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with the remainder triisopropyl borate.

Dimethyl (1,1-Dichloroethyl)boronate (3b). A solution of 285 mmol of LDA in 300 mL of THF prepared as described in the preceding paragraph was cooled with a dry ice/acetone bath (–78 °C) and added dropwise through a cannula over a period of 1 h to a stirred solution of 25 mL (0.3 mol) of 1,1-dichloroethane and 30 mL (0.265 mol) of trimethyl borate in 300 mL of THF in a 2-L three-neck flask cooled with dry ice/acetone. The mixture was allowed to warm to –50 °C, then cooled again to –78 °C, and treated with gaseous hydrogen chloride to the methyl orange endpoint. The slurry became too thick for efficient stirring and was diluted with sufficient diethyl ether to fluidize it. Filtration, washing the salts with ether, and distillation of the solvents through a packed column was carried out as described in part A of the preceding paragraph. The residue of dimethyl (1,1-dichloroethyl)boronate (**3b**) was distilled; 26.8 g (79%). It is essential that overheating of this compound (~100 °C) be avoided in order to prevent loss of hydrogen chloride and polymerization. NMR (90 MHz, $CDCl_3$): δ 2.08 (s, 3, CCH_3), 3.79 (s, 6, OCH_3). Anal. Calcd for $C_4H_9BCl_2O_2$: C, 28.12; H, 5.31; B, 6.33; Cl, 41.51. Found: C, 27.80; H, 5.15; B, 6.36; Cl, 41.49.

Dimethyl (1,1-Dichloroethyl)boronate (3b) from Preformed (1,1-Dichloroethyl)lithium. A solution of 42 mL (0.5 mol) of 1,1-dichloroethane in 300 mL of ether and 300 mL of THF was cooled to –110 °C (internal temperature), and a solution of 0.53 mol of *sec*-butyllithium in cyclohexane was added dropwise slowly enough that the internal temperature of the reaction mixture remained below –100 °C. The mixture was allowed to warm to –90 °C, stirred 1 h, and then cooled to –110 °C. A tan slurry of (1,1-dichloroethyl)lithium resulted. A solution of 66 mL (0.58 mol) of trimethyl borate was added dropwise, maintaining the temperature below –100 °C, and the mixture was then allowed to warm to –50 °C. The mixture was then cooled with a –78 °C bath, and gaseous hydrogens chloride was bubbled into the mixture to the methyl orange endpoint. The mixture was allowed to warm to room temperature and concentrated on a rotary evaporator. The product was distilled rapidly under high vacuum into a –78 °C trap and then redistilled; bp 48 °C (40 torr); 25.6 g (30%).

2,3-Butanediol (Diiodomethyl)boronate. Diisopropyl (dichloromethyl)boronate (**3a**) was transesterified with *d,l*/*meso*-2,3-butanediol as previously described for the *R,R* isomer.[3] Addition of 0.785 mL (5 mmol) of the resulting butanediol (dichloromethyl)boronate to a solution of 1.65 g (11 mmol) of sodium iodide in 15 mL of acetone, stirring 1 h at 20–25 °C, concentration, separation of the organic product from the sodium iodide with the aid of petroleum ether, and again concentrating yielded 1.68 g (92%) of butanediol (diiodomethyl)boronate as an oil, which was crystallized from petroleum ether; mp 30–31 °C. The *d,l*/*meso* ratio as estimated by proton NMR was originally ~88/12 and shifted to ~82/18 after three recrystallizations. NMR (90 MHz, $CDCl_3$): δ 1.35 (d, 6, CH_3), 4.18 (m, 1.6, *d,l*-OCH), 4.35 (s, 1, CHI_2), 4.72 (m, 0.4, meso-OCH). Anal. Calcd for $C_5H_9BI_2O_2$: C, 16.42; H, 2.48; B, 2.96; I, 69.39. Found: C, 16.35; H, 2.56; B, 3.12; I, 69.09.

Acknowledgment. We thank the National Science Foundation for Grant CHE8400715.

Registry No. **3a**, 62260-99-5; **3b**, 101772-81-0; triisopropyl borate, 5419-55-6; dichloromethane, 75-09-2; 1,1-dichloroethane, 75-34-3; trimethyl borate, 121-43-7; *d,l*-2,3-butanediol (diiodomethyl)boronate, 101772-82-1; *meso*-2,3-butanediol (diiodomethyl)boronate, 101772-83-2; *d,l*-2,3-butanediol, 6982-25-8; *meso*-2,3-butanediol, 5341-95-7.

Comparative Trapping Kinetics of Silylene. 1. Silylene Reactions with 1,3-Butadiene and Acetylene and with 1,3-Butadiene and Methanol

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Relative rate studies of silylene trapping by butadiene, methanol, and acetylene are reported. For the reactions $:SiH_2 + H_2C{=}CHC(H){=}CH_2 \xrightarrow{3} \overline{CH_2C(H){=}CHCH_2Si}H_2$ vs. $:SiH_2 + CH_3OH \xrightarrow{7} CH_3OSiH_3$, ln $(k_3/k_7) = (5.91 \pm 0.91) - (5846 \pm 1540)$ cal/RT (696–1016 K), and reaction 3 vs. $:SiH_2 + HC{\equiv}CH \xrightarrow{6} HC{\equiv}CSiH_3$, ln $(k_3/k_6) = (1.51 \pm 0.32) - (712 \pm 520)$ cal/RT (603–102 K). Relative rates, extrapolated to room temperature, are favorably compared to existing absolute rate constant measurements. On the basis of estimated Arrhenius parameters for the reaction 7, tentative absolute Arrhenius parameters with temperature dependencies for a number of silylene–substrate reactions are calculated.

