrightarrow{6} 2\ Me_3Si\cdot$ $\Delta H_6^0 = 80.5 \pm 1$ kcal [21]

  $2\ Me_3Si\cdot + 2\ H\cdot \xrightarrow{9} 2\ Me_3SiH$ $\Delta H_9^0 = -2(90.0 \pm 2.5)$ kcal [23]

Total: $Me_3SiSiMe_3 + 2\ H\cdot \xrightarrow{10} 2\ Me_3SiH$ $\Delta H_{10}^0 = -99.5 \pm 6.0$ kcal

Group 3: $Me_3SiSiH_3 \underset{-11}{\overset{11}{\rightleftharpoons}} Me_3SiH + SiH_2:$ $\Delta H^0 = 48.0 - E_{-11}$ [24]

  $:SiH_2 + SiH_4 \underset{-12}{\overset{12}{\rightleftharpoons}} Si_2H_6$ $\Delta H^0 = E_{12} - 49.3$ [25]

Total: $Me_3SiSiH_3 + SiH_4 \overset{13}{\rightleftharpoons} Si_2H_6 + Me_3SiH$ $\Delta H_{13}^0 = -1.3 + (E_{12} - E_{11})$

Group 4: $MeSiH_2SiH_3 \underset{-14}{\overset{14}{\rightleftharpoons}} MeSiH_2 + SiH_2:$ $\Delta H^0 = 48 - E_{14}$ [26]

  $SiH_2: + SiH_4 \underset{-12}{\overset{12}{\rightleftharpoons}} Si_2H_6$ $\Delta H^0 = E_{12} - 49.3$ [25]

Total: $MeSiH_2SiH_3 + SiH_4 \xrightarrow{15} Si_2H_6 + MeSiH_3$ $\Delta H_{15}^0 = -1.3 + (E_{12} - E_{-14})$

Group 5: $Me_2SiHSiH_2Me \underset{-16}{\overset{16}{\rightleftharpoons}} Me_2SiH_2 + CH_3\ddot{S}iH$ $\Delta H^0 = 46.1 - E_{-16}$ [27]

  $CH_3\ddot{S}iH + SiH_4 \underset{-17}{\overset{17}{\rightleftharpoons}} MeSiH_2SiH_3$ $\Delta H^0 = E_{17} - 49.9$ [26]

Total: $Me_2SiHSiH_2Me + SiH_4 \underset{-18}{\overset{18}{\rightleftharpoons}} Me_2SiH_2 + MeSiH_2SiH_3$ $\Delta H^0 = -3.8 + (E_{17} - E_{16})$

Group 6: $Me_3SiSiMe_2H \underset{-19}{\overset{19}{\rightleftharpoons}} Me_3SiH + Me_2Si:$ $\Delta H^0 = 47.3 - E_{-19}$ [27]

$\qquad$ $Me_2Si: + CH_3SiH_3 \underset{-20}{\overset{20}{\rightleftharpoons}} Me_2HSiSiH_2Me$ $\Delta H^0 = E_{20} - 46.1$ [27]

Total: $\quad Me_3SiSiMe_2H + CH_3SiH_3 \underset{-21}{\overset{21}{\rightleftharpoons}} Me_3SiH +$ $\Delta H^0_{21} = 1.2 + E_{20} - E_{-19}$

$\qquad Me_2HSiSiH_2Me$

Group 7: $Me_3SiSiMe_3 \underset{-22}{\overset{22}{\rightleftharpoons}} Me_4Si + Me_2Si:$ $\Delta H^0 = 67.4 - E_{-22}$ [21]

$\qquad Me_2Si: + MeSiH_3 \underset{-23}{\overset{23}{\rightleftharpoons}} Me_2SiHSiH_2Me$ $\Delta H^0 = E_{23} - 46.1$

Total: $\quad Me_3SiSiMe_3 + MeSiH_3 \underset{-24}{\overset{24}{\rightleftharpoons}} Me_4Si + Me_2SiHSiH_2Me$ $\Delta H^0 = 21.3 +$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (E_{23} - E_{-22})$

The group 1 overall reaction, gives $\overline{\Delta H^0_f}$ (hexamethyldisilane) in terms of $\overline{\Delta H^0_f}(CH_3^{\cdot}) = 34.3$ kcal/mol [1] and $\overline{\Delta H^0_f}(Me_4Si)$. Using the PRK and CATCH values for Me_4Si gives,

$\overline{\Delta H^0_f}$(HMDS) $= -92.5 \pm 5.8$ kcal/mol $\qquad$ CATCH (-86.8)
$\qquad\qquad\qquad = -64.3 \pm 5.8$ kcal/mol $\qquad$ PRK (-60.1)

This test, as noted by Davidson [11], tends to support the PRK heats of formation, but still lies within the experimental errors of the CATCH value.

