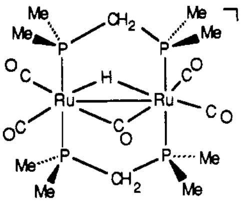
probability at the metal or at the oxygen of the bridging carbonyl ligand. Oxygen protonation is a much rarer event even with carbonyl clusters where the metal hydride is the more stable product. In previous studies of $Ru_2(dmpm)_2(CO)_5$ we reported that protonation occurs with high yield at the Ru–Ru bond, leading to structure 7.[2]



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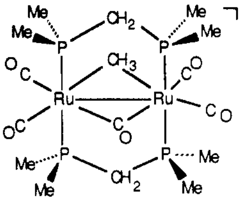

8

Because of the anticipated instability of a bridging methyl group relative to that of a terminal methyl, isolation of the analogous product (8) resulting from the methylation of the Ru–Ru bond would be unexpected. However, the most sterically accessible and electron-rich site on the dimer is the Ru–Ru bond. We propose that methylation, at least with methyl triflate, does occur on the metal–metal bond but that this rapidly rearranges through 2 to the more stable complex 3.

Studies of the solutions of 4 show that it does not convert to 3, and likewise, once 3 is formed, the only subsequent reaction is conversion to the terminal (5) and bridging (6) acetyl complexes. This suggests that k_1 and k_2 in Scheme I are both irreversible. The surprising observation that the yields of the two products are the same at all temperatures studied further suggests that $k_1 = k_2$. We conclude that the nature of the product depends simply on the side of the complex that is presented to the electrophile as the bond is being formed.

Once formed, 3 reacts rapidly with CO to form two complexes containing an acyl ligand. Unfortunately, the facile equilibrium between the terminal (5) and bridging (6) acyl complexes precludes any conclusion being drawn regarding the order of their formation from the alkyl complex.

Summary

The methylation of $Ru_2(dmpm)_2(CO)_5$ was found to result in equal amounts of metal- and oxygen-methylated products. The structure of the O-methylated product was determined by X-ray diffraction and is the first structurally characterized example of a bimetallic complex containing a μ-alkoxymethylidyne ligand. The Ru-methylated product was found to react with CO to form the η^1-acetyl species $[Ru_2(dmpm)_2(CO)_5[C(O)CH_3]]^+$. This complex loses CO at room temperature, resulting in formation of the μ-acetyl species $[Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)CH_3]]^+$. $[Ru_2(dmpm)_2(CO)_5[C(O)CH_3]]^+$ and $[Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)CH_3]]^+$ were shown to be interconvertible at room temperature. Additional studies of the reactivity of $Ru_2(dmpm)_2(CO)_5$ are in progress.

Acknowledgment. This research was supported by a grant from the National Science Foundation (Grant No. CHE-8714326).

Registry No. 1, 123810-59-3; [3][CF_3SO_3], 127356-70-1; [4][CF_3SO_3], 127356-72-3; [5][CF_3SO_3], 127356-74-5; [6][CF_3SO_3], 127356-76-7; $CF_3SO_3CH_3$, 333-27-7.

Supplementary Material Available: Listings of hydrogen atom positions, anisotropic temperature factors, and non-hydrogen bond distances and angles (7 pages); a listing of structure factors (27 pages). Ordering information is given on any current masthead page.

Decomposition Kinetics of 1,1,2- and 1,1,1-Trimethyldisilane

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Received January 18, 1990

The thermal decomposition kinetics of the titled disilanes obtained from static system investigations under conditions of maximum quenching of silylene chains are reported. Single-pulse shock-tube kinetic results on the 1,1,2-trimethyldisilane decomposition as well as relative rate kinetics of silylene insertions into silane and methylsilane at elevated temperatures are also given. Comparisons of the latter with room-temperature absolute rate constants support the consecutive-step, double-transition-state hypothesis for these reactions.