Introduction

1,3-Butadiene and other 1,3-dienes are known to be efficient trapping agents for both silylenes[1] and disilenes.[2,3] The former reaction is complex in that the initial addition of the silylene has been shown to be 1,2 to form an allylsilacyclopropane.[4] Allylic resonance assisted openings of this ring followed by 5-membered ring closing of the intermediate biradicals produces silacyclopentene trapping products. This is illustrated for silylene and 1,3-butadiene in Scheme I. [The minor product (sila-2-cyclopentene) has not been reported for this exact reaction, but is a product in a number of other 1,3-diene trapping reactions.]

Silacyclopentenes are thermally stable products: hence 1,3-dienes are often the silylene trapping agents of choice for quenching studies of organosilicon compound reactions at elevated temperatures.

Dienes are also used as trapping agents for disilenes and silenes. These reactions are probably concerted Diels–Alder processes as shown in Scheme II.

Unfortunately little kinetic data, either absolute or comparative, are available for these reactions. Thus to our knowledge, only one absolute rate measurement has been reported for a silylene–1,3-diene reaction:[5] PhMeSi: reacts

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[1] Weyenberg, D. R.; Atwell, W. H. *Pure Appl. Chem.*, **1969**, *19*, 343.

[2] Jenkins, R. L.; Kedrowski, R. A.; Elliot, L. E.; Tappen, D. C.; Schlyer, D. L.; Ring, M. A. *J. Organomet. Chem.* **1975**, *86*, 347.

[3] Masamune, S.; Murakami, S.; Tobita, H. *Organometallics* **1983**, *2*, 1466.

[4] Lei, D.; Hwang, R.; Gaspar, P. P. *J. Organomet. Chem.* **1984**, *271*, 1.

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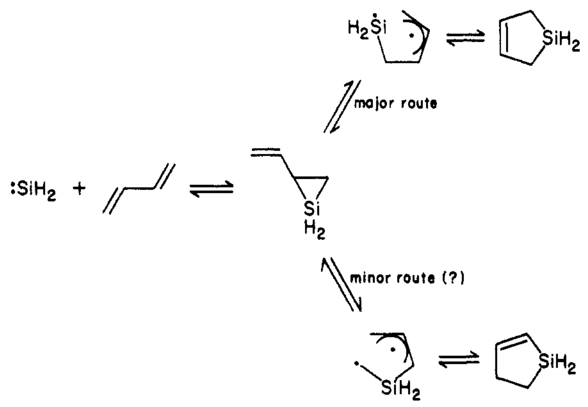
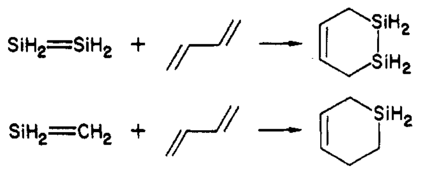
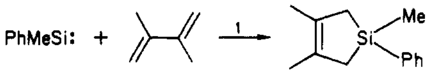
Scheme I



Scheme II

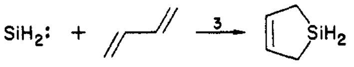


with 2,3-dimethylbutadiene in cyclohexane at room temperature (reaction 1) with a rate constant of $k_1 = (2 \pm 1) \times 10^5$ M^{-1} s^{-1}.



Relative rate results are similarly limited. For the reactions of silylene with silane and 1,3-butadiene (reactions 2 and 3),[6] between 658 and 733 K, Gaspar found $k_2/k_3 = (0.18 \pm 0.03)e^{2600\pm300\mathrm{cal}/RT}$ and, in a separate study, $k_2/k_3 = 9 \pm 1$ at room temperature.[7]

$$SiH_2\!: + SiH_4 \xrightarrow{2} SiH_3SiH_3$$



In these labs, for the reaction of silylene with disilane and butadiene (reaction 4 vs. reaction 3)[2] at 658 K, $k_4/k_3 \approx 4.2$, while for the reaction of silylene with trimethylsilane and butadiene (reaction 5 vs. reaction 3)[8] at 930 K, $k_5/k_3 \approx 1$.

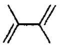
$$SiH_2\!: + Si_2H_6 \overset{4}{\rightleftharpoons} Si_3H_8$$

$$SiH_2\!: + Me_3SiH \overset{5}{\rightleftharpoons} Me_3SiSiH_3$$

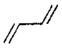
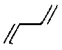
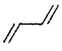
Absolute and relative rate kinetic data for other commonly employed silylene trapping substrates (e.g., acetylene, olefins, alcohols, etc.) are summarized in Tables I and II.

Table I. Absolute and Relative Rate Data for Silylene Reactions

A. Absolute Rate Data

reactants	rate const, M^{-1} s^{-1}	temp, K	ref
Me_2Si: + Et_3SiH	2.0×10^6	293	9
Me_2Si: + MeOH	3.1×10^7	293	9
MePhSi: + O_2	$(6 \pm 4) \times 10^8$	298	5
MePhSi: + EtOH	$(8 \pm 5) \times 10^6$	298	5
MePhSi: + 	$(2 \pm 1) \times 10^5$	298	5
MePhSi: + Et_3SiH	$\leq 10^4$	298	5

B. Relative Rate Data

substr	rel rate	temp, K	ref
Reference Reaction: $:SiH_2 + SiH_4 \rightleftharpoons Si_2H_6$			
SiH_4	1.0		
$MeSiH_3$	1.38	658–733	6
$MeSiH_3$	1.3	560	10
	0.73	650	6
	0.95	743	6
Si_2H_6	4.9 ± 1.9	300[a]	11
Si_2H_6	3.2	590	12
Reference Reaction: $:SiH_2 + Si_2H_6 \rightleftharpoons Si_3H_8$			
Si_2H_6	1.0		
$MeSiH_3$	0.90	594	12
$MeSiH_3$	0.20	623	13
Me_2SiH_2	0.53	594	12
Me_2SiH_2	0.23	623	13
Me_3SiH	0.51	594	12
Me_3SiH	0.27	623	13
	0.24	658	2
SiH_4	0.20 ± 0.04		11
SiH_4	0.31	590	12

[a] Silylene generated from PH_3 + ^0n reaction.

