8719843) for financial support of this work. We thank the San Diego Supercomputer center for computer time for the MOPAC/AM1 calculations, and we thank Professor Mark Midland for providing us with PCMODEL (Serena Software) which was used for the MM2 calculations.

Note Added in Proof. We thank reviewer 1 for the following observation. A minor decomposition pathway of hexamethyldisilane produces dimethylsilylene and tetramethylsilane.[16] While the kinetics of this process are quite different from the other disilane decompositions reviewed here, the overall thermochemistry should be similar, i.e., $\Delta H^\circ \approx 52$ kcal. With heats of formation of −55.7 kcal/mol for Me_4Si and 32 kcal/mol for Me_2Si:, this reaction enthalpy gives a heat of formation of −75.7 kcal/mol for hexamethyldisilane, in good agreement with the Table III "kinetic" estimate.

Registry No. $MeSiH_3$, 992-94-9; Me_2SiH_2, 1111-74-6; Me_3SiH, 993-07-7; Me_4Si, 75-76-3; Si_2H_6, 1590-87-0; $MeSiH_2SiH_3$, 13498-43-6; $Me_2SiHSiH_3$, 16342-86-2; $MeSiH_2SiH_2Me$, 870-26-8; Me_3SiSiH_3, 18365-32-7; $Me_2SiHSiH_2Me$, 814-74-4; Me_3SiSiH_2Me, 81633-92-3; $Me_2SiHSiHMe_2$, 814-98-2; $Me_3SiSiHMe_2$, 812-15-7; $Me_3SiSiMe_3$, 1450-14-2; SiH_2, 13825-90-6; $MeSiH$, 55544-30-4; Me_2Si, 6376-86-9.

Certainties and Uncertainties in the Heats of Formation of the Methylsilylenes

R. Walsh

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, U.K.

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Recent discrepancies in values for $\Delta H_f^\circ(SiMe_2)$ and $\Delta H_f^\circ(SiHMe)$ are examined in detail. For values arising from the analysis of the kinetics of methylated disilane pyrolyses, it is shown that disagreements in the dissociation enthalpies are small. The main differences in ΔH_f° for the silylenes arise from different choices for the experimentally uncertain enthalpies of formation of the disilanes. It is argued that the high values for $\Delta H_f^\circ(SiHMe)$ and $\Delta H_f^\circ(SiMe_2)$ arising from ion–molecule studies represent upper limits only. In addition various thermochemical trends and correlations are shown to support a value of $\Delta H_f^\circ(SiMe_2) = 25.7 \pm 3$ kcal mol^{-1} with a divalent state stabilization energy of ca. 28 kcal mol^{-1} for $SiMe_2$.

Introduction

The thermochemistry of reactive transients is inextricably bound up with our knowledge and understanding of the kinetics and mechanisms involving these transients. Thus we recently published an analysis of kinetic data on the thermal decompositions of various methyldisilanes[1] which led to $\Delta H_f^\circ(SiMe_2) = 26 \pm 2$ kcal mol^{-1} and $\Delta H_f^\circ(SiHMe) = 44 \pm 3$ kcal mol^{-1}. A reexamination of the same data supplemented by further kinetic studies has led O'Neal, Ring, Richardson, and Licciardi[2] (ORRL) to values for these quantities which are somewhat higher, viz., 32 and 48 kcal mol^{-1}. Theoretical calculations by Gordon[3] at the MP2/6-31G(d,p) level on isodesmic reactions involving silylenes are consistent with the latter numbers. The group of Shin and Beauchamp,[4] using FTICR spectroscopy to study the deprotonation of the $MeSiD_2^+$ ion, obtain $\Delta H_f^\circ(SiHMe) = 53 \pm 4$ kcal mol^{-1} and derive $\Delta H_f^\circ(SiMe_2) = 37 \pm 6$ kcal mol^{-1}. With these estimates spanning a range of 11 kcal mol^{-1} for $SiMe_2$ and 9 kcal mol^{-1} for SiHMe, it seems worthwhile to examine the methods and assumptions underlying these estimates to see whether any reconciliation can be achieved.

In order to understand the present uncertainties over $SiMe_2$ and SiHMe, it is helpful to recapitulate, briefly, the situation concerning $\Delta H_f^\circ(SiH_2)$. Until ca. 1985, the generally accepted[5] value for this quantity was 58 kcal mol^{-1}, based on pyrolysis studies of the dissociations of SiH_4 and Si_2H_6 combined with estimates of rates of reaction of SiH_2 with H_2 and with SiH_4.[6] The situation changed dramatically, and suddenly when first high level theoretical calculations by two groups[7,8] pointed to significantly higher values for $\Delta H_f^\circ(SiH_2)$ and secondly the first time-resolved experiments with SiH_2, carried out by Jasinski,[9] revealed a reactivity (with H_2) ca. 10^4 times greater than expected on the basis of the earlier estimates. This was followed rapidly by an FTICR study of the deprotonation of SiH_3^+ which also yielded a higher value for $\Delta H_f^\circ(SiH_2)$.[10] These studies led to values in the range 64–69 kcal mol^{-1}, and subsequent experimentation[11-16] has not narrowed this range. Thermal kinetic studies[11-14] involving neutral SiH_2 (combination of pyrolysis kinetics with reverse insertion rates) tend to support values of 64–65 kcal mol^{-1}, while ion–molecule studies[15,16] favor 68–69 kcal mol^{-1}. Theory has given values at both ends of the range, but in the most recent theoretical paper