Introduction

It is now known[1] that the only important primary dissociation reactions (PDR's) of disilanes containing Si–H bonds are 1,2-H-shift silylene eliminations, as illustrated for 1,1-dimethyldisilane:

$$Me_2SiHSiH_3 \rightarrow Me_2SiH_2 + SiH_2 \quad (1)$$

$$\rightarrow SiH_4 + Me_2Si \quad (2)$$

It has also been established that disilane decompositions leading to the same products can be induced by silylene chain processes.[2] Thus, in the neat 1,1-dimethyldisilane decomposition eqs 3–5 are very important and eq 4 is the main source of silane.

$$SiH_2 + Me_2SiHSiH_3 \rightleftharpoons Me_2SiHSiH_2SiH_3 \quad (3)$$

$$Me_2SiHSiH_2SiH_3 \rightleftharpoons Me_2SiHSiH + SiH_4 \quad (4)$$

$$\rightleftharpoons Me_2SiH_2 + SiHSiH_3 \quad (5)$$

Such chains can be difficult to quench. In the above system, complete quenching was not achieved even with

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[1] (a) Estacio, P.; Sefcik, M. D.; Chan, E. K.; Ring, M. A. *Inorg. Chem.* **1970**, *9*, 1068. (b) Baird, R. B.; Sefcik, M. D.; Ring, M. A. *Inorg. Chem.* **1971**, *10*, 883. (c) Bowrey, M.; Purnell, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 2594. (d) Vanderwielen, A. J.; Ring, M. A.; O'Neal, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 993.

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Table I. Arrhenius Parameters from Neat System Studies of the Primary Decomposition Reactions of Trimethyldisilanes

reacn[a]	eq no.	log *A*	*E*	ref
$Me_2SiHSiH_2Me \rightarrow Me_2SiH_2 + MeSiH$	7	13.66 ± 0.55	46.2 ± 1.4	4
$Me_2SiHSiH_2Me \rightarrow MeSiH_3 + Me_2Si$	8	12.56 ± 1.8	46.1 ± 5.3	4
$Me_3SiSiH_3 \rightarrow Me_3SiH + SiH_2$	9	14.5 ± 0.3	48.0 ± 0.8	5

[a] Temperature ranges were 620–665 K for $Me_2SiHSiH_2Me$ and 530–560 K for Me_3SiSiH_3.

a 60-fold excess of butadiene, an excellent silylene trap. Thus, identification of product silane formation kinetics with the PDR kinetics in disilane pyrolyses requires a demonstration of complete silylene chain suppression.

Early kinetic studies of disilane pyrolyses (i.e., studies on Si_2H_6,[3] $Me_3SiSiHMe_2$,[4] $MeSiH_2SiH_3$,[1d] Me_3SiSiH_3,[5] and $Me_2SiHSiH_2Me$[4]) were made on their neat reactions. Reexaminations of the first three of these systems have, within the errors, revised only slightly the PDR Arrhenius parameters of the pentamethyl-[6,7] and methyldisilane[8] reactions but significantly revised upward the parameters of disilane.[9]

Davidson[6] was the first to note that *A* factors of disilane PDR's appeared to correlate with the nature of the eliminated silylene

$$\begin{aligned} \log A &\approx 15.3 \pm 0.3 \quad SiH_2 \text{ eliminations} \\ \log A &\approx 14.0 \pm 0.3 \quad MeSiH \text{ eliminations} \qquad (6) \\ \log A &\approx 12.9 \pm 0.3 \quad Me_2Si \text{ eliminations} \end{aligned}$$

and the recent disilane pyrolysis studies support this observation. On this basis, the trimethyldisilane Arrhenius parameters (Table I, eqs 7–9) obtained from the early neat system studies seem somewhat low and suggest the possibility of silylene chain complications.

$$\begin{aligned} Me_2SiHSiH_2Me &\rightarrow Me_2SiH_2 + MeSiH \qquad (7) \\ &\rightarrow MeSiH_3 + Me_2Si \qquad (8) \\ Me_3SiSiH_3 &\rightarrow Me_3SiH + SiH_2 \qquad (9) \end{aligned}$$

We report here reexaminations of the decomposition kinetics of the two trimethyldisilanes (i.e., 1,1,1-trimethyldisilane (111TMDS) and 1,1,2-trimethyldisilane (112TMDS)) under conditions of maximum inhibition using either 1,3-butadiene (BD) or 2,3-dimethyl-1,3-butadiene (DMBD) as trapping agents. The study objectives were to accurately determine the PDR parameters of these two systems and to determine the importance of silylene chain effects in their neat pyrolyses. We also report results on relative Si–H insertion rates of dimethylsilylene with silane and methylsilane. Absolute rate constants for these insertions, determined by laser absorption methods at room temperature,[10] show a surprising 9-fold faster rate for insertion into methylsilane, and it was of interest to see if this same rate difference held at the higher temperatures required for disilane pyrolyses.