The sparsity of trapping reaction rate data is a serious problem in that the only important intermediates of most organosilicon compound pyrolyses are silylenes, silenes, and disilenes. We have therefore initiated a series of relative rate investigations employing 1,3-butadiene as the reference substrate. In this first paper of the series we report results on comparative reaction rates of silylene toward the substrate pairs acetylene/1,3-butadiene (reaction 6 vs. reaction 3)[17] and methanol/1,3-butadiene (reaction 7 vs. reaction 3).[18]

$$SiH_2\!: + C_2H_2 \overset{6}{\rightleftharpoons} CH{\equiv}CSiH_3$$

$$SiH_2\!: + MeOH \overset{7}{\rightleftharpoons} MeOSiH_3$$

Experimental Section

Silylene was generated through the thermal decomposition of disilane. Since activation energies of the trapping reactions (reactions 3, 6, and 7) are expected to be small and their differences to be even smaller, relative rate studies over as large a temperature range as possible were desirable. To this end, two kinetic methods were employed: stirred flow for the lower temperatures ($T \approx 700$ K) and single pulse shock tube for the higher ($T \approx 1000$ K). The general design and modes of operation for these systems have been described.[19,20] Compositions of the reaction mixtures and other reaction data are summarized in Table III. Reaction rates were monitored in terms of product formation: sila-3-cyclopentene (SCP) for the butadiene trapping reaction, methoxysilane (MeOS)

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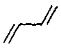
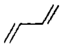
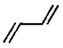
Table II. Arrhenius Parameters and Activation Energies for $:SiH_2$ Reactions

A. Relative Arrhenius Parameters

T(range), K	x[a]	A_x/A_y	$(E_x - E_y)$, cal	y[b]	ref
572–610	$MeSiH_3$	0.46	–794	Si_2H_6	12
572–610	Me_2SiH_2	0.35	–498	Si_2H_6	12
572–610	Me_3SiH	0.15	–1244	Si_2H_6	12
578–607	Si_2H_6	1.41	–910	SiH_4	16
578–607	H_2	0.25	4200	SiH_4	16
658–733	$MeSiH_3$		0	SiH_4	6
658–733		5.56	2600	SiH_4	6
697–1016		370	5846	CH_3OH	this work
603–1032	HC≡CH	0.22	–712		this work

B. Activation Energies for Silylene Reactions

reactants	E_{act}, kcal/mol	temp, K	ref
Me_2Si: + HCl	6.6	423–478	14
Me_2Si: + Me_3SiH	≤0.2	413–510	14
$:SiH_2$ + HCl	≤1.3	295–414	15

[a] The reaction being monitored is $:SiH_2$ + x. [b] The reference reactions: ($:SiH_2 + y \rightarrow$) are $:SiH_2 + Si_2H_6 \rightleftharpoons Si_3H_8$ and $:SiH_2 + SiH_4 \rightleftharpoons Si_2H_6$.

Table III. Reaction Mixtures and Reaction Conditions

	Acetylene vs. 1,3-Butadiene
stirred-flow mixture (in argon)	14.73% acetylene, 7.16% disilane, 14.73% butadiene
stirred-flow conditions	reaction time = 2.0–8.5 s; total reaction pressure = 5.9 ± 1.7 torr
shock-tube mixtures (in argon)	5.12% acetylene, 1.03% disilane, 5.14% butadiene
shock-tube conditions	reaction time = 305–352 μs; reaction pressure = 2963 ± 61 torr
	Methanol vs. 1,3-Butadiene
stirred-flow mixture (in argon)	9.97% methanol, 2.01% disilane, 2.02% butadiene
stirred-flow conditions	reaction time = 50–100 s; total reaction pressure = 7.5 ± 0.5 torr
shock-tube mixture (in argon)	7.00% methanol, 0.18% disilane, 0.46% butadiene
shock-tube conditions	reaction time = 264–363 μs; reaction pressure = 2750 ± 200 torr

for the methanol trapping reaction, and ethynylsilane (ES) for the acetylene trapping reaction. No other significant trapping products were observed under our reaction conditions.

Product analyses were made on a Varian 3700 FID gas chromatograph equipped with a Hewlett-Packard 3390 A integrator. A porapak N (150/200 mesh, 1/8 in. × 4 ft) column was used in the acetylene vs. 1,3-butadiene studies and a Squalene (80/100 mesh, 1/8 in. × 10 ft) column was used in the methanol vs. 1,3-butadiene studies. Although the latter column effected the best separation of MeOS of many columns tried, errors in MeOS analyses were still large as MeOS appeared as a leading shoulder on the disilane peak. Authentic samples of the trapping products were synthesized and identified by mass spectroscopy (Hitachi Perkin-Elmer RMU-6) and infrared spectroscopy (Perkin-Elmer 337). Retention times on the Varian 3700 GC were reproducable to 0.10 min; hence proper identification of the products was assured. Trapping product thermal stabilities were examined by running argon diluted mixtures under stirred-flow and shock reaction conditions. The SCP and MeOS products were found to be quite stable. However ES was found to be somewhat unstable under stirred-flow conditions (but not shock conditions), and corrections for its subsequent decomposition had to be made (see Table V). To this end, a complete kinetic study of the ethynylsilane pyrolysis was made and will be reported in a subsequent paper.