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Table I. Arrhenius Parameters for Pentamethyldisilane Dissociation

temp range/K	log (A/s^{-1})	E_a/kcal mol^{-1}	ref
620–699	12.93 ± 0.31	47.35 ± 0.93	18
683–743	13.3 ± 0.1	48.4 ± 0.3	19
591–639	12.83 ± 0.09	46.63 ± 0.25	20

Curtiss and Pople[17] have argued in favor of ca. 65 kcal mol^{-1}.

Regarding $\Delta H_f°(SiMe_2)$ our own first estimate[5] of 26 kcal mol^{-1} was based on the assumption of a Me-for-H substitution energy of −16 kcal mol^{-1}, transferred from the $\Delta H_f°$ data for the stable methylsilanes (not under dispute). Application of this figure, today, yields values for $\Delta H_f°(SiMe_2)$ of 32–37 kcal mol^{-1}. Can the earlier figure for $\Delta H_f°(SiMe_2)$ be so simply revised as has happened in the case of $\Delta H_f°(SiH_2)$? The situation is not so simple.

Although our present figure[1] is the same as that originally proposed, this is merely fortuitous, since the arguments currently under discussion are based on the latest information (not available at the time of the original estimate). Most of the experimental attempts to determine $\Delta H_f°(SiMe_2)$ seem to center around either the methylated disilane decomposition reactions or the silene ⇄ silylene isomerization process. In this paper data for these systems are examined again, and in addition we take another look at the Me-for-H substitution argument.

Uncertainties in the Methylated Disilane Decomposition Kinetics

Our most recent analysis[1] together with that of ORRL[2] is based on the reactions:

$$Si_2H_xMe_{6-x} \rightleftarrows SiH_yMe_{2-y} + SiH_zMe_{4-z} \qquad (1)$$

where $x = 0$–6, $y = 0$–2, and $z = x - y$. The object is to combine forward and reverse activation energies to obtain the enthalpy difference, viz.

$$\Delta H°_{1,-1} = E_1 - E_{-1} \qquad (A)$$

Then provided the heats of formation of the silanes SiH_zMe_{4-z} and the disilanes $Si_2H_xMe_{6-x}$ are known the heats of formation of the silylenes SiH_yMe_{2-y} can be obtained. There are thus two potential areas of uncertainty here. The first concerns the reliability of the kinetic studies and the second the reliability of heats of formation of methylsilanes and methyldisilanes. In order to simplify the discussion, we limit it to consideration of the single reaction

$$Me_3SiSiMe_2H \rightleftarrows SiMe_2 + Me_3SiH \qquad (2)$$

which illustrates all the problems.

The forward reaction has been investigated by Davidson et al.[18,19] and by ourselves,[20] and the rate data are shown in Table I. There appears to be resonable agreement between all three determinations, on both rate constants and Arrhenius parameters. Since these data were obtained both with and without inhibitors and extrapolated to initial stages of the reaction, it is unlikely that there is significant error here. It seems reasonable to assume that step 2 represents the rate-controlling step in the pyrolysis of pentamethyldisilane. This is important since we had previously suggested[1] that mechanistic complexities might exist in this pyrolysis, leading to erroneous (low) Arrhenius parameters for step 2 (i.e. we were wrong).

The reverse reaction has been investigated only by ourselves[21] (using time-resolved techniques) and only at 298 K, yielding $k_{-2} = (2.7 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1}.

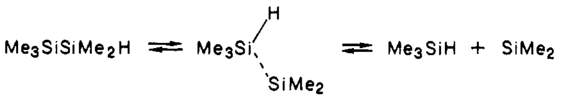
The difficulty of combining forward and reverse rate constants for step 2 is that they are not carried out at the same temperature. Therefore an extrapolation of either k_2 or k_{-2} is needed. We chose to extrapolate k_{-2} from 298 to 650 K on the general grounds that because of its high value, k_{-2} could not possess a large activation energy and was therefore unlikely to change significantly with temperature. In the event we assumed $A_{-2} = 10^{10}$ dm^3 mol^{-1} s^{-1} and $E_{-2} = 0.8$ kcal mol^{-1}. In combination with a thermodynamic estimate of $\Delta S°_{2,-2} = 34.2$ cal K^{-1} mol^{-1} this led us[1] to the estimate

$$\log(k_2/s^{-1}) = 15.3 - 54.4 \text{ kcal mol}^{-1}/RT \ln 10$$

and also to $\Delta H°_{2,-2}$ (298 K) = 55.1 kcal mol^{-1}.