Table II. Rate Constants for the Decomposition of Me_3SiSiH_3 in the Presence of 1,3-Butadiene or 2,3-Dimethyl-1,3-butadiene[a]

	rate const, 10^4 s^{-1}			no. of runs	
T, K	111TMDS loss[b]	111TMDS loss[c]	Me_3SiH[c,d]	*b*	*c*
560.5	0.68 ± 0.01	0.68 ± 0.01	0.69 ± 0.01	17	15
575.7	2.33 ± 0.05	2.21 ± 0.01	2.17 ± 0.02	18	20
588.2	5.42 ± 0.15	5.66 ± 0.04	5.23 ± 0.08	7	16
590.7	7.04 ± 0.14			6	
596.9		10.14 ± 0.08	10.54 ± 0.08		15
605.6	18.55 ± 0.44	18.26 ± 0.14	18.70 ± 0.15	9	14
615.2	36.72 ± 1.08	34.10 ± 0.45	34.33 ± 0.45	9	13

[a] See Table V for an Arrhenius summary. Errors are $\pm\sigma$. [b] Rate constants determined and runs made in excess 1,3-butadiene. [c] Rate constants determined and runs made in excess 2,3-dimethyl-1,3-butadiene. [d] Rate constants determined from Me_3SiH formation.

Experimental Section

111TMDS was produced by the room-temperature reaction of $KSiH_3$ (prepared by the method of Fieselmann and Dickson[11]) with Me_3SiCl in glyme. 112TMDS was obtained directly from Petrarch. Both compounds were purified by low-temperature trap-to-trap distillations, and their final purities of better than 98% were verified by GLC. In particular, no contamination by the main silane products could be detected (i.e., product concentrations relative to those of reactants were less than 0.004%).

The decomposition of 111TMDS was studied statistically in a 250-cm^3 quartz reactor immersed in a well-insulated, resistively heated, air bath furnace. Temperatures were controlled with a Bayley 124 proportional controller to better than ±0.1 °C as measured with a chromel–alumel thermocouple connected to a Doric 412A trendicator. Temperatures were checked by measurements of the cyclopropane isomerization rate constant with use of its well-established Arrhenius parameters[12] after making minor adjustments for pressure falloff. Product and reactant concentrations were chromatographically analyzed on a Carle Model 8000 thermal conductivity chromatograph coupled with a HP 3390A integrator using a 10 ft × $^1/_8$ in. stainless steel column packed with 20% squalene on Supelcoport. Reaction mixtures contained tetramethylsilane (S) as a GC internal standard and either 1,3-butadiene (BD) or 2,3-dimethyl-1,3-butadiene (DMBD) in varying excess proportions. Compositions of the two reactant mixtures employed in the 111TMS studies were as follows: (1) BD/A/S = 24/1/1; (2) DMBD/A/S = 29/1/1.4 (where A = reactant). Initial pressures of the first mixture varied from 10 to 40 Torr and those of the second from 10 to 24 Torr. As would be expected, rate constants were totally pressure-independent.

The 112TMDS static reactor system was essentially the same as the above except that product analyses were made on a Varian 3700 FID chromatograph using a Supelco SE-30 packed column. Compositions of the two reaction mixtures studied were BD/A/S = 30/1/1 and BD/A/S = 57/1/1, where S = the analytical internal standard, Me_4Si. The butadiene-inhibited 112TMDS decomposition was also studied by the comparative-rate single-pulse shock-tube technique[13] (CR-SPST) with cyclobutanone as the comparative rate standard and with the apparatus and procedures described previously.[14]

Results

1,1,1-Trimethyldisilane. The decomposition of 111TMDS was studied between 560 and 616 K in the presence of both BD and DMBD. Products were trimethylsilane and very small yields of the silacyclopentene

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trapping products. Reasons for low yields of the latter under our reaction conditions have been given.[15] In contrast to the neat reaction, no silane and no 1,1,1-trimethyltrisilane was produced in the presence of either butadiene trapping agent. This is consistent with a single PDR (eq 10) and with complete quenching of the silylene chain sequence (eqs 11 and 12).

$$\text{111TMDS} \rightarrow \text{Me}_3\text{SiH} + \text{SiH}_2 \qquad (10)$$

$$\text{SiH}_2 + \text{111TMDS} \rightleftharpoons \text{Me}_3\text{SiSiH}_2\text{SiH}_3 \qquad (11)$$

$$\text{Me}_3\text{SiSiH}_2\text{SiH}_3 \rightleftharpoons \text{Me}_3\text{SiSiH} + \text{SiH}_4 \qquad (12)$$

