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gram for a metal/η^2-CS_2 interaction,[12] the electron is expected to be transferred to a $\pi_{\perp}^*$ antibonding MO of CS_2, centered mainly on the carbon atom, as indicated in structure G. This orbital energy is slightly lower in cation **2** than in its precursor Fe(η^2-CS_2) derivative. (ii) The second step may be related to the elimination of one PPh_3 group from G and the formation of the unsaturated species H. Indeed, we have shown[27] that although the Ph_3P groups are strongly bonded to iron in cation **2**, these groups are immediately displaced by PMe_3 groups on electrocatalytic reduction to afford complex **2f**. Under conditions corresponding to that of **2** → **3** but in the presence of PMe_3 the dimerization into **3** was not observed. Instead substitution of PPh_3 groups occurs. (iii) The electronic unsaturation at the iron center in species H may promote the homolytic cleavage of the Fe–C(SR) bond to give species I.[28] (iv) The nature of I would then explain its dimerization into J. (v) The intermediate J would become **3** by coordination of each sulfur atom to the second metal center, allowing the iron atoms to reach their 18-electron configuration.

Conclusion

The above results show an example of the striking influence of ancillary ligands on the reactivity of a metal–substrate moiety. The reaction of $Fe(\eta^2\text{-}CS_2R)(CO)_2(L)_2^+$ cations **2** (L = PPh_3 or $P(OMe)_3$), with either borohydride or sodium amalgam, shows that the nature of the reaction products depends not only on the electron donor capability of L but also on the Fe–L lability and the reduction potential of the cation. The latter is related to both steric and electronic effects of L. Our study of cations **2** shows that the influence of L = PPh_3 is to favor monoelectronic processes, and this leads to reactions different from those with L = PMe_3. By contrast, L = $P(OMe)_3$ shows, as indicated by its reduction potential and not by its electronic effect, a behavior that is in between that of L = PPh_3 and that of L = PMe_3. It is thus shown that the nature of L in cations **2** determines the behavior of the $Fe(\eta^2\text{-}CS_2R)^+$ moiety.

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Registry No. 1, 64424-68-6; **2a** (X = I), 72598-18-6; **2a** (X = PF_6), 71004-19-8; **2b**, 111002-63-2; **2c**, 110904-33-1; **2d**, 110904-35-3; **2e**, 110904-37-5; **2h**, 71004-17-6; **3a**, 97390-97-1; **3b**, 110904-38-6; **3c**, 110904-39-7; **3d**, 110904-40-0; **3e**, 110904-41-1; **4a**, 97390-96-0; **4b**, 110904-42-2; **4c**, 110904-43-3; **4d**, 110904-44-4; **4e**, 110904-45-5; **5**, 110904-48-8; **6**, 110904-46-6; **7**, 110904-49-9; **8**, 110904-47-7; **9**, 97403-35-5; $Fe(\eta^2\text{-}CS_2)(CO)_2(P(OMe)_3)_2$, 64424-66-4; pulegone, 89-82-7; benzylideneacetone, 122-57-6; dimethyl acetylenedicarboxylate, 762-42-5.

Supplementary Material Available: Anisotropic thermal parameters for the structure of **3a** (Table S3) and **4a** (Table S4) (3 pages); listings of observed and calculated structure factor amplitudes (Tables S1 and S2) (19 pages). Ordering information is given on any current masthead page.

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[27] Fillaut, J. L.; Touchard, D.; Dixneuf, P., unpublished results.

[28] Homolysis of the M–C bond in Rh(η^2-CS_2) complexes has already been shown and rationalized[12] on account of an intended but avoided crossing of two levels centered on the metal and carbon atoms, respectively. In that case the conditions were the proper ones for the formation of a diradical species. In the case of the species H the M–C dissociation pathway is complicated by the fact that the carbon is taken as having already a radical character.

Kinetics of Alkyldisilane Pyrolyses and Heats of Formation of Methylsilylenes

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It is shown that Arrhenius parameters for various methylated disilane decomposition reactions are not consistent with recent time-resolved rate measurements for SiH_2 and $SiMe_2$. Possible reasons for this are discussed, and existing data are reassessed to provide heats of formation of 26 (± 2) and 44 (± 3) kcal mol^{-1} for $SiMe_2$ and SiHMe, respectively.