ORRL[2] chose to extrapolate k_2 from ca. 700 to 298 K, arguing that an uncertainty with a given numerical magnitude corresponded to less in terms of enthalpy at 298 than at 700 K, and was therefore preferable. While this is not in dispute, there remains the question of how reliable the extrapolation of k_2 actually is. For instance the three different sets of Arrhenius parameters for step 2 in Table I lead to extrapolated values differing by a factor of ca. 7 (or $10^{0.85}$) at 298 K assuming the Arrhenius equation is valid over the temperature range. In fact ORRL[2] used a transition-state theory fit to the data for k_2 as the basis of extrapolation. This may or may not be more reliable. Their procedure leads to $\Delta H_{2,-2} = 52.1$ kcal mol^{-1}. In general this approach[2] led to an agreeable consistency in that $\Delta H°_{1,-1}$ was found to be 51.8 ± 1.0 kcal mol^{-1} for all the methyldisilane systems studied (some 12 reactions).

There is clearly an unsettled issue here, since if rate constants were available for both forward and back reactions at all temperatures within the range, it should not matter at what temperature the comparison is made, the same value for $\Delta H°_{2,-2}$(298 K) should emerge. The only resolution of this problem which we can envisage (apart from errors in the published rate constants) is that the dissociation is not a straightforward elementary process but rather proceeds in two stages, viz.:



There are thus two bottlenecks, the first involving the 1,2-H-transfer transition state leading to a weakly bound association complex which dissociates via a second transition state simply by loss of SiMe$_2$. The first transition state should be tight and the second transition state loose. This combination could potentially give rise to a situation in which, at high temperatures, the first stage is predominantly rate determining (with effectively "low" Arrhenius parameters) while at low temperatures the second stage (with "high" Arrhenius parameters) becomes rate-determining. This would lead to a situation of non-Arrhenius behavior over a wide temperature range.

A more detailed analysis is presented in our study of pentamethyldisilane decomposition,[20] but the consequence for k_2 or k_{-2} over a wide temperature range is that Arrhenius plots should be curved. k_{-2} will show a negative

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[22] There are small differences in entropy estimates between ourselves[1] and O'Neal and Ring,[2] but these make very little difference to values for $\Delta H°$.

temperature dependence, decreasing by a factor of at least 4 between 298 and 650 K. [This possibility was hinted at earlier[1], even though we did not then favor it. Experiments are planned to test this.] The Arrhenius plot for k_2 will show curvature such that a linear extrapolation from 650 downwards to 298 K will lead to an overestimate. The use of a transition-state theory model for temperature extrapolation will not circumvent this problem since the rate-determining process is changing over this temperature range.

If we assume a factor of 4 reduction in k_{-2} between 298 and 650 K, as opposed to our previous treatment leading to ca. a factor of 2 *increase* in k_{-2}, this alters $\Delta G°_{2,-2}$(650 K) by $RT \ln 8$, i.e., 2.7 kcal mol^{-1}, and reduces our estimate of $\Delta H°_{2,-2}$(298 K) from 55.1 to 52.4 kcal mol^{-1}. Alternatively if we assume a factor of 4 reduction in the value of k_2 at 298 K obtained by ORRL,[2] this leads to an increase in $\Delta G°_{2,-2}$(298 K) by $RT \ln 4$, i.e., 0.8 kcal mol^{-1}, and increases ORRL's estimate for $\Delta H°_{2,-2}$ (298 K) from 52.1 to 52.9 kcal mol^{-1}. Thus the two values for $\Delta H°_{2,-2}$ become virtually identical and therefore independent of the method of extrapolation. Of course there remains the question of experimental corroboration of these non-Arrhenius effects. This together with small uncertainties in the thermodynamic estimates leads us to suggest $\Delta H_{2,-2} = 52.6 \pm 1.5$ kcal mol^{-1}.

It must be confessed that, although our analysis of this decomposition is somewhat different from that of ORRL,[2] the resulting value for $\Delta H°_{2,-2}$ is, at least in the case of pentamethyldisilane, considerably closer to their value (52.1 kcal mol^{-1}) than our original estimate (55.1 kcal mol^{-1}). There remains then the question of the heats of formation of the methylsilanes and dimethyldisilanes. This is dealt with in the next section.