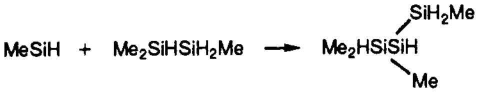
In the presence of BD the 111TMDS decomposition was studied in terms of reactant loss only, as the GC peak for BD overlapped with the trimethylsilane product peak. Rate constants (Table II), obtained over a conversion range of 20–80% with use of the usual integral rate equation I and the experimental GC peak area ratios (A/S), were the same as those of the prior neat reactant study[5] within the experimental errors.

$$\ln\left[(A/S)_0/(A/S)_t\right] = kt \qquad A = \text{reactant};\ S = \text{Me}_4\text{Si} \qquad (\text{I})$$

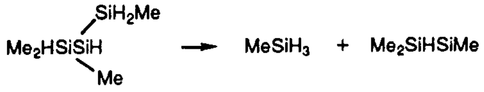
In the presence of DMBD, it was possible to follow the course of reaction in terms of the trimethylsilane appearance as well as reactant loss. Rate constants based on Me_3SiH (P) formation (Table II) were evaluated via eq I with $(A/S)_t = (A_0/S_0 - (P/S)_t \times \text{CF})$, where CF is a conversion factor converting the trimethylsilane GC area into an equivalent reactant area on a mol/mol basis. CF was determined by 'infinite time' pyrolyses of 111TMDS at 605.6 K.

Arrhenius parameters obtained from the rate constant data are given in the Arrhenius summary table (Table V). The collective parameters, k_9 (s^{-1}) = $10^{15.06 \pm 0.21}e^{-(49\,285 \pm 560\ \text{cal})/RT}$, which can be identified with the primary dissociation reaction of 111TMDS, show an *A* factor in good agreement with expectation for an SiH_2 elimination process.

1,1,2-Trimethyldisilane Decomposition (Static and CR-SPST Systems). The decomposition of 112TMDS was studied in a static reaction system over the temperature range 573 ± 630 K. Variations in the silane product ratios ($\text{Me}_2\text{SiH}_2/\text{MeSiH}_3$ = DMS/MS) with degrees of inhibition show clear evidence of silylene chains, especially in the neat reaction. Thus, Davidson et al.[4] reported DMS/MS = 11.4 at low conversions for the neat reaction; we found 17.3 for five runs on the neat reaction at 620 K. Significantly higher DMS/MS ratios (i.e., 38.3 ± 1.9 and 38.5 ± 1.3 for BD/A = 30 and BD/A = 57, respectively; see Table III) were found for the reaction under inhibition. Thus, it is clear that the silylene chain sequence producing methylsilane (eqs 13 and 14) is very important in the neat reaction even at very low conversions. In addition, the invariance of the DMS/MS product ratios at inhibition levels above 30/1 indicates that complete quenching of the silylene chains was effectively achieved in our studies.



$$\text{MeSiH} + \text{Me}_2\text{SiHSiH}_2\text{Me} \longrightarrow \text{Me}_2\text{HSiSiH(SiH}_2\text{Me)(Me)} \qquad (13)$$



$$\text{Me}_2\text{HSiSiH(SiH}_2\text{Me)(Me)} \longrightarrow \text{MeSiH}_3 + \text{Me}_2\text{SiHSiMe} \qquad (14)$$

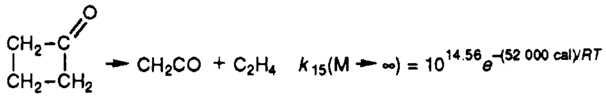
Table III. Static System Rate Constants[a] for the Decomposition of $\text{Me}_2\text{SiHSiH}_2\text{Me}$ in Excess Diene: BD/112TMDS = 30/1 and 57/1

	k, 10^4 s^{-1}			
T, K	reactant loss[b]	product formation[c]	DMS/MS[d]	no. of runs
	BD/112TMDS = 30/1			
581.9	1.99 ± 0.14	2.08 ± 0.40		3
594.9	4.75 ± 0.41	5.12 ± 0.20	40.3	4
609.9	13.2 ± 0.35	14.4 ± 1.0	40.0	5
617.1	22.8	23.8	37.5	1
630.2	44.2 ± 1.5	46.3 ± 5.5	35.6	4
	BD/112TMDS = 57/1			
573.1	1.20 ± 0.05	1.11 ± 0.05	39.3	7
582.0	2.16 ± 0.04	2.19 ± 0.05	37.7	5
583.1	2.46 ± 0.20	2.32 ± 0.04	41.5	3
590.5	4.21 ± 0.19	4.00 ± 0.08	37.5	4
597.7	6.34 ± 0.14	6.28 ± 0.13	37.7	5
602.0	9.19 ± 1.7	8.70 ± 0.41	36.9	8
612.3	19.3 ± 3.2	16.5 ± 1.2	39.3	3
613.2	18.9 ± 1.4	17.5 ± 0.4	39.0	3
623.1	28.7 ± 2.4	31.6 ± 1.0	37.9	5

