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ENTHALPIES OF FORMATION OF SILANES

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Summary - Benson's electrostatic model for calculating enthalpies of formation has been applied to the methylsilanes and some disilanes, confirming recent conclusions from electron-impact measurements that these silanes essentially follow bond additivity rules, with very small interaction corrections. These findings are shown to be consistent with recently measured bond dissociation energies.

There are few, if any, reliable enthalpies of formation of silanes, because of the formidable experimental difficulties associated with calorimetric measurements on silicon compounds. The most comprehensive collection of thermochemical data is in the "CATCH" Tables,[1] a critical compilation in which best values have been arrived at by computer-aided statistical analysis. More recently, Potzinger, Ritter and Krause[2] (PRK) have published enthalpies of formation derived from a large number of electron impact experiments by application of a modified version of Allen's bond-interaction scheme,[3] which had previously been applied to silicon compounds,[4] notably by Quane,[5] who sought to reconcile the best thermochemical and electron impact data available in 1971. For the monosilanes SiH_4 to $SiMe_4$, PRK's results closely corroborate Quane's, but differ significantly from the CATCH Tables, as shown in Table 1.

Table 1 also shows PRK and CATCH figures for disilane and for hexamethyldisilane, where the disagreement is particularly large. The first two $\Delta\Delta H_f^o$ columns in Table 1 show the differences between successive enthalpies of formation in the CATCH and PRK schemes, while the last column gives these differences derived directly from PRK's experimental appearance potentials.[2] It should be noted that Quane and PRK favour an essentially constant value of $\Delta\Delta H_f^o$ for monosilanes, conforming closely to simple bond additivity, with very small interaction terms.

TABLE 1

Enthalpies of Formation of Silanes

	ΔH_f^o/kcal. mol^{-1}*			$\Delta\Delta H_f^o$/kcal. mol^{-1}*		
COMPOUND	CATCH[1]	QUANE[5]	PRK[2]	CATCH	PRK CALC.	PRK EXPT.
SiH_4	8.2	5.7	8.2	16.0	12.5	9
$MeSiH_3$	- 7.8	- 4.0	- 4.3	12.2	12.5	11
Me_2SiH_2	-20.0	-15.2	-16.8	17.4	12.8	13
Me_3SiH	-37.4	-28.0	-29.6	19.1	12.8	12
Me_4Si	-56.5	-42.2	-42.4			
Si_2H_6	19.1		17.1	104.9	77.2	
Si_2Me_6	-85.8		-60.1			

* 1 kcal. mol^{-1} ≡ 4.184 kJ mol^{-1}

In seeking to assess the relative merits of the CATCH and PRK figures in Table 1, we first consider deductions based on bond dissociation energies, there now being a few reliable dissociation energies of organosilanes which have been measured kinetically. Thus, for hexamethyldisilane,[6] $D(Me_3Si\text{-}SiMe_3) = 80.5 \pm 1$ kcal. mol^{-1}; for trimethylsilane,[7] $D(Me_3Si\text{-}H) = 90 \pm 2.5$ kcal. mol^{-1}; and for tetramethylsilane,[8] $D(Me_3Si\text{-}Me) = 85 \pm 1.5$ kcal. mol^{-1}. Hence, for $Me_3SiH + Me\cdot \rightarrow Me_4Si + H\cdot$ $\Delta H = D(Me_3Si\text{-}H) - D(Me_3Si\text{-}Me) = 5$ kcal. mol^{-1} and $\Delta\Delta H_f^o(Me_3SiH - Me_4Si) = 52.1 - 34.3 - 5 = 12.8$ kcal. from the well-established enthalpies of formation of H• and Me•.[9] This result agrees very well with PRK, but differs by 6 kcal. from the CATCH figure. For $Me_6Si_2 + 2\ Me\cdot \rightarrow 2\ Me_4Si$ $\Delta H = 80.5 - 2(85) = -89.5$ kcal, and $\Delta H_f^o(Me_6Si_2) - 2\ \Delta H_f^o(Me_4Si) = 89.5 - 2(34) = 21.5$ kcal. This result is closer to PRK than to CATCH. These few bond dissociation energies therefore lend some support to the PRK figures.

Considerable success in the calculation of enthalpies of formation of hydrocarbons and simple organic compounds has been achieved by use of Benson's electrostatic model,[10] which can reproduce enthalpies of formation of alkanes to ± 0.2 kcal. mol^{-1}. As in Allen's scheme,[3] there are additive and interactive terms, but the latter are calculated from the coulombic interactions in the molecule. We have applied Benson's model to all of the compounds in Table 1, assuming all molecules to be tetrahedral with the following bond lengths: C-H, 1.093 Å (as in hydrocarbons[10]); Si-H, 1.48 Å; and Si-C, 1.87 Å. These molecules may have three types of formal charge: $\bar{C}\text{-}\overset{+}{H}$, denoted by $\pm\underline{y}$; $\overset{+}{Si}\text{-}\bar{H}$, denoted by $\pm\underline{z}$; and $\overset{+}{Si}\text{-}\bar{C}$, denoted by $\pm\underline{w}$. The value of $\underline{y}$ was taken to be 1.059, as in hydrocarbons,[10] giving the following expressions for the electrostatic energy:

SiH_4, $-E_{el}$/kcal. $mol^{-1} = 8.328w^2$
$MeSiH_3$, " " $= 0.535z^2 + 3.311z + 7.339 + 4.840w^2 + 2.538wz + 0.737w$
Me_2SiH_2, " " $= 1.812z^2 + 7.194z + 14.550 + 2.289w^2 + 3.385wz + 0.983w$
Me_3SiH, " " $= 3.831z^2 + 11.649z + 21.633 + 0.676w^2 + 2.538wz + 0.737w$
Me_4Si, " " $= 6.592z^2 + 16.673z + 28.587$
Si_2H_6, " " $= 9.180w^2$
Si_2Me_6, " " $= 6.937z^2 + 21.716z + 43.505$

In the absence of reliable thermochemical data $\underline{w}$ and $\underline{z}$ cannot be evaluated accurately, but they may be estimated from dipole moments. The dipole moment of methylsilane is 0.7 D, considered[11] to be made up of the following bond moments: $\mu(Si\text{-}H) = 1.0$ D, $\mu(Si\text{-}C) = 0.6$ D, and $\mu(H\text{-}C) = 0.3$ D. From these, and the bond lengths quoted above, $\underline{w} \sim 2.6$ and $\underline{z} \sim 1.2$. The resulting values of E_{el} are in Table 2.

TABLE 2

Electrostatic Energies based on w = 2.6 and z = 1.2

COMPOUND	$-E_{el}$/kcal. mol^{-1}	ΔE_{el}	$\Delta\Delta H_f^o$/kcal. mol^{-1}
SiH_4	56.30		
		-1.66	8.5
$MeSiH_3$	54.64		
		-0.26	9.9
Me_2SiH_2	54.38		
		+1.15	11.4
Me_3SiH	55.53		
		+2.56	12.8*
Me_4Si	58.09		
Si_2H_6	62.06		
		+17.49	
Si_2Me_6	79.55		

* Experimental value, see text.

For the monosilanes, ΔE_{el} is seen to be small and to change little within the series. This series may be thought of as resulting from successive methylene insertions into silicon-hydrogen bonds, i.e. $\{SiH_4(CH_2)_n\}$, n = 0 - 4. The figures for the corresponding series of alkanes[10] are in Table 3.

TABLE 3

Enthalpies of Formation of Hydrocarbons

COMPOUND	$-E_{el}$/kcal. mol^{-1}	ΔE_{el}	ΔH_f^o/kcal. mol^{-1}	$\Delta\Delta H_f^o$
CH_4	12.63		-17.9	
		1.02		2.3
C_2H_6	13.65		-20.2	
		2.89		4.6
C_3H_8	16.54		-24.8	
		4.76		7.3
i-C_4H_{10}	21.30		-32.1	
		6.61		8.2
neo-C_5H_{12}	27.91		-40.3	

It is evident that ΔE_{el} in the hydrocarbons is considerably greater than in the monosilanes (in the hydrocarbons ΔE_{el} ranges from 8% of E_{el} at the start of the series to 31% of E_{el} at the end; the corresponding figures for the silanes are 3% and 4.6%). Hence, the electrostatic model confirms the conclusion of Quane and PRK that the enthalpies of formation of the silanes closely approximate to bond additivity, with very small interaction corrections. This conclusion was foreshadowed by O'Neal and Ring, who suggested that enthalpies of formation of alkylsilanes not conforming to simple additivity were probably erroneous.[12]

It has previously been shown from bond dissociation energies that $\Delta\Delta H_f^o(Me_3SiH - Me_4Si)$ is 12.8 kcal. mol^{-1}. Since ΔE_{el} for these compounds is 2.6 (Table 2), the CH_2 increment is 10.2 kcal. mol^{-1}. Hence the other values of $\Delta\Delta H_f^o$ in the last column of Table 2 were obtained. These strikingly resemble the experimental $\Delta\Delta H_f^o$ obtained by PRK (last column of Table 1). Applying this CH_2 increment to the disilanes, we have $\Delta\Delta H_f^o(Si_2H_6 - Si_2Me_6) = 6\ (CH_2) + \Delta E_{el} = 6 \times 10.2 + 17.49 = 78.7$ kcal., close to the PRK value in Table 1. Hence, the electrostatic model is seen to be much more consistent with the Quane and PRK figures in Table 1 than with CATCH, especially so far as hexamethyldisilane is concerned. It seems that the PRK enthalpies of formation are to be preferred as the best available at present.