The Heats of Formation of Methyldisilanes (in Particular Hexamethyldisilane)

The heats of formation of the methylsilanes are known within uncertainties of ±1 kcal mol^{-1} via equilibrium studies.[23] Heats of formation of the methyldisilanes are mostly unmeasured. Earlier electron-impact values[24] are no longer thought to be reliable. Additivity schemes[25] and semiempirical theory[26] have been used to estimate values, but these depended substantially on the figure for $\Delta H_f°(Si_2Me_6)$. Hexamethyldisilane is the only methylated disilane for which values not based on either kinetics or mass spectrometry exist. $\Delta H_f°(Si_2Me_6)$ has been determined by combustion calorimetry by two groups.[27,28] The modern calorimetric method for organosilicon compounds involves combustion in the prsence of an auxiliary fluorocarbon to try to ensure complete reaction. Using this method Pedley and Rylance[29] quote $\Delta H_f° = -86.8 \pm 2.1$ kcal mol^{-1} obtained from Pedley's earlier work[27] while more recently Smeaton and Steele[28] have obtained -82.9 ± 2.2 kcal mol^{-1}. These values ought to be considered reliable on the basis of the technique used. However, at least in the case of the earlier study,[27] doubts are raised by the values obtained for other organosilanes,[30] which are no longer thought to be correct.[31]

As far as other methods are concerned, kinetic data may be used in the case of Si_2Me_6 for the decomposition

$$Me_3SiSiMe_3 \rightleftarrows 2Me_3Si \qquad (3)$$

for which both forward and reverse processes have been studied. This decomposition, although different from that of Si_2Me_5H, in that it produces free radicals, nevertheless poses the same problems of how to combine the forward and reverse rate constants measured at different temperatures. The decomposition has been studied by Davidson and Howard[32] who obtained, in the temperature range 770–872 K

$$\log (k_3/s^{-1}) = 17.2 - 80.5 \text{ kcal mol}^{-1}/RT \ln 10$$

while the gas-phase recombination of trimethylsilyl radicals has been measured by flash photolysis by Shimo et al.[33] at 298 K, yielding $k_{-3} = 1.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. [This value, obtained by real time monitoring, is taken as more reliable than earlier gas-phase or solution-phase values cited in ref 33.] The high value for k_{-3} is consistent with a high value for A_3 (i.e. a loose transition state for a bond fission process). If the room-temperature value for k_{-3} is used at 820 K where $k_3 = 5.4 \times 10^{-5}$ s^{-1}, this leads to $\Delta G°_{3,-3} = 47.4$ kcal mol^{-1}. In combination with $\Delta S° = 45.4$ cal K^{-1} mol^{-1} [34] this gives $\Delta H°_{3,-3}$(820 K) = 84.6 kcal mol^{-1}. Correction to room temperature yields $\Delta H°_{3,-3}$(298 K) = 84.7 kcal mol^{-1}. In combination with $\Delta H_f°(Me_3Si) = -0.8 \pm 1.7$ kcal mol^{-1} [1,31,35] this leads to $\Delta H_f°(Si_2Me_6) = -86.3 \pm 2.5$ kcal mol^{-1}.[36] The uncertainties here come from the uncertainty in the radical heat of formation (combined vectorially), but probably the result is more uncertain because of the assumption of a temperature invariant k_{-3}. If it is assumed that k_{-3} varies as $T^{-1.5}$, as is the case for the *tert*-butyl radical combination,[37] then k_{-3}(820 K) = 3.3×10^9 dm^3 mol^{-1} s^{-1} and the same calculation as above yields $\Delta H°_{3,-3}$(298 K) = 82.2 kcal mol^{-1} and $\Delta H_f^0(Si_2Me_6) = -83.8$ kcal mol^{-1}. This is probably more realistic in terms of the radical recombination process. The alternative of extrapolation of k_3 to room temperature and combination with the measured k_{-3} again depends on the method of extrapolation. Using either an Arrhenius or a transition-state theory, form leads to values for $\Delta H_f°(Si_2Me_6)$ in the range −83 to −84 kcal mol^{-1}. [A similar calculation by ORRL[2] leads to a value of −82.4 kcal mol^{-1}]. We thus suggest a value of -83.5 ± 3.5 kcal mol^{-1} for $\Delta H_f°(Si_2Me_6)$ as being most consistent with currently available data on the bond fission process for hexamethyldisilane. ORRL[2] have derived $\Delta H_f°(Si_2Me_6) = -75.0$ kcal mol^{-1} by combining the data for pairs of reactions (1, −1) which produce the same silylene from different methyldisilane precursors. In order to obtain $\Delta H_f°(Si_2Me_6)$ it is necessary to obtain $\Delta H_f°$ for the other methylated disilanes up to Si_2Me_5H by successive combination of different pairs of reactions

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Table II. Standard Enthalpies of Formation of Hexamethyldisilane from Various Sources

value/kcal mol^{-1}	method	ref
-86.8 ± 2.1	combustion calorimetry	29, 27
-82.9 ± 2.2	combustion calorimetry	28
-83.5 ± 3.5	kinetics of dissociation and recombination	see text
-75.0	kinetics of other disilane decompositions	2
-78.45	MM2 modified	2
-79.60	AM1 modified	2
-77.86	EECBA modified	2
-83 ± 3	preferred value	this work