[a] For an Arrhenius summary, see Table V. Errors are $\pm\sigma$. [b] Rate constants determined directly from reactant loss data. [c] Rate constants determined from product formation data (see text). [d] Dimethylsilane/methylsilane product yields: $\langle\text{DMS/MS}\rangle_{30/1}$ = 38.3 ± 1.9 and $\langle\text{DMS/MD}\rangle_{57/1}$ = 38.5 ± 1.3 in the 601 ± 29 K range.

Rate constants for the 112TMDS decomposition in the presence of butadiene are shown in Table III. Overall decomposition rate constants were obtained directly from eq I with A = 112TMDS and S = Me_4Si on the basis of reactant loss data and indirectly from eq I with $(A/S)_t = [(A/S)_0 - (\text{MS} \times \text{CF}_{\text{MS}}/S)_t - (\text{DMS} \times \text{CF}_{\text{DMS}}/S)_t]$ on the basis of product formation data. As before, the CF terms are conversion factors converting GC product areas into mole equivalent reactant areas, all referred to the internal standard. For complete quenching of silylene chains, reactant loss must equal monosilane product formation: $\Delta[\text{A}] = \Delta[\text{MS}] + \Delta[\text{DMS}]$. That this was the case within the errors is evident from the excellent agreements between rate constants evaluated by the two methods and by their resulting Arrhenius parameters (Tables III and V).

The DMS/MS product yield ratios under maximum inhibition are direct measures of the PDR ratios (k_7/k_8), and the Table III values appear to decrease slightly with increasing temperature. A least-squares Arrhenius treatment gives $\ln(k_7/k_8) = (2.98 \pm 0.67) + (797 \pm 978)/RT$. Clearly the errors are such that this trend cannot be adequately quantified via the static system data alone; hence, a number of CR-SPST kinetic runs were made on the inhibited system in order to obtain data at much higher temperatures. The CR-SPST results, obtained relative to the cyclobutanone decomposition (eq 15), are shown in Table IV. Note that RRKM falloff calculations on the 112TMDS and cyclobutanone systems indicate that both reactions are slightly dependent on the total pressure under shock-tube reaction conditions (i.e., 3200 Torr, 958 ± 52 K). To obtain high-pressure rate constants, the Table IV experimental values must be scaled by the calculated k/k_∞ values.



$$\longrightarrow \text{CH}_2\text{CO} + \text{C}_2\text{H}_4 \quad k_{15}(\text{M} \rightarrow \infty) = 10^{14.56}e^{-(52\,000\ \text{cal})/RT} \qquad (15)$$

The CR-SPST results confirm that DMS/MS yield ratios do decrease with temperature, and their decrease is somewhat stronger than the static reaction data suggest. A least-squares treatment of the 12 SPST reaction

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[15] Martin, J. G.; O'Neal, H. E.; Ring, M. A. *Int. J. Chem. Kinet.*, in press.

Table IV. Single-Pulse Shock Tube Results[a] for the Pyrolysis of 1,1,2-Trimethyldisilane under 30/1 Butadiene Inhibition[b]

k_{exp}, 10^{-3} s^{-1}		falloff[c]		DMS/	
std[a,d]	A[a]	$(k/k_\infty)_{std}$	$(k/k_\infty)_A$	MS yield[e]	T, K
0.103	0.405	0.98	0.98	16.1	906.4
0.383	1.13	0.97	0.90	16.0	949.9
0.399	1.34	0.97	0.90	17.8	951.3
0.601	2.09	0.96	0.89	18.3	965.6
0.623	2.25	0.96	0.89	19.5	966.9
0.697	2.42	0.96	0.88	18.1	971.1
0.993	3.27	0.95	0.85	19.5	984.0
1.027	3.34	0.95	0.85	19.7	985.2
1.086	4.17	0.95	0.85	15.0	987.5
1.202	4.49	0.95	0.84	18.2	991.3
1.285	5.21	0.95	0.84	11.9	993.8
1.966	6.04	0.94	0.82	16.0	1010.3