Results and Discussion

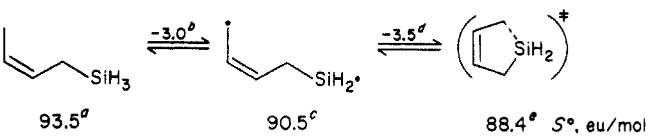
Methanol vs. 1,3-Butadiene. The only trapping products observed were sila-3-cyclopentene (SCP, from reaction 3) and methoxysilane (MeOS, from reaction 7). Therefore reactions 3 and 7 appear to be exclusive reaction pathways under our conditions. Results of the stirred-flow and shock-tube relative rate studies for methanol vs. 1,3-butadiene are given in Table IV. The relative trapping

Table IV. Relative Rate Data on $:SiH_2$ Trapping by Butadiene and Methanol

T, K	(SCP/MeOS)[a]	$[MeOH]/[C_4H_6]$[b]	(k_3/k_7)	Y(SCP)[c]	Y(MeOS)[c]
		Stirred Flow			
698.5	0.587	10.2	5.99	0.065	0.111
696.7	0.579	10.2	5.91	0.073	0.126
699.2	0.430	10.5	4.52	0.063	0.147
698.4	0.470	11.0	5.17	0.060	0.128
		Shock Tube			
977	1.51	15.6	23.6	0.185	0.123
978	2.02	15.6	31.5	0.340	0.168
987	1.09	16.2	17.7	0.227	0.208
1003	1.15	15.4	17.7	0.154	0.134
1000	0.96	15.9	15.3	0.297	0.303
1016	0.89	16.1	14.3	0.309	0.340
1011	1.21	16.4	19.8	0.448	0.370

[a] These are mole ratios where SCP is sila-3-cyclopentene, $\overline{CH_2C(H){=}CHCH_2SiH_2}$, and MeOS is methoxysilane, CH_3OSiH_3. [b] Average trapping reactant concentrations. [c] Product yields are moles of products per mole of disilane decomposed, which assumes one $:SiH_2$ for each Si_2H_6 reacted.

Scheme III



[a] Intrinsic entropy of the model compound obtained from group additivities.[22] [b] Entropy loss due to the restriction of rotation due to resonance development in the biradical and the loss of two H atoms. [c] Intrinsic entropy of the biradical. [d] Entropy loss due to internal rotation restriction on movement to the transition state. [e] Real entropy of the transition state correcting for optical activity ($n^{\ddagger} = 2$).

rate constant ratios (k_3/k_7) shown in column 4 were calculated in the usual fashion from eq I utilizing the product

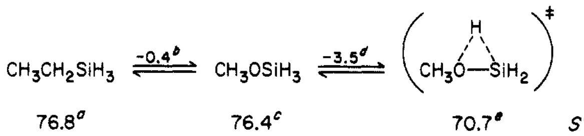
$$k_3/k_7 = ([\mathrm{SCP}]/[\mathrm{MeOS}])\,(\overline{[\mathrm{MeOH}]/[\mathrm{butadiene}]}) \qquad \text{(I)}$$

mole (or yield) ratios (column 2) and the average trapping reactant concentration ratios (column 3). The latter differ from the initial reactant ratios, particularly in the stirred-flow studies, because 1,3-butadiene polymerized significantly during the course of reaction. Under shock-tube reactions conditions, 1,3-butadiene loss by this route was much reduced. [Butadiene loss is accompanied by very small yields of C_2H_2 and C_2H_4. No other gaseous products are observed; hence the loss is mainly due to polymerization.] A least-squares Arrhenius analysis of the rate constant ratios gives

$$\ln (k_3/k_7) = 5.91 \pm 0.91 - (5849 \pm 1529)\ \mathrm{cal}/RT$$

where the errors shown represent the 95% confidence level. The results of the methanol vs. 1,3-butadiene studies indicate a substantial activation energy for trapping of :SiH_2 by butadiene. Surprising as this result may appear, it nevertheless agrees with absolute rate constant measurements of Gaspar[5] on analogous reactions of phenylmethylsilylene. At 25 °C, PhMeSi: reacts with 2,3-dimethylbutadiene and ethanol with rate constants of $k'_3 = (2 \pm 1) \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$ and $k'_7 = (8 \pm 5) \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ (see Table IA). Thus at 25 °C, $k'_3/k'_7 = 2.5 \times 10^{-2}$, extrapolating our results to 25 °C gives $k_3/k_7 = 1.90 \times 10^{-2}$. If one assumes that steric and energy effects roughly cancel in the two diene/alcohol silylene trapping studies, which seems reasonable, then using Gaspar's rate constant ratio $k'_3/k'_7 = 2.5 \times 10^{-2}$ (25 °C) along with the data of Table IV in an extended Arrhenius treatment considerably reduces the errors in the Arrhenius parameters. Thus one obtains, $\ln (k_3/k_7) = (5.78 \pm 0.35) - (5620 \pm 451)$. These parameters and errors have been adopted in the subsequent treatment.

Scheme IV



[a] Intrinsic entropy from group additivities.[22] [b] Entropy loss due to H atoms on replacement of O for CH_2 group. [c] Intrinsic entropy of the ether. [d] Entropy loss due to internal rotation restriction. [e] Real entropy including symmetry of 3. [f] Entropies are in eu/mol based on the 1 atom standard state.

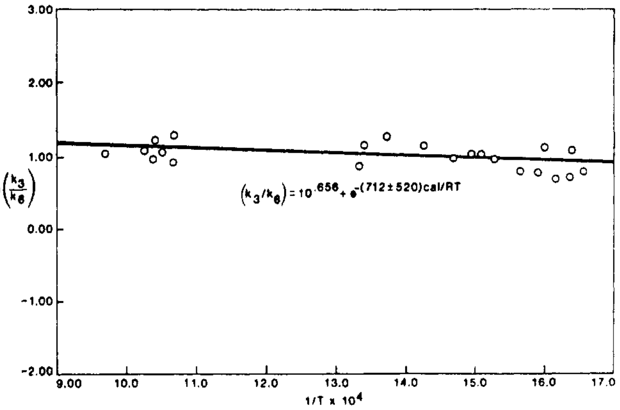
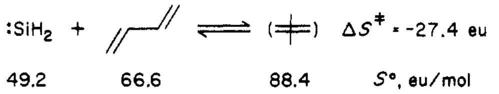


Figure 1. Arrhenius plot of comparative rate of silylene trapping by acetylene vis. 1,3-butadiene.