Similarly, the group 2 overall reaction gives $\overline{\Delta H^0_f}$(HMDS) in terms of $\overline{\Delta H^0_f}(H^{\cdot}) = 52.1$ kcal/mol and $\overline{\Delta H}^0_f(Me_3SiH)$. With the PRK and CATCH values for Me_3SiH one obtains,

$\overline{\Delta H^0_f}$(HMDS) $= -86.3 \pm 6$ kcal/mol $\qquad$ CATCH (-86.8)
$\qquad\qquad\qquad = -63.9 \pm 6$ kcal/mol $\qquad$ PRK (-60.1)

This group of reactions clearly favors the CATCH values. It is apparent that an evaluation of the accuracy of the CATCH relative to the PRK data sets cannot be made on the basis of these two "kinetic" tests. However, if one accepts the CATCH enthalpies one must conclude that the reaction enthalpy for methyl fission in tetramethylsilane is too low by about 3 kcal/mol. This is quite possible since, although complete suppression of free radical chains was assumed in the kinetic study [22], any small residual chain component to the reaction could easily lower the observed activation energy by this amount. In a similar fashion we can use the overall reactions of groups 3 through 7 to calculate the activation energy differences for silylene and methylsilylene insertions into different kinds of bonds. The PRK and CATCH heats of formation predict very similar values for these insertion activation energy differences. The "apparent" disagreements for groups 3 and 4, in fact, arise mainly from the different disilane heats of formation adopted by the two sets *. If the calculated heats of formation are used, the differences are identical, see terms

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* In this regard PRK erred in adopting the updated heat of formation of silane (i.e., 7.2 → 8.2 kcal/mol) without similarly employing the disilane updated value (17.1 → 19.1) kcal/mol).

Group 3: $E_{12} - E_{-11}$ = 4.5   CATCH [4,22]
                = 2.8   PRK

Group 4: $E_{12} - E_{-14}$ = 2.3   CATCH [2.2]
                = 0.2   PRK

Group 5: $E_{17} - E_{-16}$ = 6.0   CATCH [5.7]
                $\doteq$ 6.3   PRK

Group 6: $E_{20} - E_{-19}$ = 0.5   CATCH [0.3]
                = —1.0   PRK

Group 7: $E_{23} - E_{-22}$ = —18.0   CATCH [—19.5]
                = —21.1   PRK

in brackets above. This indicates that in the estimations of reaction enthalpies of zero mole change involving only heat of formation differences, it is possible to use either the PRK enthalpies or the CATCH enthalpies with good results. However, it seems most reasonable to adopt the CATCH values, or better still, the Benson EECBA scheme calculated CATCH based enthalpies, as the more accurate heat of formation values. This minimizes the experimental errors in the CATCH values.

On this basis (i.e., from the calculated CATCH based heats of formation of Table 1), we have derived the Benson type group additivity enthalpy values of Table 7. These groups can be used to estimate the heat of formation of all non-strained alkylsilanes or alkyldisilanes. The accuracy of such estimates should greatly exceed that of Pedley's individual experimental measurements (which average 4.3 kcal/mol and range from 1.8 to 11.4 kcal/mol), and we believe they should be accurate to about ±1—2 kcal/mol. Corrections for next to nearest neighbour repulsions in highly branched structures can not be made at this time. *Gauche* and *cis* interactions, that is, the next to nearest neighbor bulky group repulsions found in hydrocarbons, are apparently unimportant in polysilanes, presumably because of the longer Si—Si and Si—C bond lengths. However, H—H repulsions in highly branched structures do occur, and comparisons of space filling models of compounds with experimental heats of formation may eventually aid in estimations of the magnitudes of these effects.