[a] Std = cyclobutanone; A = 112TMDS. For Arrhenius summaries, see Table V. [b] The reaction mixture contained 3.67% in argon of the components BD, A, Std, and Si in the ratio 45.5/1/1.35/1.75, where Si = Me_4Si. Total reaction pressures were 3200 Torr. [c] Both reactions are in their unimolecular falloff regimes. The k/k_∞ values were calculated by RRKM methods[20] with use of sets of frequencies that reproduce the experimental activation entropies and with collision efficiencies (calculated by the methods of Troe[21]) based on assumed values at 550 K of $\beta_c = 0.95$ for all "heavy" substrates and $\beta_c = 0.29$ for argon. [d] The internal rate standard was cyclobutanone (log A = 14.56, E = 52 000 cal).[12] [e] $\langle$DMS/MS$\rangle_{30/1}$ = 17.2 ± 2.2 in the temperature range 958 ± 52 K.

DMS/MS values and the 13 static system reaction values gives ln $(k_7/k_8) = (1.53 \pm 0.17) + (2520 \pm 266\ \text{cal})/RT$. Thus, the activation energy for Me_2Si elimination is higher than that for MeSiH elimination by more than 2.5 kcal, a trend noted in a prior analysis of methylated disilane decompositions.[15]

An Arrhenius treatment of the shock-tube rate constant data gives parameters for the overall decomposition rate constant that are significantly higher than those found from the static system studies (see Table V). However, since the shock reaction rate constant errors are rather large and 10 of the 12 rate constant determinations fall within a relatively narrow 50 K range, these parameters are not very reliable. However, the shock-tube data used with the static reaction data in an extended Arrhenius treatment (i.e., a temperature range of 437 K and a rate constant range of 6 orders of magnitude) provide quite reliable Arrhenius parameters: $k_{overall} = k_7 + k_8 = 10^{14.08 \pm 0.06} e^{-(47\,256 \pm 200\ \text{cal})/RT}$ s^{-1}. This collective treatment is in excellent agreement with the combined static reaction result (see Table V).

When the overall decomposition rate constant parameters are combined with the k_7/k_8 parameters, one obtains Arrhenius parameters of the individual PDR's: $k_7 = 10^{13.81 \pm 0.06} e^{-(47\,157 \pm 200\ \text{cal})/RT}$ s^{-1} for the dimethylsilane formation (MeSiH elimination) reaction and $k_8 = 10^{13.15 \pm 0.13} e^{-(49\,677 \pm 466\ \text{cal})/RT}$ s^{-1} for the methylsilane formation (Me_2Si elimination) reaction. Again, A factors of the individual PDR's are consistent with the Davidson[6] thesis. Thermochemical kinetic A-factor estimates for 1,2-H-migration, silylene-elimination reactions all fall in the $10^{13 \pm 0.5}$ s^{-1} range, very close to those observed for Me_2Si eliminations. The A-factor increases of about 1 order of magnitude above the "expected" values with each H for Me replacement on the eliminated silylene are surprising and signify a considerable loosening in the MeSiH and SiH_2 elimination transition states. A plausible reason for this loosening, involving a consecutive-step decomposition with the possibility of two different transition states, has been advanced by Walsh.[7]

Table V. Arrhenius Parameter Summary[a]