Introduction

Silylenes, SiH_nMe_{2-n} (n = 0, 1, or 2) are implicated as intermediates in many high-temperature organosilane reactions.[1] Mechanistic understanding of such reaction systems has reached the point where analytical and kinetic data are routinely fitted with kinetic modeling schemes.[2,3] Much information on the behavior of silylenes has come from studies of the thermal decompositions of the methyldisilanes

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

where x = 0–6, y = 0–2, and z = x–y. For example, a knowledge of the activation energy E_1 for such a process, combined with the reverse activation energy E_{-1}, leads to $\Delta H_{1,-1}$. The heat of formation of the silylene, $\Delta H_f°(SiH_yMe_{2-y})$, can then be obtained provided the heats of formation of the silane SiH_zMe_{4-z} and disilane $Si_2H_xMe_{6-x}$ are known.

Several gas-phase kinetic studies of methyldisilanes have been carried out,[4-7] and activation energies obtained. Until

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[1] Gaspar, P. P. *Reactive Intermediates* (*Wiley*) **1978**, *1*, 229; **1981**, *2*, 335; **1985**, *3*, 333.

[2] See for example: Davidson, I. M. T.; Hughes, K. J.; Scampton, R. J. *J. Organomet. Chem.* **1984**, *272*, 11.

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Table I. Absolute Rate Constants[a] for Some Silylene Insertion Reactions (298 K)

	Silylene	
substrate	SiH_2	$SiMe_2$[e]
SiH_4	6.6×10^{10}[b,f]	1.2×10^{8}
$MeSiH_3$	5.7×10^{10}[c]	1.1×10^{9}
Me_2SiH_2	5.5×10^{10}[c]	3.3×10^{9}
Me_3SiH	3.1×10^{10}[d,f]	2.7×10^{9}

[a] Units: $dm^3\ mol^{-1}\ s^{-1}$ ($M^{-1}\ s^{-1}$). [b] Reference 8. [c] Reference 14. [d] Reference 15. [e] Reference 10. [f] Recent work suggests even higher values (SiH_4, ref 28, Me_3SiH, ref 29).

recently no absolute rate data were available for the reverse silylene insertion reactions and so this information could not be properly exploited. However, in the last 2 years time-resolved kinetic studies of reactions of SiH_2 by Inoue and Suzuki[8] and also Jasinski[9] and of $SiMe_2$ by ourselves[10] have been carried out. One of the implications of the new data on SiH_2 has been an upward revision of $\Delta H_f°(SiH_2)$ to 65.3 ± 1.5 kcal mol^{-1}.[11] Another was that the earlier published activation energy for Si_2H_6 decomposition was too low.[11] Reinvestigations of the kinetics of this latter system[12,13] have now led to higher Arrhenius parameters, which are in accord with this prediction.

The purpose of this paper is to explore the implications of our recent studies of $SiMe_2$ and to expand further on those for SiH_2. For ease of reference the available data are summarized in Table I.

Thermodynamic Calculations and Decomposition *A* Factors

To assess the kinetics of the methyldisilane decomposition reactions (1) we have first estimated the entropy changes associated with these decompositions and then used these in conjunction with the reverse insertion *A* factors (A_{-1}) to calculate values for the forward *A* factors (A_1).[16] To calculate the entropy changes, absolute entropy values are required for all species involved. Data are available for the stable molecules, i.e. the methyldisilanes[17] and methylsilanes,[18] but not for the methylsilylenes, and so the values for the methyl sulfides were used (based on the structural analogue principle (ref 19, pp 50–56)). For those reactions that produce $SiMe_2$ the results are shown in Table II, together with the implied decomposition *A* factors. These are evaluated from the relationship (ref 19, pp 8–12)

$$\log (A_1/s^{-1}) = \log (A_{-1}/M^{-1}\ s^{-1}) + [\Delta S°/R - (1 + \ln R'T)]/\ln 10$$