From the group values and the reported heats of formation of the three cyclic compounds (1,1-dimethylsilacyclobutane, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, and 1,1-dimethylsilacyclopentane) one can calculate the ring strain corrections to be applied to four and five-membered carbosilane rings. Thus the reported heat of formation of 1,1-dimethylsilacyclobutane is,

$$\overline{\Delta H^0_f} \quad \left(\text{Me—}\overset{\text{Me}}{\underset{}{\text{Si}}}\!\!\sqsupset \right) \quad = -33.03 \pm 3.4 \text{ kcal/mol. Expressed in terms of group}$$

additivities we have,

$$\Delta H^0_f = 2[\text{C—(H)}_3(\text{Si})] + [\text{Si—C})_4] + 2[\text{C—(H)}_2(\text{C})(\text{Si})] + [\text{C—(H)}_2(\text{C})_2] + \underset{\text{strain}}{\overset{\text{Si}}{\Box}}$$

$$-33.03 = 2(-10.2) + (-18.3) + 2(-3.08) + (-4.93) + \underset{\text{strain}}{\overset{\text{Si}}{\Box}}$$

Solving for the ring strain, gives $\underset{\text{strain}}{\overset{\text{Si}}{\Box}}$ = 16.8 kcal/mol, a value not too

different from the corresponding ring containing sulfur ($\boxed{}^{\,S}$ = 19.4 kcal/mol).

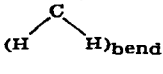In a similar fashion, the strain energy in 1,1,3,3-tetramethyl 1,3-disilacyclo-butane is E_{st} ($\boxed{}^{Si}_{Si}$) = 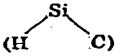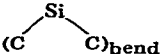24.6 ± 2.6 kcal/mol; while in 1,1-dimethylsilacyclo-pentan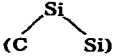e the strain energy is calculated to be E_{sy} ($\langle\rangle^{Si}$) = 11.3 ± 1.8 kcal/mol. These latter values are surprisingly high. However, as we will show in a subsequent paper, kinetic data tend to support the "high" strain energy of the 1,3-disilacyclobutane ring.

Entropies and heat capacities

Entropy and heat capacity tabulations for silicon compounds appear to be limited to silane, disilane, the methylsilanes, vinylsilane, silyl acetylene, a few siloxanes and some halosilanes [1].

However, IR and Raman spectroscopic data have been reported for a number of polysilanes [28], and complete or partial normal mode vibrational assignments have been made for tetramethylsilane [29], mono; di- and tri-methylsilane [30], and hexamethyldisilane [31,32]. These data, coupled with some judicious generalizations regarding normal mode frequency assignments (see later and Tables 2 and 3) have been used to calculate, by well known statistical thermodynamic methods [33], molar entropies and heat capacities for all possible methylated silanes and disilanes, and also for a number of polysilanes including disilane, trisilane, isotetrasilane, and neopentasilane. In all cases,

TABLE 2

ASSIGNED [a] AND GENERALIZED [b] FREQUENCY [c] ASSIGNMENTS IN METHYLSILANES

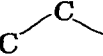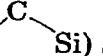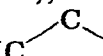| Vibrations	CH$_3$SiH$_3$	(CH$_3$)$_2$SiH$_2$	(CH$_3$)$_3$SiH	HMDS [d]	Generalized [b]
(C—H)$_{str}$	(?)				2960
(Si—H)$_{str}$	2 (?), 2169				2130
(H $\diagup$C$\diagdown$ H)$_{bend}$	2 (1412)	4 (1380—1440)	6 (1425—1467)		(1450) 2
	1266	2 (1260)	1257, 1263		(1260) 1
(H $\diagup$Si$\diagdown$ C)	2 (?)				690
	943				
(CH$_3$)$_{rock}$	2 (870)	919, 963	2 (900)		850
		802, 867	850, 835		
(Si—C)$_{str}$	701	728, 654	2 (711), 625		700
(SiH$_2$)$_{w,t}$		643, 591			610
(SiH$_3$)$_{rock}$	2 (539)				555
(SiH$_2$)$_{rock}$		467			460
(C $\diagup$Si$\diagdown$ C)$_{bend}$		223	2 (252, 216)		225
Si—Si				184	185
(C $\diagup$Si$\diagdown$ Si)				404	400
(Si—C)				638	2 (685)
					1 (640)

[a] Ref. 30. [b] Assignments by authors with the help of Professor W.D. Jones. [c] All frequencies in units of cm^{-1} units. [d] HMDS = Hexamethyldisilane.

