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Kinetic Determinations of the Heats of Formation of Methylated Disilanes and of Silylene, Methylsilylene, and Dimethylsilylene

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The thermal decomposition kinetics of disilane and a number of methylated disilanes have been analyzed with the aid of transition-state theory and their back-reaction rate constants to obtain heats of formation of the reactant disilanes and heats of formation of their product silylenes. On the basis of comparisons of the values so obtained with semiempirical and ab initio molecular orbital calculations and with existing literature values, recommendations for the heats of formation of the methylated disilanes and for silylene and the methylated silylenes are made (e.g., to an estimated accuracy of ±2 kcal/mol, heats of formation for Me_6Si_2, SiH_2, MeSiH, and Me_2Si are −78, 64, 48, and 32 kcal/mol, respectively).

Introduction

Kinetic studies of the thermal decompositions of disilanes[1-6] (e.g., reactions 1–3) have been important to heat of formation determinations of their product silylenes.

$$Si_2H_6 \xrightarrow{1} SiH_4 + SiH_2$$

$$MeSiH_2SiH_3 \xrightarrow{2} SiH_4 + MeSiH$$

$$Me_3SiSiHMe_2 \xrightarrow{3} Me_3SiH + Me_2Si$$

Thus assuming back reaction activation energies of zero, decomposition activation energies have been equated with reaction enthalpies at mean study temperatures (T_m), heat capacity corrected to the 298 K condition, and combined with the "known" heats of formation of the disilane reactants and silane products to obtain heats of formation for the product silylenes. In this way early kinetic data[1,3,5] yielded[7] values of about 59, 40, and 22 kcal/mol for the silylene, methylsilylene, and dimethylsilylene heats of formation, respectively. We now believe these values to be low by 5–10 kcal/mol.

There are several problems in the above analysis. First, identification of the observed kinetic parameters with those for the 1,2-H shift silylene elimination reactions may be incorrect. Most of the early kinetic studies were done without added silylene trapping agents, and it is now known that silylene-induced chain reactions can occur in these systems.[8] Second, back reactions may have nonzero activation energies. Absolute rate constant measurements for Si–H insertion reactions of SiH_2[9,10] and Me_2Si[11] (see Table I) have only recently been determined, and while the rate constants for the SiH_2 reactions suggest near zero activation energies, those for Me_2Si leave room for nonzero values. As yet, there are no absolute rate constant data for MeSiH reactions, nor are there data on the temperature dependencies of any silylene reaction. Third, heats of formation of the reactant disilanes are not really "known". Thus while heats of formation of methylated monosilanes are reasonably well established (to about ±1 kcal/mol by equilibrium disproportionation studies[12]), the only calorimetric data on disilanes is for hexamethyldisilane[13] and this is questionable (see later). Therefore heats of formation for methylated disilanes have either been calculated by additivity schemes,[14] or they have been estimated by assuming a linear change in heats of formation with increasing methylation between disilane (calorimetrically determined at 19.1 kcal/mol[15]) and hexamethyldisilane (kinetically determined at around −83 kcal/mol[7,13,15-18]).

Table I. Absolute Rate Constants (298 K) of Silylene Insertion Reactions

	k, M^{-1} s^{-1}			
substr	SiH_2[11]	Me_2Si[10]	MeSiH[a]	MeSiH[b]
SiH_4	6.6 ± 10^{10}	1.2×10^8	(2.8×10^9)	(6.3×10^9)
$MeSiH_3$	5.7×10^{10}	1.1×10^9	(7.9 ± 10^9)	(4.0 ± 10^{10})
Me_2SiH_2	5.5×10^{10}	3.3×10^9	(1.3×10^{10})	(3.7×10^{10})
Me_3SiH	3.1×10^{10}	2.7×10^9	(9.1×10^9)	

[a] Estimated as the mean of the SiH_2 and Me_2Si rate constants. [b] Derived from the kinetics (see text).