The *A* factor for trapping by methanol is expected to be in the "normal" range; therefore, $A_3/A_7 = 323$ indicates a surprisingly high *A* factor for trapping by 1,3-butadiene. Standard thermochemical estimates[21] of A_3 and A_7, however, shows that this experimental result is not unreasonable. Thus, assuming the "loose" transition-state biradical consecutive step mechanism verified by Gaspar for 1,3-diene trapping,[4] a transition-state entropy of $S°(\ddagger) = 88.4$ eu/mol can be estimated by the difference method[21] starting from the model compound *cis*-2-butenylsilane with $S°(\mathrm{model}) = 93.5$ eu/mol (see Scheme III). Then for the activation process at 25 °C



$A_3 = (ekT/h)e^{\Delta S^{\ddagger}/R}eR'T = 10^{9.1 \pm 0.3}\ \mathrm{M^{-1}\ s^{-1}}$. Similarly, for the silylene trapping by methanol (reaction 7) using $CH_3CH_2SiH_3$ as the model compound, one obtains $S°(\ddagger) \approx 70.7$ eu/mol (see Scheme IV), and this gives for the (reaction 7) activation entropy at 25 °C, $\Delta S^{\ddagger}_7 = -35.8$ eu (see below). Hence

$$\begin{array}{lllll} :SiH_2 & + \ CH_3OH & \rightleftharpoons & (\ddagger) & \Delta S^{\ddagger}_{25\,°C} = -35.8\ \mathrm{eu} \\ 49.2 & 57.3 & & 70.7 & S°,\ \mathrm{eu/mol} \end{array}$$

$A_7 = (e^2kT/h)(R'T)e^{\Delta S'^{\ddagger}/R} = 10^{7.2 \pm 0.3}\ \mathrm{M^{-1}\ s^{-1}}$ at 25 °C. The thermochemical estimate of the *A* factor ratio in ln form is therefore, $\ln (A_3/A_7) = 4.4 \pm 1.4$, which agrees with the experimental value within the estimate errors. The outside limits of the *A* factor estimates give agreement with the experimental values, and we have adopted those values: thus $A_3 = 10^{9.41}\ \mathrm{M^{-1}\ s^{-1}}$ and $A_7 = 10^{6.9}\ \mathrm{M^{-1}\ s^{-1}}$. It should be noted that while the *A* factors and activation energies of both trapping reactions will, by transition-state theory, increase with temperature, the *A* factor ratios and activation energy differences should remain relatively constant. [*A* factor in $\mathrm{M^{-1}\ s^{-1}}$ units increase with T^2 even without $\Delta C^{\ddagger}_p$ increases, and activation energies increase as $2RT$. Changes will occur if $\Delta(\Delta C^{\ddagger}_p) \neq 0$. However, differences in activation heat capacities should be small for these reactions.]

Acetylene vs. 1,3-Butadiene. The only trapping products observed in the competitive trapping of silylene by acetylene and 1,3-butadiene were ethynylsilane (ES, reaction 6) and silacyclopentene. Kinetic results are shown in Table V. The trapping rate constant ratios (k_3/k_6) were obtained from eq II, where the factor $(1 + k_{\mathrm{ES}}t_{\mathrm{res}})$ corrects for the subsequent decomposition of ethynylsilane (see Appendix I).

$$k_3/k_6 = \frac{([\mathrm{SCP}]/[\mathrm{ES}])(\overline{[C_2H_2]/[C_4H_6]})}{(1 + k_{\mathrm{ES}}t_{\mathrm{res}})} \qquad \text{(II)}$$

The Arrhenius plot of the rate constant ratios (k_3/k_6) is shown in Figure 1, and least-squares treatment of these data give

$$\ln (k_3/k_6) = (1.51 \pm 0.32) - (712 \pm 520)\ \mathrm{cal}/RT$$

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Table V. Acetylene vs. 1,3-Butadiene Trapping of $:SiH_2$

Stirred-Flow Data

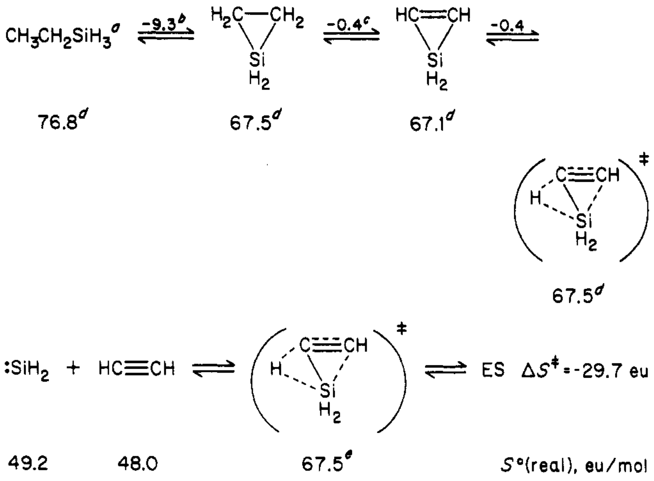
T, K	([SCP]/[ES])[a]	($[C_2H_2]/[C_4H_6]$)[b]	($1 + k_{ES}t_{res}$)[c]	Y(SCP)[d]	Y(ES)[d]	k_3/k_6[e]
627.7	2.218	1.052	1.09	0.366	0.165	2.140
603.1	2.301	1.076	1.12	0.140	0.060	2.211
624.6	3.168	1.056	1.08	0.287	0.091	3.097
618.4	1.950	1.084	1.09	0.112	0.057	1.939
609.4	3.317	1.090	1.21	0.181	0.054	2.988
610.1	2.289	1.070	1.20	0.121	0.052	2.041
638.6	2.233	1.105	1.12	0.161	0.071	2.203
654.0	2.380	1.111	1.07	0.137	0.057	2.471
661.8	2.817	1.116	1.11	0.128	0.045	2.832
667.6	2.872	1.106	1.14	0.169	0.058	2.786
680.7	2.817	1.132	1.20	0.130	0.046	2.657
700.8	3.322	1.131	1.16	0.216	0.064	3.239
728.3	3.879	1.183	1.22	0.246	0.063	3.761
756.4	4.353	1.247	1.56	0.297	0.067	3.480
749.1	4.439	1.249	1.90	0.299	0.066	2.918
745.7	4.214	1.215	1.45	0.149	0.035	3.531