TABLE 3

OBSERVED [a] AND GENERALIZED [b] FREQUENCIES [c] IN POLYSILANES

Vibration	Si_3H_8	$n\text{-}Si_4H_{10}$	$i\text{-}Si_4H_{10}$	$neo\text{-}Si_5H_{12}$	2,2-disilyl tetrasilane	2,3-disilyl tetrasilane	Generalized [b]
$(Si\text{—}H)_s$	2147	2146	2145	2143	2144	2146	2130
	2130	2129	2116		2118	2108	
(H $\diagdown$Si$\diagup$ H)	920	930, 917	932	926, 909	925, 913	927	2(920)
	873	900	895	845	891	893	1(880)
$(SiH_2)_{w,t}$	698	682, 652			679	679	700
		744, 714				743	
(H $\diagup$ $\diagdown$ Si)			693				690
$(SiH_3)_r$	564	540	567	574	567	541	555
$(SiH_2)_r$	466	467			457	452	460
$(Si\text{—}Si)$	392	427	450	440	444, 393	385	425 [d]
		377	352	309	282, 303	330	325 [e]
(Si $\diagup$ $\diagdown$ Si)	109	127	118	98	131	137	110
			100		98	95	

[a] Ref. 28. [b] Assignments by authors with the help of Professor W.D. Jones. [c] All frequencies listed in cm^{-1} units. [d] Asymmetric stretches. [e] Symmetric stretches.

tetrahedral bond angles and standard bond lengths (i.e., C—H = 1.093 Å, Si—H = 1.48 Å, Si—C = 1.87 Å, and Si—Si = 2.30 Å) were assumed. The results, based on free rotations of all groups and the "generalized" assigned frequencies of Tables 2 and 3, are given in Table 4. For the compounds whose vibrational mode assignments are available, free rotor calculations employing the generalized frequencies produced values which agreed quite well with those reported and with those calculated using the exact frequency assignments. Thus the average deviations in the 300 K entropies and in the 300 and 1500 K heat capacities were 0.06, 0.31, and 0.41 e.u./mole respectively. We therefore believe that the generalized frequencies can be used to obtain fairly reliable estimates of free rotor entropies and heat capacities for the methylated silanes and disilanes of Table 4. The entropies and heat capacities of the compounds shown in Table 5 cannot be considered to be as reliable since a number of low frequency vibrations, for which there are no data, had to be assigned.

The skeletal bends (C $\diagdown$ Si), set at 300 cm^{-1}, and (Si $\diagdown$ Si) set at 195 cm^{-1}, were assigned from the (C $\diagdown$ C) $\simeq$ 400 cm^{-1} vibration utilizing the square root reduced mass relation, $w_1/w_2 \simeq \left(\dfrac{\mu_2}{\mu_1}\right)^{1/2}$. This relation appears to hold reasonably well for skeletal bends and stretches. In addition, we have assigned $(CH_2)_r$ and $(CH_2)_{w,t}$ for CH_2 groups bonded to silicon, frequencies of 620 cm^{-1}, and 925 cm^{-1}, respectively on the basis of the 23% reduction observed in the CH_3 group rocks when CH_3 is bonded to silicon as opposed to carbon.

To obtain estimates of the real entropies and heat capacities of the compounds of Tables 4 and 5, it is necessary to correct their listed free rotor values

TABLE 4

FREE-ROTOR [a] THERMODYNAMIC ENTROPIES AND HEAT CAPACITIES OF METHYLATED SILANES, METHYLATED DISILANES AND SOME POLYSILANES