Walsh has argued that reported Arrhenius parameters for most methylated disilane decompositions are too low to be identified with their direct silylene elimination reactions.[19] He supported this conclusion with thermo-

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(15) $\Delta H°(Si_2H_6)$ = 19.1 kcal/mol[13] and $\Delta H_f°(SiH_4)$ = 8.2 kcal/mol,[17] determined calorimetrically by Gunn and Green,[17] are recognized standards for the silicon hydrides. $\Delta H_f°(Me_6Si_2)$ has been determined from the thermal decomposition kinetics of hexamethyldisilane (E_a = 80.5 ± 1 kcal[16]) and the iodination kinetics of trimethylsilane which yields $\Delta H_f°(Me_3Si^\bullet)$ = −0.8 ± 2.0 kcal/mol.[18] Note the considerable error in the latter's $\Delta H_f°$.

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Table II. Kinetic Data Analysis for the Determinations of the Heats of Formation of Methylated Disilanes and Silylenes

	exptl		at 298 K					
reactant (A)	log A_d	E_d	$-\log k_d$	$-\log K_{eq}$	$\Delta S°$	$\Delta H°$	$\Delta H_f°$ (Si:–A)	Δ
			(A) Silylene Eliminations (SiH_2=Si:)					
Si_2H_6[2]	15.75	52.20	22.14	31.57	32.6	52.8	44.6	
$MeSiH_2SiH_3$[3]	15.28	50.75[a]	21.62	30.99	31.6	51.7	58.7	14.1
$Me_2SiHSiH_3$[21]	15.50	50.99	21.56	30.89	33.3	52.0	74.7	16.0
Me_3SiSiH_3[20]	15.11	49.40	20.82	29.92	36.3	51.6	90.6	15.9
			(B) Dimethylsilylene Eliminations (Me_2Si:=Si:)					
$Me_2SiHSiH_3$[21]	13.12	51.79	24.91	31.60	32.6	52.8	44.6	
$Me_2SiHSiH_2Me$[20]	13.11	49.42	23.18	30.84	32.2	51.6	58.5	13.9
$Me_2SiHSiHMe_2$[21]	13.17	48.17	22.20	30.33	35.2	51.8	74.5	16.0
$Me_3SiSiHMe_2$[6]	13.30	48.40	22.22	30.26	36.3	52.1	91.2	16.0 (17.5)
			(C) Methylsilylene Eliminations (MeSiH=Si:)					
$MeSiH_2SiH_3$[3]	14.14	49.89[b]	22.36	(30.77)	33.4	(51.8)	(43.7)	
$MeSiH_2SiH_2Me$[6]	14.30	47.90	20.64	(29.85)	33.9	(50.8)	(57.7)	14.0[e]
$Me_2SiHSiH_2Me$[20]	14.26	47.82	20.64	(29.82)	34.7	(51.0)	(73.7)	16.0[e]
Me_3SiSiH_2Me		no data		(29.25)	37.0	(51.0)	(90.0)	16.3[e]

[a] Arrhenius parameters for the major pathway of the neat, uninhibited decomposition. Probably reliable, but need confirmation. [b] Arrhenius parameters for the minor, uninhibited decomposition. Need to be redetermined under silylene chain; inhibition may be low. [c] $\Delta H_f°$ (Si:–A) is the heat of formation difference between the product silylene and the reactant disilane. [d] Δ is the incremental difference in successive reactant disilane heats of formation eliminating the same silylene. [e] Increments assigned on the basis of the average Me_2Si and SiH_2 series increments.

chemical estimates of minimum and preferred *A* factors for silylene eliminations using eq I, where $\Delta S°$ is the de-

$$\ln A_{\mathrm{dec},T_m} = \ln A_b\ (\mathrm{M^{-1}\ s^{-1}}) + \Delta S°/R - \ln(eR'T_m) \qquad \text{(I)}$$

composition reaction entropy at the mean decomposition temperature (T_m), $R' = 0.082$ L/(mol deg), and A_b is the back-reaction *A* factor in the units shown.