Table III. Possible Values for Standard Enthalpies of Formation of the Methyldisilanes (kcal mol^{-1})

compd	upper limit	lower limit	preferred
Si_2H_6	+19.1	+19.1	+19.1
$MeSiH_2SiH_3$	+3.4	+1.5	+2.1
$Me_2SiHSiH_3$	-12.3	-16.2	-14.9
$MeSiH_2SiH_2Me$	-12.3	-16.2	-14.9
Me_3SiSiH_3	-27.9	-33.8	-31.9
$Me_2SiHSiH_2Me$	-27.9	-33.8	-31.9
Me_3SiSiH_2Me	-43.6	-51.5	-49.0
$Me_2SiHSiHMe_2$	-43.6	-51.5	-49.0
$Me_3SiSiHMe_2$	-59.3	-69.1	-66.0
$Me_3SiSiMe_3$	-75.0	-86.8	-83.0

starting from Si_2H_6 with its known $\Delta H_f° = 19.1 \pm 0.3$ kcal mol^{-1}.[30] This procedure accumulates successively all the errors involved in estimating each $\Delta H°_{1,-1}$ value from the kinetic data for each decomposition. Thus while each $\Delta H°_{1,-1}$ value may have an uncertainty of only ca. ±1.5 kcal mol^{-1}, the accumulation may be substantial. In addition the final increment for Si_2Me_5H to Si_2Me_6 is assumed.

For Si_2Me_6 these heats of formation are collected in Table II together with three other values estimated by semiempirical schemes as modified by ORRL.[2] These latter estimates are not those of the original schemes but have been modified to fit the methylmonosilanes and one particular disilane (Si_2H_6 or $MeSi_2H_5$). It is our view that minor modifications of the parametrization of these schemes can alter these values sufficiently to provide reasonable consistency with any of the existing experimental values. The key to this problem is a reliable *experimental* value for $\Delta H_f°(Si_2Me_6)$. We are at present at risk of drowning in values of uncertain reliability. Although our preference at present is for a value of ca. -83 ± 3 kcal mol^{-1}, it must be admitted that the basis for this is still a little shaky.

As we have pointed out before,[38] Si_2Me_6 is a key compound for heat of formation studies because other disilane heats of formation depend on it. Because no independent values for these other disilanes exist, it is necessary to estimate them by some kind of empirical or semiempirical scheme. All the schemes proposed previously[2,25,26] have suggested an approximately constant for Me-for-H replacement increment. (with one exception, viz., that of Bell, Perkins and Perkins[26]). A truly constant increment is the equivalent to the law of bond additivity. [Bond additivity appears to work quite well with organosilicon compounds, especially where no polar groups are involved.[23,31]] Slight deviations arising from polarization or steric effects might be expected, but these are likely to be below the level of uncertainty in the increment value itself. If we assume bond additivity and pin the scheme on $\Delta H_f°$ for Si_2H_6 and Si_2Me_6, the value for Me-for-H replacement lies in the range -15.75 to -17.65 kcal mol^{-1}. The values corresponding to the extremes are shown in Table III. The average Me-for-H replacement enthalpy in the methylmonosilanes[23,31] is -16.0 ± 0.3 kcal mol^{-1}, close to the lower end for the methyldisilanes. Our preferred values are based on those required to fit the preferred value for $\Delta H_f(Si_2Me_6)$. It is clear, however, that the greater the extent of methyl substitution the more uncertainty there is.

If we take our preferred value for $\Delta H_f°(Si_2Me_5H)$ of -66.0 ± 2.5 kcal mol^{-1} together with the derived value for $\Delta H°_{2,-2}$ and $\Delta H_f°(Me_3SiH) = -39.1 \pm 1$ kcal mol^{-1},[23,31] this leads to $\Delta H_f°(SiMe_2) = 25.7 \pm 3.1$ kcal mol^{-1}. This estimate almost identical with that proposed previously[1] but supersedes it in the sense that it is now based on the most recent available data. It is clear that the difference with ORRL[2] is wholly dependent on the choice of $\Delta H_f°(Si_2Me_5H)$. They prefer a value of ca. -60 kcal mol^{-1} (i.e. at the lower limit of Table III) which yields 31.3 kcal mol^{-1} (their preferred value of 31.6 kcal mol^{-1} comes from average data from several decompositions rather than basing it all on reaction 2). It is thus clear that reliable thermochemistry of penta- or hexamethyldisilane will settle this question.