Compound	$\overline{S}^0$ (298 K)	$\overline{C}_p^0$ (cal/deg mol)				
		298 K	500 K	800 K	1000 K	1500 K
Si_2H_6	64.89	18.26	25.17	31.64	34.43	38.31
Si_3H_8	82.33	25.82	36.06	44.95	48.69	
iso-Si_4H_{10}	98.53	35.18	47.26	58.22	62.87	
neo-Si_5H_{12}	111.8	44.06	58.40	71.53	77.10	
$MeSiH_3$	60.93	14.90	21.68	28.64	31.80	36.55
Me_2SiH_2	72.68	20.09	29.34	38.86	43.30	50.19
Me_3SiH	81.99	25.51	36.98	49.04	54.76	63.81
Me_4Si	87.81	29.93	43.94	58.89	65.99	77.33
MeH_2SiSiH_3	78.81	23.11	32.91	42.08	46.13	52.16
$Me_2HSiSiH_3$	88.93	28.86	40.90	52.50	57.77	65.80
Me_3SiSiH_3	95.12	33.41	48.12	62.54	69.15	79.24
MeH_2SiSiH_2Me	90.15	28.62	40.92	52.54	57.80	65.82
$Me_2HSiSiH_2Me$	101.15	34.04	48.84	62.93	69.37	79.57
$Me_2HSiSiHMe_2$	109.86	39.98	56.81	73.33	81.05	93.24
Me_3SiSiH_2Me	107.49	38.91	56.12	72.99	80.82	93.13
$Me_3SiSiHMe_2$	117.61	44.33	63.89	83.31	92.36	106.80
$Me_3SiSiMe_3$	122.73	48.74	70.93	93.24	103.69	120.37

[a] Real $\overline{S}^0$ and $\overline{C}_p^0$ values require rotational barrier corrections (see Table 6).

TABLE 5

FREE ROTOR THERMODYNAMIC ENTROPIES AND HEAT CAPACITIES OF SOME CARBOSILANES [a, b]

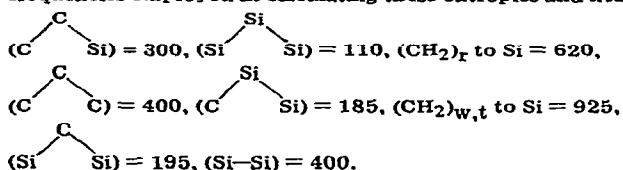| Compound	$\overline{S}^0$ (298)	$\overline{C}_p^0$ (Cal/deg mol)				
		298 K	500 K	800 K	1000 K	1500 K
$SiH_3C(CH_3)_3$	86.89	28.49	44.38	60.51	67.74	78.71
$(SiH_3)_2C(CH_3)_2$	92.87	32.25	48.34	63.86	70.65	80.63
$(SiH_3)_3CCH_3$	97.39	36.04	52.31	67.22	73.56	82.55
$SiH_3CH(CH_3)_2$	81.81	23.74	36.78	49.93	55.18	64.69
$(SiH_3)_2CHCH_3$	86.87	27.29	40.64	53.24	58.69	66.59
$(SiH_3)_3CH$	93.14	33.17	46.94	58.58	63.27	69.56
$SiH_3CH_2SiH_3$	76.80	22.10	32.64	42.38	46.54	52.46
$(SiH_3)_4C$	99.20	39.50	56.13	70.51	76.42	84.45
$(SiH_3)_2SiHCH_3$	93.56	30.93	43.52	55.12	60.17	67.47
$(SiH_3)_2Si(CH_3)_2$	101.10	36.24	51.18	65.37	71.69	81.12
$(SiH_3)_3SiCH_3$	106.02	39.31	54.40	68.27	74.28	82.89
$(C_2H_5)_2SiH_2$	97.13	29.85	45.72	61.12	68.08	78.81

[a] See Table 2 for vibration frequency assignments employed to generate these data. [b] Additional assigned frequencies employed in calculating these entropies and heat capacities are:

(C$\diagup^{C}\diagdown$Si) = 300, (Si$\diagup^{Si}\diagdown$Si) = 110, (CH$_2$)$_r$ to Si = 620,

(C$\diagup^{C}\diagdown$C) = 400, (C$\diagup^{Si}\diagdown$Si) = 185, (CH$_2$)$_{w,t}$ to Si = 925,

(Si$\diagup^{C}\diagdown$Si) = 195, (Si—Si) = 400.