Minimum *A* factors were obtained by equating *A* factors for the reverse reactions at T_m to their measured absoluted rate constants at room temperature. Preferred *A* factors were obtained by assuming similar and "loose" transition states for all silylene Si–H insertions with *A* factors on a per H basis of 10^{10} M^{-1} s^{-1}. The product silylene heats of formation following from the preferred *A* factor analysis were as follows: SiH_2, 65; MeSiH, 44; and Me_2Si, 26 (in kcal/mol).[19] The Walsh analysis is reasonable and intuitively appealing; however, it is not supported by recent kinetic data on methylated disilane decompositions under maximum inhibition conditions.[6,20,21] Thus preferred *A* factors for Me_2Si elimination reactions were in the $10^{15\pm0.3}$ s^{-1} range, and minimum *A* factors ranged from $10^{12.5}$ s^{-1} (for $Me_2SiHSiH_3$) to $10^{14.8}$ s^{-1} (for Me_5Si_2H). By contrast, the highest experimental value (i.e., $10^{13.3}$ s^{-1} for Me_5Si_2H; see Table II) is 30 times lower than the calculated *A* factor minimum.

If the latest experimental rate parameters of the inhibited reactions are indeed those of the silylene eliminations, the assumption of similar and loose transition states for all silylene eliminations is in error. Instead, transition-state tightening with increasing alkylation of the eliminated silylene is indicated. Davidson[6] was first to note that *A* factors for SiH_2, MeSiH, and Me_2Si eliminations seem to fall in the respective ranges $10^{15.5\pm0.3}$, $10^{14\pm0.3}$, and $10^{12.8\pm0.2}$ s^{-1}, and our subsequent studies tend to confirm these ranges.[2,20,21] While Walsh's analysis relative to the preferred disilane decomposition Arrhenius parameters (and therefore also his suggested silylene heats of formation following from those preferred parameters) appears to be incorrect, his $A_{\min}$ calculations still indicate serious correlation problems between the disilane experimental decomposition kinetics and the decomposition reaction thermochemistries. In addition, before reliable silylene heats of formation can be determined by kinetic analysis, accurate heats of formation of the reactant disilanes must be available. This paper addresses these problems (i.e., the apparent inconsistencies of the kinetics and thermodynamics of the disilane decompositions and the accuracies of the heats of formation of the reactant methylated disilanes).

Results and Discussion

Kinetic Data Analysis Yielding Disilane and Silylene Heats of Formation. We believe that the disilane decomposition rate data obtained under conditions of maximum inhibition of silylene chains are valid measures of the silylene elimination kinetics. To obtain silylene heat of formation estimates from these data, we have varied the usual kinetic analysis in a manner that should reduce errors. Thus the disilane decomposition kinetics are extrapolated to the 298 K condition by using transition-state theory relationships (eq II and III)[22] and by assigning

$$A_T = \mathrm{rpd}(ekt/h)e^{\Delta S^{\ddagger}/RT} \qquad \text{(II)}$$

$$E_{a,T} = \Delta E^{0\ddagger} + \Delta(H_T - H_0)^{\ddagger} + RT \qquad \text{(III)}$$

vibrational frequencies to the reactants and transition states that are consistent with the experimental $\Delta S_{T_m}{}^{\ddagger}$. The $\Delta E^{0\ddagger}$ values (from III) and room-temperature rate constants (k_d, s^{-1}) are then calculated. These rate constants are combined with the experimental back-reaction rate constants (k_b, atm^{-1} s^{-1}) to give equilibrium constants (K_{eq}, atm), which in turn (with reaction entropies) give reaction enthalpies (all values at 298 K). Product monosilane and reactant disilane heats of formation, provided they are "known", then give heats of formation of the product silylenes.