Shock-Tube Data

T, K	([SCP]/[ES])[a]	($[C_2H_2]/[C_4H_6]$)[b]	k_3/k_6[f]
935.5	3.575	1.021	3.650
937.5	2.520	1.005	2.533
951.5	2.887	0.998	2.881
960.6	3.541	0.982	3.477
962.5	2.623	0.993	2.605
975.6	3.081	0.961	2.961
976.6	3.125	0.967	3.022
1032	3.004	0.950	2.854

[a] Product mole ratios: SCP is $\overline{CH_2C(H){=}CHCH_2Si}H_2$ and ES is ethynylsilane ($HC{\equiv}CSiH_3$). [b] Average trapping reactant ratios (acetylene/1,3-butadiene). [c] Correction for ES subsequent decomposition (see Appendix I). [d] Trapping product yields based on disilane loss. [e] k_3/k_6 = (mol of SCP/mol of ES) ($[C_2H_6]/[C_4H_6]$)($1/(1 + k_{ES}t_{res}$). [f] $k_{ES}t_{res} \ll 1.0$ in the shock tube runs, therefore no correction for subsequent decomposition of ES was needed.

Scheme V



[a] Model compound for difference method estimation. [b] Entropy loss in cyclization (see ref 21). [c] Entropy loss for ring unsaturation. [d] Intrinsic entropy. [e] For the transition state $n^\ddagger = 1$, $\sigma = 1$.

Hence, $A_3/A_6 = 4.53$ and $(E_3 - E_6) = 712 \pm 520$ cal. Using our deduced absolute Arrhenius parameters for butadiene trapping to silacyclopentene, the above gives for acetylene trapping to ethynylsilane $A_6 = 10^{8.75}(T/298)^2$ M^{-1} s^{-1} and $E_6 = (2507 + 2RT) \pm 1790$ cal. The above A factor compares quite well with transition-state estimates. Thus, by the difference method,[21] the activation entropy is estimated to be $\Delta S_6^\ddagger = -29.7$ eu at 25 °C (see Scheme V); hence A_6(estimated) $\approx 10^{8.6\pm0.3}$ M^{-1} s^{-1}.

Mechanism of Silylene Trapping by Acetylene. When silane is pyrolyzed in the presence of acetylene at relatively low temperatures and high concentrations, the products are ethynylsilane, ethylene, vinylsilane, ethynylvinylsilane, and ethynyldivinylsilane.[23] The most reasonable mechanism for the reaction under these conditions is shown in Scheme VI From the static system product yields and rates of formation it is clear that vinylsilylene production is the favored mode of silacyclopropene decomposition (i.e., $k_a > k_b \approx k_c$; $k_{a'} > k_{b'}$). This probably remains true at stirred-flow and shock reaction temperatures as well; however, the VSiH and V_2Si: prod-

Scheme VI

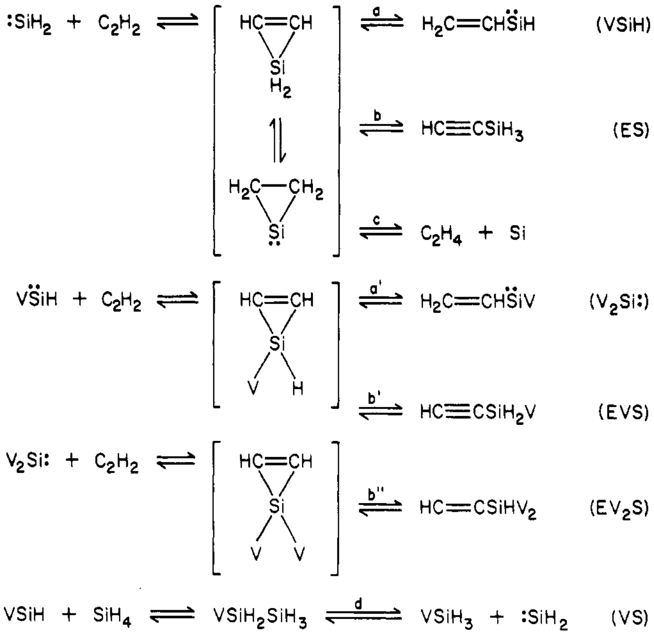


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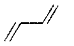
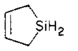
Table VI. Measured and Recommended Arrhenius Parameters for Silylene Reactions