TABLE 6

ROTATIONAL BARRIER CORRECTIONS [a] TO FREE ROTOR ENTROPIES AND HEAT CAPACITIES AT VARIOUS ROTATIONAL BARRIERS

V_0 (kcal)	ΔS^0 (corr)	ΔC_p^0 (corr)				
		300	500	800	1000	1500
1.0	0.3	0.4	0.2	0.1	0.0	0.0
1.7	0.7	0.9	0.5	0.2	0.1	0.0
2.0	0.8	1.1	0.6	0.3	0.2	0.1
2.5	1.1	1.1	0.8	0.4	0.3	0.1
3.0	1.4	1.2	1.0	0.6	0.4	0.2
4.0	1.7	1.1	1.2	0.8	0.6	0.3
6.0	2.2	1.0	1.1	1.1	1.0	0.6

[a] Corrections are to be subtracted from the free rotor values for each internal rotation.

for rotational barrier restrictions. With the exception of the rotational barriers in methylsilane (reported as 1.70 kcal from a microwave study) [34], and disilane (estimated as 1.10 kcal) [35] there are no data on the barriers to rotation in these compounds. Hence in the absence of such information, we suggest barriers of 1.7 kcal for all methyl groups, and 1.0 kcal for all rotations about Si—Si bonds. In highly branched compounds, this latter assumption certainly fails, but to what degree is not presently known. Approximate corrections [33] for hindered rotations at various barrier heights are shown in Table 6. These corrections must be subtracted from the free rotor entropies and heat capacities to obtain estimates of the "real" entropies and heat capacities. Exact corrections depend also on the corresponding free rotor partition function values, but since this is a minor effect compared to barrier height uncertainties (i.e., no more than a few tenths of an entropy unit for partition function variations of from 3 to 100), the partition function dependence of the rotational barrier corrections can readily be ignored.

The free rotor entropies and heat capacities of Tables 4 and 5 can be used to obtain the corresponding free rotor based group additivity values needed to estimate entropies and heat capacities of other similar and related compounds. These group values are shown in Table 7. To illustrate the use of the additivity values, we show below estimates of the entropies and heat capacities of 1,1,1-trimethyldisilane and of trisilane.

1,1,1-Trimethyldisilane, (CH₃)₃SiSiH₃

$\sigma = \sigma_{ext} \times \sigma_{int} = 3 \times 3^4$ Rotational barrier: 3 $(CH_3 \longrightarrow \infty)$ at $V_0 = 1.7$ kcal/mol
                                                                      1 $(SiH_3 \longrightarrow \infty)$ at $V_0 = 1.0$ kcal/mol

Groups: $3[C—(H)_3(Si)] + [Si—(Si)(C)_3] + [Si(Si)(H)_3]$

$\bar{S}^0$(intrinsic): $3(30.41) + [-20.48] + [35.32] = 106.07$ e.u./mole

$\bar{C}_p^0(300)$: $3(6.19) + (5.84) + 9.04 = 33.45$ e.u./mole

$\bar{S}^0$(real, hindered rotors) $= 95.16 - 3(0.7) - (0.3) = 92.8$ e.u./mole

$\bar{C}_p^0$(real, hindered rotors) $= 33.45 - 3(0.9) - (0.4) = 30.4$ e.u./mole

Trisilane SiH₃SiH₂SiH₃

$\sigma = \sigma_{ext} \times \sigma_{int} = 2 \times 3^2$ Rotational barriers: 2 $(SiH_3 \longrightarrow Si_2H_5)$ at $V_0 = 1.0$ kcal/mol