There are several advantages to treating the kinetic data this way. First, with use of room-temperature equilibrium constants to establish reaction enthalpies, errors in those enthalpies are significantly reduced. Thus a 2.5 kcal "error" in the activation energy of the Si_2H_6 decomposition,

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Table III. Kinetically Derived and MM2, AM1, and EECBA Calculated Heats of Formation of the Methylated Silanes and Disilanes

	calculated heats of formation ($\Delta H_f°$), kcal/mol					
compound	MM2[a,h]	AM1[b]	EECBA	EECBA[c]	BA[e]	kinetics
MeSiH$_3$[f]	−6.65	−5.58	−6.96	−7.95	−7.8	
Me$_2$SiH$_2$[f]	−22.95	−22.82	−22.68	−23.98	−23.7	
Me$_3$SiH[f]	−39.26	−39.54	−38.93	−39.92	−39.8	
Me$_4$Si[f,d]	−55.74	−55.74	−55.74	−55.74	−55.74	
Si$_2$H$_6$	19.1[d]	20.68	19.1	19.1[d]	19.1	19.1
MeSiH$_2$SiH$_3$[d]	3.37	3.37	4.71	2.76	3.2	5.0
Me$_2$SiHSiH$_3$	−12.57	−13.44	−10.22	−13.46	−12.8	−11.0
MeSiH$_2$SiH$_2$Me	−11.67	−13.86	−9.68	−13.54	−12.8	(−9.0)[g]
Me$_3$SiSiH$_3$	−28.99	−29.70	−25.69	−29.57	−28.8	−26.9
Me$_2$SiHSiH$_2$Me	−29.33	−30.62	−24.57	−29.71	−28.8	−24.9 (−25.0)[g]
Me$_3$SiSiH$_2$Me	−44.83	−46.69	−40.02	−45.73	−44.7	−41.3[g]
Me$_2$SiHSiHMe$_2$	−44.66	−47.33	−40.24	−45.83	−44.7	−40.9
Me$_3$SiSiHMe$_2$	−62.20	−63.32	−54.91	−61.87	−60.8	−57.5
Me$_3$SiSiMe$_3$	−78.45	−79.60	−70.40	−77.86	−76.7	−75.0

[a] After Si–C and Si–Si bond energy term adjustments (see text). Pop and Torr corrections are included. [b] After scaling the directly calculated monosilane and disilane values by constant amounts to fit Me$_4$Si and MeSiH$_2$SiH$_3$ (see text). [c] Lower minimum values according to the EECBA method (see text). [d] Reference compounds (see text). [e] Simple bond additivity based on SiH$_4$, Si$_2$H$_6$, and Me$_4$Si assuming heats of formation of 8.2, 19.1, and −55.74 kcal/mol, respectively. [f] Determined by equilibrium studies[12] to be MeSiH$_3$, −6.9, Me$_2$SiH$_2$, −22.7, and Me$_3$SiH, −39.0 (all values to ±1 kcal/mol). [g] From MeSiH elimination kinetics (see text for assumptions made). [h] Preferred heats of formation.

for example, was found to produce an extrapolation "error" in the derived room-temperature rate constant of about a factor of 10; this corresponds to an error of only 1.4 kcal in the resulting 298 K reaction enthalpy. Also, errors of the former analysis methods, e.g., errors arising from uncertainties in back-reaction rate constant temperature variations and errors in heat capacity extrapolations of reaction enthalpies from T_m to 298 K, are completely avoided. Further, we have found that the rate constant extrapolations are moderately insensitive to choices of reaction path degeneracies (rpd) and of transition state and reactant frequencies as long as these choices are consistent with the experimental *A* factor at T_m. Thus changing the disilane decomposition rpd from 6 to 18 produced less than a 1% change in rate constant extrapolation, and even a totally unrealistic change in rpd and frequencies for the 1,1-dimethyldisilane system (as judged by the corresponding changes in the $\Delta(H_T - H_0)^{\ddagger}$ values from −0.84 to −3.4 kcal) resulted in a factor of 2.8 difference in the calculated room-temperature rate constants. Even this latter unrealistic extrapolation "error" produces only a 0.6 kcal error in the room-temperature reaction enthalpy. All factors considered, then, the above kinetic analysis should provide reasonably good estimates of room-temperature decomposition reaction enthalpies (i.e., we believe errors are less than ±1 kcal).

Results of our kinetic data analysis are summarized in Table II. Reactions producing SiH$_2$ and Me$_2$Si were analyzed as described above; MeSiH eliminations, however, because their back-reaction rate constants have not been determined, were analyzed differently (see later). The Table II results for the MeSiH eliminations are therefore less reliable and have been placed in parentheses to indicate this fact.