inhibition[b]	log A,s^{-1}	E, cal	basis
Static System Me_3SiSiH_3 Decomposition (T = 588 ± 27 K)			
BD/A = 24	15.18 ± 0.43	49 583 ± 1 170	k_9 (A loss)
DMBD/A = 29	14.96 ± 0.26	49 030 ± 573	k_9 (A loss)
DMBD/A = 29	15.05 ± 0.38	49 286 ± 1 025	k_9 (P formn)
combined	15.06 ± 0.21	49 285 ± 560	k_9 (best value)
Static Decomposition of 1,1,2-Trimethyldisilane (601 ± 29 K)			
BD/A = 30	14.19 ± 0.89	47 627 ± 2 440	$k_7 + k_8$ (A loss)
BD/A = 30	14.18 ± 0.86	47 541 ± 2 369	$k_7 + k_8$ (P formn)
BD/A = 57	14.01 ± 0.90	47 003 ± 2 473	$k_7 + k_8$ (A loss)
BD/A = 57	14.16 ± 0.24	47 476 ± 650	$k_7 + k_8$ (P formn)
BD/A = 30, 57	14.01 ± 0.39	47 048 ± 1 063	$k_7 + k_8$ (both)
BD/A = 30, 57	0.665 ± 0.074[f]	−2 520 ± 266[f]	k_7/k_8 (see text)
CR-SPST Decomposition of 1,1,2-Trimethyldisilane[c] (T = 958 ± 52 K)			
BD/A = 30	15.58 ± 0.92	53 901 ± 4 035	$k_7 + k_8$ (P formn)
Static and CR-SPST Combined Results (T = 792 ± 218 K)			
complete[d]	14.08 ± 0.06	47 256 ± 200	$k_7 + k_8$ (all data)
complete[d]	0.664 ± 0.074[f]	−2 520 ± 266[f]	k_7/k_8 (all data)
complete[d,e]	13.81 ± 0.06	47 157 ± 200	k_7 (Me_2SiH_2 formn)
complete[d,e]	13.15 ± 0.13	49 677 ± 466	k_8 ($MeSiH_3$ formn)

[a] Errors are ±2σ. [b] Abbreviations: BD = 1,3-butadiene; DMBD = 2,3-dimethyl-1,3-butadiene; A = reactant; P = product; formn = formation. [c] See text regarding reliability. [d] Complete inhibition achieved at all levels of inhibition. [e] Calculated from the overall rate constant parameters ($k_7 + k_8$) and the rate constant ratio (k_7/k_8) parameters from the combined single-pulse shock tube and static system rate constant data. [f] log (A_7/A_8); $E_7 - E_8$ in calories.

If the rate constants of eqs 8 and 9 (i.e., Me_2Si and SiH_2 elimination reactions, respectively) are extrapolated with use of transition-state theory to the 298 K condition and coupled with the observed rate constants of their reverse room-temperature reactions,[10] one obtains equilibrium constants $K_8 = 1.1 \times 10^{-31}$ and $K_9 = 1.3 \times 10^{-30}$ in units of atm. Even though these decompositions may involve more than one transition state (see later), equilibrium constant errors larger than 1 order of magnitude, corresponding to enthalpy errors of less than 1.4 kcal, are unlikely.[16] Therefore, coupling the reaction entropies[17] (ΔS°_8 = 32.2 cal/deg and ΔS°_9 = 36.6 cal/deg, atmospheric standard state) with these equilibrium constants gives for the corresponding reaction enthalpies at 298 K ΔH°_8 = 51.8 ± 1.4 kcal and ΔH°_9 = 51.6 ± 1.4 kcal. If one assumes that the heats of formation of the two reactant trimethyldisilanes are the same (AM1, MM2, and EECBA calculations[16] all support this assumption), then the two decomposition reactions can be added to obtain the heat of formation difference between the product silylenes. Thus, with $\Delta H^\circ_f(MeSiH_3)$ = −6.9 kcal/mol and $\Delta H^\circ_f(Me_3SiH)$ = −39.0 kcal/mol,[18] one obtains $\Delta H^\circ_f(SiH_2) - \Delta H^\circ_f(Me_2Si)$ = 31.9 kcal/mol. Further, if $\Delta H^\circ_f(SiH_2)$ = 64 ± 2 kcal/mol, this gives $\Delta H^\circ_f(Me_2Si)$ = 32.1 ± 2 kcal/mol. These values and their difference are in excellent agreement with Gordon's[19] high-level (MP4/6-

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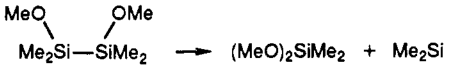
Table VI. Relative Rates of Me_2Si Insertions into $MeSiH_3$ and SiH_4

T, K	$\langle k_{18}/k_{17}\rangle^a$	no. of runs	T, K	$\langle k_{18}/k_{17}\rangle^a$	no. of runs
527.6	8.47	11	567.5	8.44	12
533.7	8.34	16	572.7	8.37	9
545.3	8.42	9	584.0	8.12	15
552.8	7.51	13			

[a] Average values of k_{18}(into methylsilane)/k_{17}(into silane) for the stated number of runs.