TABLE 7

FREE ROTOR-BASED [a] GROUP ADDITIVITIES FOR SILICON COMPOUNDS

Group	$\Delta \overline{H}_f^0$ (298 K)	$\overline{S}^0$ (298 K)	$\overline{C}_p^0$				
			300 K	500 K	800 K	1000 K	1500 K
[Si—(H)₃(Si)]	9.55	35.32	9.04	12.56	15.83	17.24	19.16
[Si—(H)₂(Si)₂]	9.50	17.43	7.74	10.94	13.29	14.21	
[Si—(H)(Si)₃]	8.05	1.30	8.06	9.58	10.79	11.15	
[Si—(Si)₄]	5.10	−15.81	7.90	8.16	8.21	8.14	
[Si—C)(H)₃]	2.10	34.89	8.71	12.28	15.62	17.03	18.97
[Si—(C)₂(H)₂]	−4.4	17.60	7.71	10.54	12.82	13.76	15.03
[Si—(C)₃(H)]	−11.3	−0.51	6.94	8.78	9.98	10.45	11.07
[Si—(C)₄]	−18.3	−20.16	5.17	6.34	6.81	6.91	7.01
[C—(Si)(H)₃]	−10.2	30.41	6.19	9.40	13.02	14.77	17.58
[C—(Si)₄]	−7.95	−26.69	4.66	7.01	8.03	8.30	8.57
[C—(Si)₃(C)]	−2.91	−26.78	3.72	6.07	7.34	7.70	8.06
[C—(Si)₂(C)₂]	2.46	−27.62	2.45	4.98	6.58	7.05	7.53
[C—(Si)(C)₃]	8.14	−28.32	1.21	3.90	5.83	6.40	7.00
[C—(Si)₃(H)]	−8.83	−2.80	7.04	10.10	11.72	12.18	12.65
[C—(Si)₂(H)₂]	−9.62	12.76	4.68	8.08	11.14	12.48	14.52
[C—(Si)₂(C)(H)]	−2.91	−6.77	3.68	6.68	8.98	9.86	11.07
[C—(Si)(C)₂(H)]	3.03	−7.35	2.64	5.70	8.27	9.24	10.56
[Si—(Si)₃(C)]	−0.92	−19.44	6.00	7.32	7.76	7.79	7.83
[Si—(Si)₂(C)₂]	−6.83	−20.25	5.78	7.26	7.67	7.67	7.65
[Si—(Si)₂(C)(H)]	1.50	−0.94	6.66	9.00	10.44	10.92	11.47
[C—(Si)(C)(H)₂]	−3.08	12.23	4.88	8.19	11.13	12.39	14.31
[Si—(Si)(H)₃]	9.55	35.32	9.04	12.56	15.83	17.24	19.16
[Si—(Si)(C)(H)₂]	2.55	17.53	8.08	11.06	13.25	14.11	15.36
[Si—(Si)(C)₂(H)]	−4.70	−0.86	7.54	9.58	10.62	10.95	11.47
[Si—(Si)(C)₃]	−12.2	−20.48	5.84	7.31	7.59	7.56	7.43
(ring structure, Si)	16.8(?) [b]						
(ring structure, Si—Si)	24.6 [b]						
(pentagon ring, Si)	11.3 [b]						
[C—(H)₃(C)] [c]	−10.2	−30.41	6.19	9.40	13.02	14.77	17.58
[C—(H)₂(C)₂] [c]	−4.93	9.42	5.50	8.25	11.07	12.34	14.25
[C—(H)(C)₃] [c]	−1.90	12.07	4.54	7.17	9.31	10.05	11.17
[C—(C)₄] [c]	0.50	−35.10	4.37	7.36	8.77	8.76	8.12
[C_d—(H)₂] [c, d]	6.26	27.61	5.10	7.51	10.07	11.27	13.19
[C_d—(H)(C)] [c, d]	8.59	7.97	4.16	5.81	7.65	8.45	9.62
[C_d—(C)₂] [c, d]	10.34	−12.70	4.10	4.99	5.80	6.08	6.36

[a] Corrections for hindered rotation must be made for each internal rotation using the correction terms of Table 6. [b] These values correspond to strain energies of the rings. Verification is needed. [c] See ref. 1. [d] C_d represents doubly bonded C atoms.

Groups: $2[Si—(H)_3(Si)] + [Si—(Si)_2(H)_2]$

$\overline{S}^0$(intrinsic): $= 2(35.32) + 17.43 = 88.07$ e.u./mole

$\overline{S}^0$(real, free rotor): $= 88.07 — R \ln(18) = 82.33$ e.u./mole

$\overline{S}^0$(real, hindered rotor): $= 82.33 — 2(0.3) = 81.7$ e.u./mole

$\overline{C}_p^0$(real, free rotor): $2(9.04) + 7.44 = 25.52$ e.u./mole

$\overline{C}_p^0$(real, hindered rotor): $= 25.52 — 2.0(4) = 24.7$ e.u./mole

Similarly, the heat of formation of the compound $(CH_3)_3SiCH_2SiH(CH_3)_2$ can be estimated as follows:

$$\overline{\Delta H_f^0} = 5[C—(H)_3(Si)] + [Si—(C)_4] + [C—(H)_2(Si)_2] + [Si—C)_3(H)]$$

$$= 5(-10.2) + (-18.3) + (-9.62) + (-11.3)$$

$$= -90.2 \text{ kcal/mol}$$

While the enthalpy group additivities presented here are the easiest way to estimate silane and organosilane compound heats of formation, it should be noted that they have been derived from values calculated by the Benson EECBA method. If one has the computer facilities available, the best way to generate heat of formation enthalpies is with this method, via eq. 1, with the fixed dipole charges and bond additivity values given earlier and found to provide estimates consistent with the latest, apparently reliable, calorimetric data.