The Relative Stabilities of Silenes and Silylenes

In 1986 we attempted a best estimate calculation of $\Delta H°$ for

$$Me_2Si \rightleftarrows MeSiH{=}CH_2 \quad (4)$$

and obtained a value of 0 ± 6 kcal mol^{-1}, based on the assumption that the π-bond energy, $D_\pi(Si{=}C)$, in silenes was a transferable quantity (of magnitude 41 ± 5 kcal mol^{-1}). Clearly if $\Delta H°_{4,-4}$ can be estimated and $\Delta H_f°(MeSiH{=}CH_2)$ is known, this offers a route to obtaining $\Delta H_f°$ ($SiMe_2$). Unfortunately neither of these quantities appears to be established sufficiently well to provide a definitive value. It is known from chemical evidence that Me_2Si and $MeSiH{=}CH_2$ can interconvert in the gas phase if temperatures are sufficiently high,[39] and estimates have suggested a near zero enthalpy difference,[40] although uncertainties arise because of the necessity of estimating uncertain trapping rates for the silene species in these experiments. $\Delta H_f°(MeSiH{=}CH_2)$ is based on $\Delta H_f°(Me_2Si{=}CH_2)$ and has an uncertainty of ±5 kcal mol^{-1}, based on our analysis of the kinetics of decomposition of 1,1-dimethylsiletane.[38] Thus it appears that from experimental thermal studies (with neutral molecules) that no sufficiently reliable estimate of $\Delta H_f°(SiMe_2)$ can be obtained by using reaction 4.

However reaction 4 and the analogous process

$$MeSiH \rightleftarrows H_2Si{=}CH_2 \quad (5)$$

have become the subject of a controversy arising from recent ion-molecule studies[4] and theoretical calculations.[41] Some years ago Pau et al.[42] obtained an enthalpy difference between of Me_2Si and $MeSiD{=}CH_2$ by studies of deprotonation (or dedeuteronation) of Me_2SiD^+ by various bases, of ca. 28 kcal mol^{-1}. Since this value was well outside any uncertainties in $\Delta H°_{4,-4}$, we offered[38] an alternative interpretation of these experiments.

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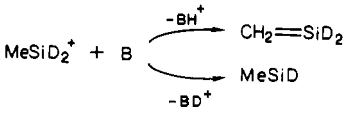
Table IV. Comparison of Incremental Methyl-for-Hydrogen Replacement Enthalpies (kcal mol^{-1}) in Methyl- and Methylchlorosilanes[a]

compd	$\Delta H_f°$	$\Delta\Delta H_f°$	compd	$\Delta H_f°$	$\Delta\Delta H_f°$
SiH_4	−8.2	−15.2	SiH_3Cl	−32.4	−17.8
SiH_3Me	−7.0	−15.6	SiH_2MeCl	−50.2	−17.2
SiH_2Me_2	−22.6	−16.5	$SiHMe_2Cl$	−67.4	−17.2
$SiHMe_3$	−39.1	−16.6	$SiMe_3Cl$	−84.6	
$SiMe_4$	−55.7		SiH_2Cl_2	−75.3	−18.6
$SiHCl_3$	−119.3	−16.7	$SiHMeCl_2$	−93.9	−17.5
$SiMeCl_3$	−136.0		$SiMe_2Cl_2$	−111.4	

[a] $\Delta H_f°$ data from ref 31.

A similar, although less extreme situation appears to have arisen in recent FTICR studies by Shin et al.[4] of the deprotonation and dedeuteronation reactions of $MeSiD_2^+$, viz.:



The measured threshold energy difference for D^+ transfer is 10 ± 3 kcal mol^{-1} higher than for H^+ transfer. In most of the reactions studied (eight different bases were used) there were at least four reaction channels with substantial yields of products suggesting pathways occurring via decomposition of an initial formed adduct ion ($MeSiD_2B^+$); e.g., for nitrogen bases there were always SiN-containing product ions. If the onset or threshold for thermoneutral D^+ transfer were slightly inhibited by fast competing adduct formation, then the MeSiD forming pathway might not become apparent until a more exothermic base was employed. Alternatively the BH^+ and BD^+ formation processes could occur via addition–elimination sequences through the intermediacy of the adduct ion as we previously suggested (although this explanation is probably inconsistent with the observed kinetics). Shin et al.[3] supported their measured energy difference for $CH_2{=}SiD_2$ and MeSiD by ab initio GVB calculations which gave ΔE(298K) = −11.6 kcal mol^{-1} for reaction 5. However, Grev et al.[41] have criticized this calculation and repeated it by using larger basis function sets and more extended electron correlation techniques. This results in $\Delta E_{5,-5}$(298K) = −3.6 kcal mol^{-1} consistent with their own earlier estimates. Although not conclusive this finding tends to support the idea that the appearance energies for silylenes in the base-induced H^+ or D^+ transfer processes from silyl cations are all overestimated to some extent. We thus regard the derived $\Delta H_f°$ values for SiH_2 (69 ± 3), SiHMe (53 ± 4) and $SiMe_2$ (37 ± 6) as all representing upper limits rather than actual values and therefore not inconsistent with the other proposed values discussed in the present work.