reaction (:SiH_2 + X)			T = 298 K			
X			A,[a,b] M^{-1} s^{-1}	E,[b] cal	$\Delta H^{\ddagger}_{298}$, cal	notes
SiH_4	$\xrightarrow{2}$	Si_2H_6	$10^{8.66}$	1803	618	*c*
	$\xrightarrow{3}$		$10^{9.41}$	4403	3218	*a*
Si_2H_6	$\xrightarrow{4}$	Si_3H_8	$10^{8.81}$	893	−292	*d*
Me_3SiH	$\xrightarrow{5}$	SiH_3SiMe_3	$10^{7.99}$	−356	−1536	*d*
$HC{\equiv}CH$	$\xrightarrow{6}$	$HC{\equiv}CSiH_3$	$10^{8.75}$	3691	2506	*a*
CH_3OH	$\xrightarrow{7}$	CH_3OSiH_3	$10^{6.90}$	−1217	−2402	*b, e*
$MeSiH_3$	$\xrightarrow{8}$	SiH_3SiH_2Me	$10^{8.47}$	99	−1086	*d, g*
Me_2SiH_2	$\xrightarrow{9}$	SiH_3SiHMe_2	$10^{8.35}$	395	−790	*c*
H_2	$\xrightarrow{10}$	SiH_4	$10^{8.06}$	6003	4818	*c, f*

[a] Estimated errors in A are the errors reported in the various relative rate studies times two (i.e., the estimated error in A_7). [b] Assuming $\Delta C^{\ddagger}_p \approx 0$, the Arrhenius parameters have the following temperature dependence: $A_T = A_{298}(T/298)^2$ and E_T, $= \Delta H^{\ddagger}_{298} + 2RT$. [c] Based on the relative rate data of Table IIA. [d] Based on results of this study. [e] Reference reaction (see text). [f] This reaction is in the fall off (pressure dependent region). High-pressure Arrhenius parameters are higher. $E_\infty \approx 10.3$ kcal and log A_∞ (M^{-1} s^{-1}) ≈ 10.3.[25] [g] Preferred parameters are log $A_{25\,°C} = 9.25$, E (cal) = 1160, and $\Delta H^{\ddagger}$(cal) = −25.

ucts (VS, EVS, and EV_2S) are not formed under our reaction conditions because the RSi–H and C_2H_2 concentrations are too low (stirred-flow studies have $[C_2H_2] \approx 10^{-6}$ M) in the stirred-flow reactor and the VSiH concentrations are too low in the shock tube system. [The reaction :SiH_2 + $C_2H_2 \rightleftharpoons H_2C{=}CHSiH$ is exothermic by 53.1 kcal; therefore the VSiH concentration decreases rapidly with temperature.] Thus the silacyclopropene $\overset{a}{\rightleftharpoons}$ vinylsilylene equilibrium at shock temperatures is essentially displaced by reaction of silacyclopropene via reaction b to ES. Formation of ES is not totally exclusive, however, since reaction c (to ethylene) must compete with reaction b (to ES). We are presently unable to determine the degree of this competition since, while ethylene is an observed product, it is also produced in the background decomposition of butadiene. The silylene–acetylene trapping rate constants reported here, then, are lower limiting values for overall acetylene trapping. As a measure of the latter they should not be in error by more than a factor of 2 since $k_b \approx k_c$.

Absolute Arrhenius Parameters of Silylene Reactions (See Note Added in Proof). It would be advantageous to have absolute Arrhenius parameters for silylene trapping reactions; however, no absolute rate constants exist for :SiH_2. From the absolute rate constant measurements of PhMeSi:[5] and MeSi:[9] with alcohols we note a factor of 4 increase for the latter which can reasonably be assigned to a decrease steric effect. Assuming another factor of 2 increase in moving from Me_2Si: to :SiH_2 gives $k_7 = 6.2 \times 10^7$ M^{-1} s^{-1}. This value should be accurate to at least a factor of 2 or 3. Coupled with the adopted $A_7 = 10^{6.9}$ M^{-1} s^{-1}, this value of k_7 gives $E_7 = -1217 \pm 800$ cal at 25 °C. This in turn establishes an absolute value for the activation energy and A factor of 1,3-butadiene trapping of silylene of $E_3 \approx 4403 \pm 1270$ cal and $A_3 = 10^{9.41\pm0.6}$ M^{-1} s^{-1} at 25 °C. [These parameters give $\Delta H^{\ddagger}_3 = 3853$ cal and $\Delta S^{\ddagger}_{p(3)} = -24.16$ eu/mol at 25 °C.] At elevated temperatures, assuming $\Delta C^{\ddagger}_{p(3)} \approx 0$, the butadiene trapping parameters for silacyclopentene formation become $k_3(M^{-1}\ s^{-1}) = 10^{9.41}\ (T/298)^2 e^{-(3218+2RT\pm1270)\mathrm{cal}/RT}$. Using these parameters for reaction 3 and the relative Arrhenius parameters of Table II, a self-consistent list of absolute Arrhenius parameters for silylene reactions with a number of substrates has been generated. [Note that the reference reaction for this tabulation is reaction 7. Even though this reaction has not been directly measured, it is unlikely that the estimated k_7, A_7, and E_7 are in error by more than factors of 2, 2, and ±820 cal, respectively. No other silylene reaction at this time is better characterized, including the silylene–silane reaction.] The parameters are shown in Table VI, and they are in fair agreement with most presently accepted values. Thus for the :SiH_2 + $SiH_4 \overset{2}{\rightleftharpoons} Si_2H_6$ reaction (perhaps the most common experimental reference reaction) the Table VI predicted A factor at disilane decomposition temperatures (T = 650 K) is $A_2 = 10^{9.33}$ M^{-1} s^{-1}, well within the errors of the $10^{9.45}$ M^{-1} s^{-1} value calculated from the experimental A_{-2} and the reaction entropy. [From ref 23, $A_{-2} = 10^{14.52}$ s^{-1}, and from the thermochemistry, $\Delta S°_{3(650K)} \approx -33.1$ eu/mol for $p = 1.0$ atm.] On the other hand, the predicted activation energy of E_2 = 3200 cal at 650 K is 1.9 kcal higher than the generally accepted value of 1.3 kcal.[16] Since the latter was obtained by a flawed method,[24] there is no reason not to accept the higher value. The calculated activation energy for silylene insertion into trimethylsilane (reaction 5) is quite low (E_5 = 292 cal, 460 K), in excellent agreement with a 0.2-kcal value reported by Davidson[14] for the analogous reaction with :$SiMe_2$. Also, the predicted $(E_3 - E_5)$ = 4.8 kcal agrees reasonably well with an estimate of 6.0 kcal obtained by us from a modeling analysis of comparative rate shock data for these reasons.[8] [Results to be published in part 2.]