311G(d,p)) isodesmic calculations and with values obtained previously from the kinetics of other disilane decomposition systems with use of the same kind of kinetic analysis.[16]

Relative Insertion Rates of Me_2Si into SiH_4 and $MeSiH_3$. The relative rates of dimethylsilylene Si–H insertions into silane and methylsilane were studied at seven temperatures between 527.6 and 584 K by decomposing tetramethyl-1,2-dimethoxydisilane (TMDMODS, an excellent source of Me_2Si) in the presence of excess silane and methylsilane. Reactants were in the ratio $SiH_4/MeSiH_3/TMDMODS = 9.63/1.00/0.435$. The operative reactions (16-18) are shown in eqs 16–18. Since TMDMODS is considerably less stable[6] than any of the product disilanes, the latter did not decompose appreciably during the period of their production. Therefore, yield ratios of the product disilanes at low conversions of TMDMODS provided direct measures of the rates of the competing insertion reactions through eq II.



$$(MeO)Me_2Si{-}SiMe_2(OMe) \longrightarrow (MeO)_2SiMe_2 + Me_2Si \quad (16)$$

$$Me_2Si + SiH_4 \longrightarrow Me_2SiHSiH_3 \quad (17)$$

$$Me_2Si + MeSiH_3 \longrightarrow Me_2SiHSiH_2Me \quad (18)$$

$$Y(Me_2SiHSiH_3)/Y(Me_2SiHSiH_2Me) = k_{17}[SiH_4]/k_{18}[MeSiH_3] \quad \text{(II)}$$

The rate constant ratios so evaluated are given in Table VI. Since no temperature variation in these ratios is evident, it seems reasonable to equate k_{18}/k_{17} with the data average: $k_{18}/k_{17} = 8.22 \pm 0.31$ in the 550 ± 30 K range. Absolute rate constants determined by laser absorption techniques at 298 K ($k_{18} = (1.1 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, $k_{17} = (1.2 \pm 0.2) \times 10^8$ M^{-1} s^{-1})[9] give the same value within the errors, i.e. $k_{18}/k_{17} = 9.17 \pm 2.4$. Thus, assuming Arrhenius behavior, $E_{18} = E_{17}$ and $A_{18}/A_{17} \approx 9$. This is a curious result as the 9-fold difference in the A factors of the insertion reactions at room temperature implies very different transition states for the two reactions, while the equivalancy of the decomposition reverse reaction A factors (i.e., $A_{-17} = 10^{13.18}$ s^{-1} and $A_{-18} = 10^{13.15}$ s^{-1}) implies very similar transition states. Thus, a single-transition-state, simple Arrhenius analysis produces a contradiction, and this provides further support for the Walsh argument of a consecutive-step reaction mechanism with the possibility of different transition states under different conditions.

Acknowledgment. We are indebted to the National Science Foundation (Grants CHE-8419089 and CHE-8719843) for financial support of this work.

Registry No. 111TMDS, 18365-32-7; 112TMDS, 814-74-4; Me_2Si, 6376-86-9; SiH_4, 7803-62-5; $MeSiH_3$, 992-94-9.

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Chemical and Structural Investigations on (Ferrocenylacyl)silanes[†,1]

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Received October 2, 1989

(Ferrocenylacyl)silanes, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)COSiR_3$ (R_3 = Me_3, Me_2Ph, $MePh_2$, Ph_3), have been synthesized and their chemical, physical, and structural properties investigated. The compounds exhibit no photochemistry and are not subject to base-catalyzed rearrangements. Attempts to synthesize acyldisilanes, $FcCOSiR'_2SiR_3$, via hydrolysis of the corresponding ferrocenyldisilyldithianes, resulted in the formation of only $FcCOSiR_3$. In a similar manner attempts to synthesize $FcCOSiMe_2SiMe_2SiMe_3$ and $FcCOSi(SiMe_3)_3$ yielded only $FcCOSiMe_3$. Basicity measurements, via H-bonding to phenol, indicate the ferrocenyl group to be responsible for a major increase in the basicity of the acylsilanes. The structures of the four acyl complexes are reported and exhibit almost identical structural parameters about the carbonyl group, illustrating that the ferrocenyl group has a dominant steric effect upon the compounds. The steric bulk of the silyl groups is shown to be $Ph_3Si > Me_3Si > Me_2PhSi = MePh_2Si$.

Introduction

Acylsilanes have been thoroughly investigated by the comprehensive studies of Brook and co-workers and have been shown to exhibit many unusual and remarkable chemical, spectral, and photochemical properties.[2-12] Treatment of acylsilanes with an alkoxide ion, depending upon the polarity of a medium, results in formation of silyl

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[†] Dedicated to Professor A. G. Brook on the occasion of his 65th birthday.

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