The Methyl-for-Hydrogen Enthalpy Increment

The frequent presumption of a constant Me-for-H replacement enthalpy in silicon compounds is worth investigating briefly since it has been used in arguments here concerning $\Delta H_f°$ for SiHMe and $SiMe_2$. Our preferred values, hardly changed from previously,[1] correspond to a Me-for-H replacement value of −20 kcal mol^{-1} in the divalent silylenes, substantially different from that in the tetravalent methylmonosilanes and for that implied by the isodesmic reaction calculations of Gordon.[3] We have recently reviewed the thermochemistry of organosilanes,[31] and a selection of data for appropriate comparisons is shown in Table IV. These show that individual values for the Me-for-H increment can vary between −15.2 and −18.6 kcal mol^{-1} among the various methylchlorosilanes. The average values for particular sequences are as follows: for the methylsilanes, −16.0 kcal mol^{-1}; for the monochloromethylsilanes, −17.4 kcal mol^{-1}; for the dichloromethylsilanes, −18.0 kcal mol^{-1}; for the trichloromethylsilanes, −16.7 kcal mol^{-1}. There are no other useful sequences of data for this analysis, but it is clear that there is some *variation in the Me-for-H increment amongst ordinary tetravalent silicon compounds.*

Table V. Comparison of Average Halogen-for-Hydrogen Replacement Enthalpies (kcal mol^{-1}) in Silicon Tetra- and Dihalides[a]

SiX_4	$\Delta H_f°$	$\Delta\Delta H$ X-for-H	SiX_2	$\Delta H_f°$	$\Delta\Delta H$ X-for-H
SiH_4	8.2		SiH_2	65.3[b]	
SiF_4	−386.0	−98.6	SiF_2	−141.0	−103.2
$SiCl_4$	−158.4	−41.7	$SiCl_2$	−40.3	−52.8
$SiBr_4$	−99.3	−26.9	$SiBr_2$	−11.0	−38.2
SiI_4	−26.4	−8.7	SiI_2	+22.0	−21.7

[a] $\Delta H_f°$ data from ref 43 unless otherwise indicated. [b] $\Delta H_f°$ data from ref 11.

Table VI. Divalent State Stabilization Energies (DSSE)[a] **and Substituent Electronegativities (UCP)**[b] **for Silylenes**

species SiX_2	DSSE, kcal mol^{-1}	UCP(X), Å^{-1}
SiH_2	19.4 ± 2.2	2.70
$SiMe_2$	28.4 ± 3.9[c]	5.19
SiF_2	49 ± 10	5.25
$SiCl_2$	38 ± 4	6.13
$SiBr_2$	34 ± 12	7.04
SiI_2	32 ± 13	9.92

[a] References 43 and 44. [b] Reference 45. [c] Derived from data in this work.

In order to address the question of whether more negative values are possible for the silylenes, a further set of comparisons is made in Table V. These show the average X-for-H replacement enthalpies for the silicon tetrahalides and dihalides. These reveal that for a given halogen, replacement of H is always *more negative for the dihalide* than for the tetrahalide. This demonstrates that silylene is more stabilized than silane by halogen substitution. The silicon halides are the only series for which data for this kind of comparison exists. Of course methyl groups may behave differently from halogens, but we have presented evidence previously[5,31] that on silicon a methyl group may act as a weakly *electronegative substituent.* It does not therefore appear unreasonable that the Me-for-H replacement enthalpy *in silylenes* could be −20 kcal mol^{-1}, although it must be admitted that this does not agree with Gordon's theoretical calculations.[3]

Divalent State Stabilization Energies

One further argument may be brought to bear on the question of $\Delta H_f°(SiMe_2)$; viz., does it give rise to a reasonable value for the divalent state stabilization energy (DSSE)? This has been defined previously as the difference between the first and second dissociation enthalpies in any SiX_4 molecule.[44] DSSE values for silylenes are collected in Table VI. Most of the values are as previously calculated but that for $SiMe_2$ is newly derived from the figures in this paper. The data in Table VI support the idea, previously pointed out of a correlation between substituent electronegativity and DSSE. Figure 1 shows a plot of DSSE against unshielded core potential (UCP) for each substituent X of the series of silylenes SiX_2. UCP has recently been proposed by Benson and Luo[45] as a

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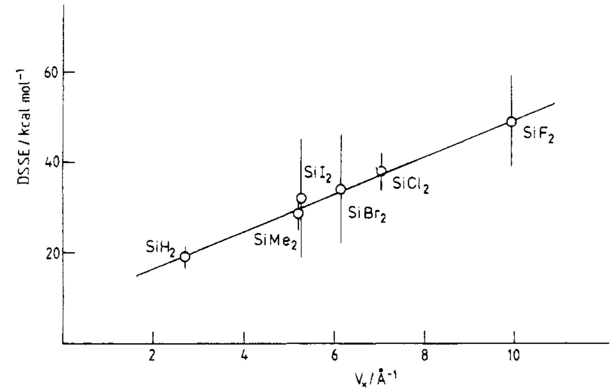