One of the most interesting results of our analysis is the near constancy of the 298 K reaction enthalpies: averages of the SiH$_2$, Me$_2$Si, and MeSiH eliminations are respectively 52.0 ± 0.4, 52.1 ± 0.4, and 51.2 ± 0.4 kcal. This can be compared to the 4.4 kcal spread in elimination reaction activation energies. Silylene heats of formation can be obtained from the Table II, column 8, terms (which show heat of formation differences between the product silylenes and their reactant disilanes) if the reactant disilane heat of formations are available. Reactant disilane heats of formation can be generated relative to disilane ($\Delta H_f°$(Si$_2$H$_6$) = 19.1 kcal/mol as reference) by way of column 8 differences shown in column 9. Column 9 differences (or increments) between successive members of each series measure heat of formation Me for H replacement effects; they appear to increase with increasing degrees of methylation. For example, increments between the first and second members of the Me$_2$Si and SiH$_2$ elimination series are about 14 kcal/mol while increments between the last (more methylated) members of these series average 16.3 kcal/mol. Extrapolation of the Me and H replacement effect suggests an increment of about 17.5 ± 0.5 kcal/mol between hexamethyl- and pentamethyldisilane. As mentioned above, the column 9 increments can be used to generate heats of formation of the reactant disilanes relative to disilane. The values obtained relative to the SiH$_2$ and Me$_2$Si elimination reactions (i.e., the only reactions for which complete kinetic data are available) are shown in the last column of Table III. Product silylene heats of formation obtained from these heats of formation and the Table II, column 8, terms give $\Delta H_f°$(SiH$_2$) = 63.7 kcal/mol and $\Delta H_f°$(Me$_2$Si) = 33.7 kcal/mol.

The MeSiH elimination reactions were analyzed by assuming a methylsilylene heat of formation equal to the silylene and dimethylsilylene mean: $\Delta H_f°$(MeSiH) = 48.7 kcal/mol. This value with the previously determined methyldisilane heat of formation and the assigned column 9 increments (14.0, 16.0, 16.3) were used to calculate terms of Table IIC in parentheses. That the resulting heats of formation [MeSiH$_2$SiH$_2$Me (−9.0 kcal/mol), Me$_2$SiHSiH$_2$Me (−25.0 kcal/mol), and Me$_3$SiSiH$_2$Me (−41.3 kcal/mol)] agree rather well with previously determined or expected values attests to the internal consistency of the kinetic data and analysis method. According to all calculations (see Table III) methylated disilanes of similar degrees of methylation have very similar enthalpies of formation.

The MeSiH terms of Table IIC in parentheses can be further tested. When the equilibrium constants (Table II, column 5) are combined with the corresponding elimination reaction rate constants (column 4), back-reaction Si–H insertion rate constants can be calculated. The values obtained (column 5, Table I) when compared to those estimated as the geometric means of the corresponding rate constants for SiH$_2$ and Me$_2$Si insertion (column 4, Table I) agree within a factor of 3 for MeSiH insertions into SiH$_4$ and Me$_2$SiH$_2$ and within a factor of 7 for MeSiH insertion into MeSiH$_3$. Even the latter difference can be considered to be a good agreement with the expected mean value since it corresponds to an "error" of less than 1 kcal in the reaction enthalpy. One can conclude, therefore, that there are no *major* discrepancies within the experimental errors between the Table I and II kinetics and thermochemistries of the disilane decomposition reactions at room temperature (including values deduced for the MeSiH elimination reactions).