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References

1 S.W. Benson, Thermochemical Kinetics, 2nd Ed., John Wiley & Sons, New York, 1976.
2 G.J. Janz, Quart. Revs. (London), 9 (1955) 229.
3 T.L. Allen, J. Chem. Phys., 31 (1959) 1039.
4 S.W. Benson and J.H. Buss, J. Chem. Phys., 29 (1958) 546.
5 S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Shaw, and R. Walsh, Chem. Reviews, 69 (1969) 279.
6 H.E. O'Neal and M.A. Ring, Inorg. Chem., 5 (1966) 435.
7 S.W. Benson and M. Luria, J. Amer. Chem. Soc., 97 (1975) 704.
8 S.W. Benson and M. Luria, J. Amer. Chem. Soc., 97 (1975) 3337.
9 S.W. Benson and M. Luria, J. Amer. Chem. Soc., 97 (1975) 3342.
10 S.W. Benson, Angewandte Chemie, 17 (1978) 812.
11 I.M.T. Davidson, J. Organometal. Chem., 170 (1979) 365.
12 CATCH TABLES, Univ. of Sussex, 1972; updated 1977.
13 P. Potzinger, A. Ritter and J. Krause, Z. Naturforsch., 30 (1975) 347.
14 S.R. Gunn and L.G. Green, J. Phys. Chem., 65 (1961) 779; ibid, 68 (1964) 946.
15 J.H. Purnell and R. Walsh, Proceedings of the Royal Soc. A, 293 (1966) 543.
16 C.G. Newman, H.E. O'Neal, M.A. Ring, F. Leska and N. Shipley, Int. Journal of Chem. Kinetics, XI (1979) 1167.
17 A. Kaczmarczyk, M. Millard, J.W. Nuss and G. Urry, J. Inorg. Nucl. Chem., 26 (1964) 421.
18 A. Kaczmarczyk, J.W. Nuss and G. Urry, J. Inorg. Nucl. Chem., 26 (1964) 427.
19 J.W. Nuss and G. Urry, J. Inorg. Nucl. Chem., 26 (1964) 435.
20 G.A. Russell, J. Amer. Chem. Soc., 81 (1959) 4815.
21 I.M.T. Davidson and A.V. Howard, J. Chem. Soc., Faraday I, 71 (1975) 69.
22 A.C. Baldwin, I.M.T. Davidson and M.D. Reed, J. Chem. Soc., Faraday I, 74 (1978) 2171.
23 J. Wells and R. Walsh, J. Chem. Soc., Faraday I, 100 (1976).
24 D.P. Paquin and M.A. Ring, J. Amer. Chem. Soc., 99 (1977) 1793.
25 M. Bowery and J.H. Purnell, Proc. Roy. Soc., A, 321 (1971) 341.
26 A.J. Vanderwielen, M.A. Ring and H.E. O'Neal, J. Amer. Chem. Soc., 97 (1975) 993.
27 I.M.T. Davidson and J.I. Matthews, J. Chem. Soc., Faraday I, 72 (1976) 1403.
28 F. Fehér and D. Skrodzki, Inorg. Nucl. Chem. Letters, Vol. 10 (1974) 577.
29 K. Shimizu and H. Murato, J. Molec. Spectroscopy, 5 (1960) 44.
30 D.F. Ball, P.L. Goggin, D.C. McKean and L.A. Woodward, Spectrochimica Acta, 16 (1960) 1358.
31 M.P. Brown, E. Cartmell and G.W.A. Fowles, J. Chem. Soc., (1959) 506.
32 H. Murata and K. Shimizu, J. Chem. Phys., 23 (1955) 1968.
33 G.L. Lewis and M. Randall (revised by K.S. Pitzer and L. Brewer), Thermodynamics, 2nd ed., McGraw-Hill Book Co., New York, 1961.
34 R.W. Kelb and L. Pierce, J. Chem. Phys., 27 (1957) 108.
35 R.A. Scott and H.A. Scheraga, J. Chem. Phys., 42 (1965) 2209.