Figure 1. Plot of correlation between divalent state stabilization energies (DSSE) and substituent electronegativity (represented by unshielded core potential, V_x) for silylenes.

modern measure of electronegativity. Although there is some scatter in the data, there is clearly a reasonable correlation in which $SiMe_2$ fits reasonably close to the best fit line. If a value of $\Delta H_f°(SiMe_2) = 31.6$ kcal mol⁻¹ had been used, then the DSSE ($SiMe_2$) = 22.5 kcal mol⁻¹. The point for Me would then lie substantially away from the correlation line. It should be noted that if the more well-known Pauling electronegativities are used for this plot, this conclusion is not altered. [The electronegativity scale of Sanderson,[46] perhaps less well-known, does not support this correlation.] The existence of this correlation may be understood in terms of a *deshielding* effect.[44] The more electronegative the substituent, the more the bonding electrons are attracted further from the silicon nucleus, thus increasing the attraction of the nucleus for the (largely s-type) lone-pair electrons. Since carbon has a higher UCP than hydrogen, this means an increased stabilization energy for $SiMe_2$ compared with SiH_2.

Acknowledgment. I thank Mark Gordon, Ed O'Neal, and Morey Ring for valuable discussions.

Registry No. $Me_3SiSiMe_3$, 1450-14-2; Si_2H_6, 1590-87-0; $MeSiH_2SiH_3$, 13498-43-6; $Me_2SiHSiH_3$, 16342-86-2; $MeSiH_2SiH_2Me$, 870-26-8; Me_3SiSiH_3, 18365-32-7; $Me_2SiHSiH_2Me$, 814-74-4; Me_3SiSiH_2Me, 81633-92-3; $Me_2SiHSiHMe_2$, 814-98-2; $Me_3SiSiHMe_2$, 812-15-7; SiH_3Me, 992-94-9; SiH_2Me_2, 1111-74-6; $SiHMe_3$, 993-07-7; $SiMe_4$, 75-76-3; $SiMeCl_3$, 75-79-6; SiH_2MeCl, 993-00-0; $SiHMe_2Cl$, 1066-35-9; $SiMe_3Cl$, 75-77-4; $SiHMeCl_2$, 75-54-7; $SiMe_2Cl_2$, 75-78-5; SiF_4, 7783-61-1; $SiCl_4$, 10026-04-7; $SiBr_4$, 7789-66-4; SiI_4, 13465-84-4; SiF_2, 13966-66-0; $SiCl_2$, 13569-32-9; $SiBr_2$, 14877-32-8; SiI_2, 13465-83-3; $SiMe_2$, 6376-86-9; SiHMe, 55544-30-4.

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Predicted Heats of Formation for Methylsilylene and Dimethylsilylene

Mark S. Gordon* and Jerry A. Boatz

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

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Ab initio calculations at the MP2/6-31G(d,p) level of computation, combined with a sequence of isodesmic reactions, have been used to predict the heats of formation of methylsilylene and dimethylsilylene to be 49.2 and 32–33 kcal/mol, respectively. These results are discussed in the light of recent experimental determinations in the accompanying experimental papers.

Introduction

The prediction of heats of formation is one of the prime goals of both ab initio and semiempirical electronic structure theory. For small molecules, Pople and coworkers[1] and Binkley and Melius[2] have demonstrated how large basis sets and fourth-order perturbation theory can be used to predict heats of formation to within 2–3 kcal/mol. For larger molecules, Dewar, Stewart, and coworkers[3] have parametrized semiempirical methods to predict this property.

Disch et al.[4] have shown that, if the heats of formation of key reference compounds are known either from experiment or from accurate electronic structure theory calculations, then the (previously unknown) heats of formation for compounds of moderate size can be predicted with a modest level of theory. The proposed procedure is to utilize the energetics of some chemical reaction which has two important features: (1) the heats of formation for all species in the reaction, except the compound of interest, are known and (2) the reaction is designed in such a way that the difference in the correlation error (implicit in the calculation at the Hartree–Fock level) for the reaction is minimized. Two such reactions may be referred to as isodesmic and homodesmic. The former is a reaction in which each formal bond type is conserved. This may be illustrated with the reaction of *n*-butane with methane to form ethane and propane:

$$CH_3CH_2CH_2CH_3 + CH_4 \rightarrow CH_3CH_3 + CH_3CH_2CH_3 \quad (1)$$

Here, both reactants and products have three CC single bonds and 14 CH bonds. Since the correlation error should be roughly constant for a given bond type, one can expect

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