For the series of H_2Si: insertions into SiH_4, $MeSiH_3$, Me_2SiH_2, and Me_3SiH (see Table VI), while the A factors follow a logical sequence according to reaction path degeneracies, the activation energies show an anomalously low value for $MeSiH_3$. Thus the activation energies in calories at 25 °C are for the above series 1803, 99, 395, and −351, respectively. Present data for the silylene eliminations from Si_2H_6 (log A = 14.50), $MeSiH_2SiH_3$[25] (log A = 15.28), and Me_3SiSiH_3[10] (log A = 14.48) indicate that the A factor for :SiH_2 insertion into $MeSiH_3$ should not be "well behaved" but rather should be correspondingly out of line by about a factor of 6. If this adjustment is made to the Table VI values, one obtains log $A_{8(298K)} = 9.25$ M^{-1} s^{-1} and $E_{8(298K)}$ = 1160 cal. These adjusted parameters, we believe, are preferable as they generate a more reasonable activation energy sequence while consistancies with their reverse reaction kinetics are maintained. The upward adjustment of roughly 1100 cal is within the errors of the original relative rate measurement.[12]

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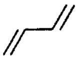
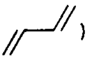
Appendix I

Reactions influencing the ES and SCP yields are

$$:SiH_2 + HC\equiv CH \overset{6}{\rightleftharpoons} ES \xrightarrow{7} \text{other products}$$

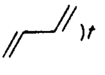
$:SiH_2 +$  $\xrightarrow{3} SCP$

Therefore, $d(ES)/dt = k_6(:SiH_2)(HC\equiv CH) - (k_{-6} + k_7)(ES)$

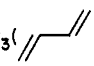
$d(SCP)/dt = k_3(:SiH_2)($  $)$

Integrating for the stirred-flow condition with $(k_{-6} + k_7) = k_{ES}$ gives

$[ES] = k_6(:SiH_2)(HC\equiv CH)t - k_{ES}[ES]t$

$[SCP] = k_3(:SiH_2)($  $)t$

From the ratio of the above one obtains

$[ES](1 + k_{ES}t)/[SCP] = k_6(HC\equiv CH)/k_3($  $)$

which rearranges to eq II.

Note Added in Proof. Serious questions were raised[26,27] concerning the reliability of some of the solution-phase absolute rate constants used as the basis for the absolute Arrhenius parameters suggested here. Any subsequent adjustments in these reference values will, of course, require corresponding changes in the Table VI values. The situation is further confused by some recent absolute[28] and relative rate constant measurements[29] of silylene reactions which suggest much higher values than those formerly accepted or those recommended here. An early resolution of these problems is not imminent. However, use of the Table VI parameters in modeling or in mechanistic prediction can still be made with confidence as such processes only require reliable relative rate constant input data.

Registry No. $:SiH_2$, 13825-90-6; Si_2H_6, 1590-87-0; 1,3-butadiene, 106-99-0; acetylene, 74-86-2; methanol, 67-56-1.

Mechanism of Thermal Decomposition of Bis(tricyclopentylphosphine)platinacyclopentane(II): Intramolecular β-Hydride Elimination from the Platinacyclopentane Ring Is Slow Relative to an Intermolecular Chain Reaction Involving Hydridoplatinum Intermediates[1]

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Received January 29, 1986

The thermal decomposition of bis(tricyclopentylphosphine)platinacyclopentane(II) (1) in cyclohexane yields 1-butene and bis(tricyclopentylphosphine)platinum(0) (2) as the major products. Minor hydrocarbon products include (*Z*)- and (*E*)-2-butenes, butadiene, *n*-butane, and cyclopentene. Decomposition is first order in 1 for initial concentrations of 1 < 15 mM; at higher initial concentrations of 1 decompositions proceed more slowly and deviate from first order. This deviation appears to be due to inhibition by 2. Decomposition is slowed by added 2 and by added tricyclopentylphosphine (L). Deuterium-labeling experiments suggest that two pathways are important in these decompositions. One involves *intermolecular* transfer of hydrogen atoms: this process appears to be a chain reaction involving reduction of the carbon–platinum bond of the platinacyclopentane moiety by a reactive hydridoplatinum species. The second involves incorporation of hydrogen from tricyclopentylphosphine into the 1-butene and probably involves initial cyclometalation. This latter process may be important, inter alia, in initiating the hydride chain reaction. A mechanism involving β-hydride elimination directly from the platinacyclopentane group is not important. Free alkyl radicals also do not seem to be intermediates in these reactions.

Introduction

The objective of this paper is to rationalize the high stability of platinacycloalkanes using a bis(trialkylphosphine)platinacyclopentane as a representative. Metallacycles are important intermediates in several homogeneous transition-metal-catalyzed reactions, including olefin metathesis,[2-9] isomerization of strained carbocyclic rings,[10,11] and cyclotrimerization of acetylenes.[12-14] They are undoubtedly also involved in heterogeneous metal-

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[1] Supported by the National Science Foundation (CHE 82-05143 and CHE 85-08702).

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