where $R = 1.987$ cal $K^{-1}\ mol^{-1}$ and $R' = 0.0821$ dm^3 atm $mol^{-1}\ K^{-1}$. For each reaction two values have been calculated. The first, *A*(min), corresponds to the assumption that the insertion *A* factor, A_{-1}, may be identified with the rate constant k_{-1} of Table I; i.e., the insertion reaction has no activation energy. It may be noted that for the two cases for which data exist, measured *A* factors are less than this. The second value, *A*(preferred), corresponds to the assumption that the per H insertion *A* factor, A_{-1}, is 10^{10} $M^{-1}\ s^{-1}$. This latter assumption implies that the trend in rate constants in Table I for $SiMe_2$ arises largely from activation energy differences. This seems more likely since for a set of similar processes (which are fast anyway) it would be unreasonable to expect large variations in activated complex structure and therefore *A* factors. Similar arguments applied to the reactions that produce SiH_2 (with a per H insertion *A* factor of 3×10^{10} $M^{-1}\ s^{-1}$) give the figures shown in Table III. In this case the preferred and minimum *A* factors differ only slightly since the reverse SiH_2 insertion reactions (Table I) are so fast that they can have very little activation energy associated with them. The most recent studies of Si_2H_6[12,13] are in agreement with these expectations but that of Me_3SiSiH_3[6] is not.

Discussion

From the foregoing analysis it seems probable that several of the measured *A* factors for the methylated disilane decomposition reactions (1) discussed here are too low. There are a number of possible mechanistic complications in the systems under original study which could have led to errors in Arrhenius parameters. These include (a) reversibility of the initial step 1, (b) instability of trisilanes[20] produced by reactions such as

$$SiMe_2 + Me_3SiSiMe_2H \rightarrow Me_3SiSiMe_2SiMe_2H$$

(c) chain reactions,[21] in which silylenes are interconverted, via higher polysilanes, and (d) complexities arising from the isomerization of $SiMe_2$,[22] viz.

$$SiMe_2 \rightarrow MeSiH{=}CH_2$$

and subsequent reactions of $MeSiH{=}CH_2$. However, it should be noted that a recent reinvestigation of $Me_3SiSiMe_2H$[7] and a study of $Me_2SiHSiHMe_2$[23] have been carried out in the presence of excess butadiene which did not significantly alter the observed Arrhenius parameters. Since 1,3-butadiene is thought to be an effective trap for silylenes, this apparently offers strong support for the original measurements. There is thus at present an unresolved conflict of evidence concerning these Arrhenius parameters. One possible solution could be that butadiene is a less effective trap than has been thought at high temperatures. Trapping of $SiMe_2$ by dienes leads to silacyclopentanes via the intermediacy of vinylsiliranes.[24] Although silacyclopentenes are reasonably stable, it is known that vinylsiliranes can regenerate $SiMe_2$ competitively with ring expansion at high temperatures.[25] There is, therefore, a case for reinvestigation of these decompositions by using

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Table II. Entropy Changes, *A* Factors, and Activation Energies for Some Methyldisilane Decompositions

reaction	ΔS/cal K^{-1} mol^{-1} [a]	$\log(A/s^{-1})$			E_a/kcal mol^{-1}	
		min[b]	exptl	preferred[b]	exptl	reevaluated
$Me_3SiSiMe_2H \rightarrow Me_3SiH + SiMe_2$	34.2	14.75	12.9 ± 0.3[c,d]	15.3	47.4	54.4
$Me_2SiHSiMe_2H \rightarrow Me_2SiH_2 + SiMe_2$	32.1	14.4		15.2		
$MeSiH_2SiMe_2H \rightarrow MeSiH_3 + SiMe_2$	29.5	13.3	12.6 ± 2.0[c]	14.8	46.0	52.7
$H_3SiSiMe_2H \rightarrow SiH_4 + SiMe_2$	29.9	12.5		15.0		

[a] T = 650 K. [b] See text. [c] Reference 5. [d] 13.3 has been obtained more recently (Table II footnote, ref. 7).

Table III. Entropy Changes, *A* Factors and Activation Energies for Some Methyldisilane Decompositions

reaction	ΔS/cal K^{-1} mol^{-1} [a]	$\log(A/s^{-1})$			E_a/kcal mol^{-1}	
		min[b]	exptl	preferred[b]	exptl	reevaluated[b]
$Me_3SiSiH_3 \rightarrow Me_3SiH + SiH_2$	36.1	16.2	14.48 ± 0.3[c]	16.2	48.0	52.6
$Me_2SiHSiH_3 \rightarrow Me_2SiH_2 + SiH_2$	32.5	15.7		15.7		
$MeSiH_2SiH_3 \rightarrow MeSiH_3 + SiH_2$	31.1	15.4	15.28 ± 0.15[d]	15.6	50.8	51.7
$Si_2H_6 \rightarrow SiH_4 + SiH_2$	32.7	15.8	15.8[e]	16.1	52.2	53.0

[a] T = 650 K. [b] See text. [c] Reference 6. [d] Reference 4. [e] Reference 12.

other traps to try to check for and eliminate possible perturbations by secondary reactions.