Calculated Heats of Formation of the Methylated Disilanes. While the elimination and insertion kinetic data and the kinetically obtained silylene and disilane heats of formation are internally consistent, the question of their accuracy and reliability still remains. To assess the latter, we have calculated heats of formation of the methylated silanes and disilanes by four methods: simple bond additivity, Stewart and Dewar's (MOPAC/AM1),[23] Allinger's (MM2),[24] and Benson's (EECBA).[25] The results are shown in Table III. The column 2 MM2 results were obtained with Allinger's 1987 suggested parameters[26] after adjusting the (Si–Me) and (Si–Si) bond energy terms from –5.230 and 6.600 to –4.848 and 7.880 kcal/mol, respectively, in order to fit the most recent heats of formation for tetramethylsilane and disilane. The column 3 MOPAC/AM1 heats of formation were obtained after scaling all the directly calculated monosilane and disilane values to fit the Me_4Si and $MeSiH_2SiH_3$ heats of formation (i.e., $\Delta H_f°$(monosilanes) = $\Delta H_f°$(calc) – 11.25 kcal/mol; $\Delta H_f°$(disilanes) = $\Delta H_f°$(calc) – 18.96 kcal/mol). Column 4 EECBA heats of formation were obtained from eq IV by using the

$$\Delta H_f° = \sum m_i \Delta H_f°(i,\text{bond}) + \sum\sum q_i q_j / r_{ij} \qquad \text{(IV)}$$

Benson C–H bond parameters (BE(C–H) = –1.1300 kcal/mol, $(x) = 0.2800 \times 10^{-10}$ esu) and the bond additivity and polarization parameters derived from the heats of formation (kcal/mol in parentheses) of SiH_4 (8.2), Si_2H_6 (19.1), Si_3H_8 (28.9), $MeSiH_3$ (–6.96), and Me_4Si (–55.74), namely, BA(Si–H) = 4.012, BA(Si–Si) = 3.663, and BA(Si–C) = 8.21 kcal/mol ($w = 0.2554 \times 10^{-10}$ and $z = 0.4406 \times 10^{-10}$ esu). Differences between these EECBA heats of formation and the MM2 and scaled AM1 heats of formation vary from an acceptable 2 kcal/mol for disilanes of lower degrees of methylation to an unacceptable 8 kcal/mol for hexamethyldisilane.[27] The (C–Si) and z terms of the EECBA calculations are fixed by the heats of formation assigned to the reference compounds $MeSiH_3$ and Me_4Si. The errors in these assigned values are given[12] at ±1.0 and ±0.8 kcal/mol, respectively. If the lower limit for $MeSiH_3$ is used (i.e., –7.96 kcal/mol), one obtains (C–Si) and z parameters (i.e., 0.558 kcal/mol and 0.1917×10^{-10} esu) which yield lower limiting values to the mono- and disilane heats of formation. (It is interesting to note that this same lower limit is imposed by the mathematics since z becomes an irrational number for heats of formation of $MeSiH_3$ lower than –8 kcal/mol.) Heats of formation obtained by the revised (C–Si) and z values (see column 5, Table III) are *much* lower for the more methylated disilanes (e.g., the EECBA adjusted heat of formation for hexamethyldisilane is within 0.6 kcal/mol of the MM2 value and lower than the original EECBA value by 7.5 kcal/mol). Obviously one cannot place much confidence in calculated EECBA values if a 1 kcal/mol variation in the heat of formation of a reference compound produces this kind of change in higher methylated disilane heats of formation. On the other hand, with a firm value for the heat of formation of hexamethyldisilane, the EECBA method of calculating organosilane heats of formation could prove to be quite reliable since this heat of formation would fix with reasonable accuracy the critical (C–Si) and z parameters.

The heats of formation of column 6, Table III, are particularly interesting in that they represent the results of simple bond additivity. Thus from SiH_4, Si_2H_6, and Me_4Si ($\Delta H_f°$ values given previously) one obtains Si–H, Si–Si, and C–Si bond additivities of 2.05, 6.90, and –2.39 kcal/mol, respectively. The heats of formation obtained from these bond additivities agree surprisingly well with the MM2 and adjusted AM1 and EECBA calculations. This makes a very strong case for using this simple method for making heat of formation estimates of organosilicon compounds (as opposed to the other more elaborate, and perhaps equally questionable, estimation methods of this paper). However, if one of the Table II sets of values is to be selected as the most reliable, we favor the MM2 set and suggest that errors of this set are probably less than ±3 kcal/mol. Unfortunately, the kinetically determined disilane heats of formation for the more highly methylated disilanes lie slightly outside this range. Since most errors in the kinetic estimates act to make the estimated values more positive and these errors are cumulative (e.g., an error in the methyldisilane heat of formation will be carried along to all higher methylated disilanes), 3–4 kcal/mol errors in the kinetic values of the more highly methylated disilane heats of formation would not be surprising. However, considering the internal consistency of the kinetic data, we believe that errors much higher than this are unlikely.