Although the agreement between the last columns of Tables 1 and 2 is excellent, this is fortuitous as it depends on the values of $\underline{w}$ and $\underline{z}$. Deriving these from bond moments is not reliable because of the influence of polarization,[13] and $\underline{w}$ and $\underline{z}$ may have significantly smaller values. However, the main conclusions are unaffected since constancy of ΔE_{el} for the monosilanes is a feature of the electrostatic expressions which is virtually independent of the values of $\underline{w}$ and $\underline{z}$, so long as these are kept within the bounds of reason. Thus, if as a reductio ad absurdum $\underline{w}$ and $\underline{z}$ are both reduced to unity, implying less charge separation in Si-C and Si-H than in C-H, ΔE_{el} for the monosilanes only varies between 10.8 and 11.0 kcal., while $\Delta\Delta H_f^o(Si_2H_6 - Si_2Me_6)$ becomes 76.2 kcal., in even better agreement with PRK than Table 2!

If the PRK enthalpies of formation are to be adopted, some previous thermochemical calculations based on CATCH have to be revised.[6,14] Combining PRK enthalpies of formation with the bond dissociation energies discussed above we obtain three values for the enthalpy of formation of the trimethylsilyl radical: 8.3 kcal. mol^{-1} from tetramethylsilane, 8.3 from trimethylsilane, and 10.2 from hexamethyldisilane. The average of these is 9 ± 1 kcal. mol^{-1}; taking into account uncertainties in the enthalpies of formation and dissociation energies, we suggest $\Delta H_f^o(Me_3Si\cdot) = 9 \pm 3$ kcal. mol^{-1}.

Estimates for some reactions involving dimethylsilylene[14] are revised as follows. In the hypothetical reaction $Me_5Si_2H + Me\cdot \rightarrow Me_6Si_2 + H\cdot$ $\Delta H = D(Me_5Si_2\text{-}H) - D(Me_5Si_2\text{-}Me)$. This difference is likely to be approximately equal to $D(Me_3Si\text{-}H) - D(Me_3Si\text{-}Me)$, say 5 ± 3 kcal. mol^{-1}. Hence, if $\Delta H_f^o(Me_6Si_2)$ is -60.1 kcal. mol^{-1} $\Delta H_f^o(Me_5Si_2H) = -47 \pm 3$ kcal. mol^{-1}. PRK[2] calculate -47.3 kcal. mol^{-1} for this enthalpy of formation. In the silylene-forming elimination: $Me_5Si_2H \rightarrow Me_2Si + Me_3SiH$, the activation energy[14] is 47.3 kcal. mol^{-1} and the back reaction is one of the most rapid known reactions of dimethylsilylene, probably with zero activation energy.[15] Hence $\Delta H_f^o(Me_2Si) = 47.3 + 29.6 - 47 = 30 \pm 3$ kcal. mol^{-1}. The second bond dissociation energy in tetramethylsilane can then be calculated: $Me_3Si\cdot \rightarrow Me_2Si + Me\cdot$ $\Delta H = 34 + 30 - 9 = 55 \pm 3$ kcal. mol^{-1}.

In the pyrolysis of hexamethyldisilane,[6] a minor reaction is the elimination of dimethylsilylene, $Me_6Si_2 \rightarrow Me_2Si + Me_4Si$, which has an experimental activation energy of 67 kcal. mol^{-1}. This is much higher than for the corresponding reaction of Me_5Si_2H because the back reaction (insertion of Me_2Si into tetramethylsilane) is "forbidden".[16] Since ΔH can be calculated from the above results to be 48 ± 3 kcal. mol^{-1}, the activation energy of this "forbidden" back reaction is seen to be ca. 19 kcal. mol^{-1}.

If PRK and Quane are correct in concluding that enthalpies of formation of silanes closely approximate to bond additivity, redistribution reactions of these compounds should be essentially thermoneutral. This is borne out by the data for redistribution reactions involving the monosilanes[17] which are given in Table 4, together with calculated values from CATCH and PRK.

TABLE 4

Enthalpy Changes in Redistribution Reactions

REACTION	ΔH/kcal. mol^{-1}		
	EXPTL.	PRK	CATCH
$SiH_4 + Me_2SiH_2 \rightleftharpoons 2MeSiH_3$	0.7	0.0	- 3.8
$MeSiH_3 + Me_3SiH \rightleftharpoons 2Me_2SiH_2$	0.2	0.3	5.2
$2MeSiH_3 + Me_4Si \rightleftharpoons 3Me_2SiH_2$	0.4	0.6	12.1
$MeSiH_3 + 2Me_4Si \rightleftharpoons 3Me_3SiH$	0.4	0.3	8.6
$Me_2SiH_2 + Me_4Si \rightleftharpoons 2Me_3SiH$	0.2	0.0	1.7

Consequently, it is simple and quite reliable to calculate differences in enthalpy of formation of organosilanes by PRK's version of Allen's method. The main outstanding difficulty is the lack of a single reliable enthalpy of formation for any silane, to convert these differences to absolute values.

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