One other possibility should be entertained. If the silylene insertion reactions had negative activation energies (in the case of $SiMe_2$ of up to −4 kcal mol^{-1}), the conflict between forward and reverse rate data might not arise. This seems on the face of it unlikely but might be possible if the process of insertion were no longer simple but occurred via an intermediate complex. Although donor–acceptor type complexes have been proposed as intermediates for silylene reactions with lone pair donors[26] (such as H_2O and NH_3), such complexes would be of a different type for insertion into Si–H bonds. To our knowledge no such complexes have been previously suggested or as yet indicated by theoretical calculations for this process. Nevertheless we plan to investigate the temperature dependence of the insertion reaction.

Thus there remains a strong argument that, as with Si_2H_6, the Arrhenius parameters for these methyldisilane decompositions should be higher. If this is so, there are important implications for the heats of formation of the silylenes that are worth evaluating. On the assumption that experimental rate constants in these studies are not in too serious error, then the measured data may be reevaluated with the *A* factors proposed here. This may be illustrated for pentamethyldisilane decomposition,[27]

$$Me_3SiSiMe_2H \xrightarrow{2} Me_3SiH + SiMe_2$$

for which the reworked Arrhenius equation

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

is obtained.

Table IV. Thermochemistry of Silylenes

silylene	$\Delta H_f°$/kcal mol^{-1}
SiH_2	65.3 (± 1.5)[a]
SiHMe	43.9 (± 3)[b]
$SiMe_2$	26.1 (± 2)[b,c]

[a] Reference 11. [b] This work. [c] See also ref 10.

With the implied E_{-2} = 0.8 kcal mol^{-1} (from the k_{-2} of Table I and an assumed A_{-2} of 10^{10} M^{-1} s^{-1}) and temperature correction, this yields $\Delta H_2°$ (298 K) = 55.1 kcal mol^{-1}. In conjunction with $\Delta H_f°(Me_3SiH)$ = −39.0 kcal mol^{-1} [18] and an estimate of $\Delta H_f°(Me_5Si_2H)$ = −68.0 kcal mol^{-1} [16] this yields $\Delta H_f°(SiMe_2)$ = −26.1 kcal mol^{-1}. This value is only altered by 0.9 kcal mol^{-1} if the *A*(min) rather than *A*(preferred) is chosen. The largest source of uncertainty lies in the $\Delta H_f°(Me_5Si_2H)$, the value of which has been obtained by linear interpolation (bond additivity) from an estimated value of $\Delta H_f°(Me_6Si_2)$ = −86.2 kcal mol^{-1}, consistent with data on Me_6Si_2 decomposition.[16]

The same exercise has been carried out on the other disilane pyrolyses in Tables II and III as well as on those (not listed here) which produce SiHMe.[16] If reasonable insertion rate constants of SiHMe are assumed (intermediate between those of SiH_2 and $SiMe_2$), then a $\Delta H_f°$ value for SiHMe is obtainable. The values summarized in Table IV each come from at least two separate calculations.

In view of the argued importance[2,3] of the processes considered here, it may well prove necessary in future modeling exercises involving methylsilylenes to employ the kinetic data and thermochemistry of this paper.

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Registry No. SiH_2, 13825-90-6; $SiMe_2$, 6376-86-9; SiH_4, 7803-62-5; $MeSiH_3$, 992-94-9; Me_2SiH_2, 1111-74-6; Me_3SiH, 993-07-7; $Me_3SiSiMe_2H$, 812-15-7; $Me_2SiHSiMe_2H$, 814-98-2; $MeSiH_2SiMe_2H$, 814-74-4; $H_3SiSiMe_2H$, 16342-86-2; Me_3SiSiH_3, 18365-32-7; $MeSiH_2SiH_3$, 13498-43-6; Si_2H_6, 1590-87-0; SiHMe, 55544-30-4.

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