Comparisons with Literature Values and Assignments of Preferred Silylene Heats of Formation. The kinetics of the thermal decomposition of hexamethyldisilane[13] (HMDS $\xrightarrow{k_d}$ $2Me_3Si^\bullet$, with $k_d = 10^{17.2\pm0.3}e^{-80.6\pm1.0\text{kcal}/RT}$ s^{-1}) can be analyzed by the same method employed here for the other disilane decompositions. Extrapolation from T_m = 820 K to room temperature gives $k_d = 9.1 \times 10^{-42}$ s^{-1}, and with the reaction entropy ($\Delta S°$ = 44.4 eu)[25] and latest measurement of the back-reaction rate constant ($k_b = 7.53 \times 10^9$ M^{-1} s^{-1}),[28] one obtains the room-temperature values $K_{eq} = 3.0 \times 10^{-50}$ atm and $\Delta H°$ = 80.8 ± 1.1 kcal. With Walsh's heat of formation for trimethylsilyl ($\Delta H_f°$) = –0.8 ± 2.0 kcal/mol),[18] one obtains $\Delta H_f°$(HMDS) = –82.4 ± 5.1 kcal/mol. This value is clearly much lower than the kinetic value of –75 kcal/mol, but it is just barely within the combined errors of the estimates. A crude error estimate of about ±3 kcal/mol in the kinetic value follows from a ±1 kcal systematic error in the rate constant extrapolations and a ±2 kcal collective error in the activation energies of the four (minimum number) kinetic systems required to fix the thermochemistries of SiH_2, Me_2Si and their reactant disilanes. The lower HMDS heat of formation is supported by calorimetric measurements: –85.8 kcal/mol[13] and more recently

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(27) The EECBA calculations show a methyl destabilization trend which is not reflected in the AM1 and MM2 calculations. There may be a plausible reason for this. In the EECBA method, the C–H bond additivity and charge polarization parameters are derived from fitting hydrocarbon heat of formation data where methyl–methyl steric interactions are always repulsive. In organosilanes, according to MM2 steric strain calculations, these same van der Waal's interactions can be attractive as well as repulsive depending on the methyl–methyl separation distance. Thus the EECBA method may underestimate the stability of more highly methylated disilanes.

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Table IV. Silylene heat of Formation Results[a]

SiH$_2$ Results

ΔH_f°, kcal/mol	system/method	level of calculatn	ref
68.4, 68.7	ab initio (corrected)	MP4/6-31G**	31
63.4, 67.9	semiempirical	MNDO, SCF-MO(AM1)	32, 33

ΔH_f°, kcal/mol	reactn	ΔH_{rxn}° (calc)	level of calculatn	ref
65.1[c]	$SiH_4 \rightleftharpoons SiH_3 + H$	91.6	GVB/CI	34
	$SiH_3 \rightleftharpoons SiH_2 + H$	69.5	GVB/CI	
63.4[c]	$CH_3SiH_3 \rightleftharpoons SiH_2 + CH_4$	52.2	MP4/6-311G(d,p)	35
65.4[c]	$SiH_4 \rightleftharpoons SiH_2 + H_2$	57.3	MP4/6-311G(d,p)	36
63.3[c]	$Si_2H_6 \rightleftharpoons SiH_2 + SiH_4$	52.4	MP4/6-311G(d,p)	37
69 ± 3	ion cyclotron resonance			38
65.6	ion cyclotron resonance			39
65.4 ± 1.6	laser-induced dissociation of SiH$_2$			41
63.7	disilane decomposition kinetics			this paper
64 ± 2	disilane decomposition kinetics			compromise

ΔH_f°, kcal/mol	reaction	ΔH_{rxn}° (calc)	level of calculatn	ref
		MeSiH Results		
48.3[c]	$CH_3SiH_3 \rightleftharpoons CH_3SiH + H_2$	55.0	MP4/6-311G(d,p)	35
53 ± 4	ion cyclotron resonance			40
48.7	disilane decomposition kinetics			this paper
48 ± 2	disilane decomposition kinetics			compromise
		Me$_2$Si Results		
37 ± 6	ion cyclotron resonance			40
33.7	disilane decomposition kinetics			this paper
32 ± 2	disilane decomposition kinetics			compromise

Silylene Differences[b,c]

	isodesmic reactn	ΔH_{rxn}°
$\Delta\Delta H^\circ$ (SiH$_2$, MeSiH) = 16.0	$MeSiH + SiH_4 \rightleftharpoons SiH_2 + MeSiH$	0.9
$\Delta\Delta H^\circ$ (Me$_2$Si, MeSiH) = 17.0	$Me_2Si + MeSiH_3 \rightleftharpoons Me_2SiH_2 + MeSiH$	0.7
$\Delta\Delta H^\circ$ (Me$_2$Si, MeSiH) = 16.3	$Me_2Si + SiH_4 \rightleftharpoons MeSiH_3 + MeSiH$	1.4
$\Delta\Delta H^\circ$ (SiH$_2$, Me$_2$Si) = 32.6	$Me_2Si + SiH_4 \rightleftharpoons SiH_2 + Me_2SiH_2$	1.4

[a] All values (heats of formation, reaction enthalpies, enthalpy differences, etc.) are in kcal at 298 K. [b] See accompanying paper of Gordon et al. [c] Silylene heats of formation and heat of formation differences were calculated by us from the reported reaction enthalpies assuming our preferred silane, disilane, and methylated monosilane heats of formation (i.e., MM2 values of Table III).

−82.9 ± 2.2 kcal/mol,[29] both from combustion in auxilary fluoride.

With regard to silylene heats of formation, there are values reported in the literature from a variety of sources: calculations by different methods at different levels of reliability[30-37] and experimental values obtained from kinetic, ion cyclotron resonance (ICR) measurements,[38-40] and photolysis.[41] Table IV contains a partial summary of these values. It is evident that both the range and errors of the tabulated values are too large to fix the formation enthalpies of the silylenes to the ±2 kcal/mol kinetically and thermodynamically desirable level. However, the Table IV values do tend to bracket the kinetic values of this work.

Conclusions

The situation regarding the heats of formation for the methylated disilanes and their product silylenes, therefore, remains unresolved. The more negative disilane heats of formation, suggested by the HMDS kinetics and the calorimetric measurements, are consistent (through the Table II reaction enthalpies) with silylene heats of formation which seem much too low when compared to the Table IV numbers, particularly the isodesmic enthalpies (e.g., a pentamethyldisilane heat of formation of about −68 kcal/mol, obtained by interpolation between disilane (19 kcal/mol) and hexamethyldisilane (−86 kcal/mol), gives $\Delta H_f^\circ(Me_2Si) \approx 23$ kcal/mol). By contrast, the kinetically derived, more positive disilane heats of formation of this work are consistent with significantly higher silylene heats of formation (i.e., up to 10 kcal/mol higher; see Table IV), and they are in good agreement with the calculated values. ICR results for the silylenes, however, support even higher values. At this time it seems necessary to adopt compromise values for both heats of formation of the reactant disilanes and their product silylenes. As indicated previously, we favor the MM2 values of Table III for the former. For the silylene heats of formation, we favor $\Delta H_f^\circ(SiH_2) = 64 \pm 2$ kcal/mol, $\Delta H_f^\circ(MeSiH) = 48 \pm 2$ kcal/mol, and $\Delta H_f^\circ(Me_2Si) = 32 \pm 2$ kcal/mol. These heats of formation are within the errors of the ICR values, they are in good agreement with the calculated and isodesmic enthalpies of Gordon (see Table IV and accompanying paper),[30] and they agree well with the kinetically determined reaction enthalpies of Table II.

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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

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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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