2596 *Organometallics* 1987, *6*, 2596-2600

Kinetics of *sec*-Butylsilylene Isomerization to 2,3-Dimethylsilacyclopropane and the Decomposition and Isomerization Kinetics of 2,3-Dimethylsilacyclopropane

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Received April 29, 1987

Silylene, generated from the thermal decomposition of silane between 643 and 689 K, reacts with 1-butene to produce *n*-butyl- and *sec*-butylsilane and *cis*- and *trans*-2-butene. The mechanism of the reaction involves butylsilylene and silacyclopropane intermediates. *sec*-Butylsilylene isomerizes to 2,3-dimethylsilacyclopropane with an activation energy of $E_{21} = 11.6 \pm 2.6$ kcal, while the activation energy for the decomposition of 2,3-dimethylsilacyclopropane (to 2-butenes and silylene) is significantly higher than the activation energy for its back reaction to *sec*-butylsilylene, $(E_{22} - E_{-21}) = 11.5 \pm 0.5$ kcal. Further, the decomposition of the silacyclopropane is several times faster than its isomerization, $k_{22}/k_{-21} \approx 5$, indicating a high A factor and consecutive step, biradical mechanism for the decomposition. The relative rate of SiH_2 trapping by 1-butene and silane (643–689 K) was found to be $k_{18}/k_{17} = 2.1$, from which an absolute value of $k_{18} = 10^{11.1}$ M^{-1} s^{-1} for the rate constant of silylene trapping by 1-butene is deduced.

Introduction

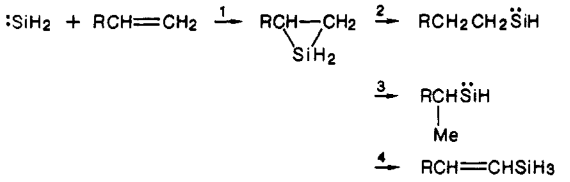
It is now known that silylenes react with olefins to produce alkylsilanes and vinylsilanes and that the dominant products of these reactions are determined by the reaction conditions: high reactant pressures and low temperatures favor alkylsilanes; low reactant pressures and high temperatures favor vinylsilanes.[1] The proposed mechanism of reaction (illustrated in Scheme I) involves the addition of silylene to the olefin to produce a silacyclopropane intermediate which then ring opens to an alkylsilylene or to a vinylsilane. Back reactions of these processes (namely, alkylsilylene[2] and vinylsilane[3] decompositions to olefin and silylene) have also been studied and are consistent with this mechanistic interpretation. Thus the observation of small yields of vinylsilane in the ethylsilylene decomposition[4] firmly supports the intermediacy of silacyclopropane in the decomposition.

Alkylsilylenes with R groups larger than ethyl can decompose to more than one olefin product. Thus the shock-induced decomposition of propylsilane[5] (between 1100 and 1240 K) produced, via the subsequent reactions of propylsilylene, ethylene as well as propylene (C_2H_4/C_3H_6 = 0.29), and the shock-induced decomposition of butylsilane[6] (1100–1250 K), via the subsequent reactions of butylsilylene, produced ethylene, propylene, 1-butene, *cis*- and *trans*-2-butene, and silacyclopentane. These observations are best explained in terms of competing intramolecular C–H bond insertions processes as shown in Scheme II.

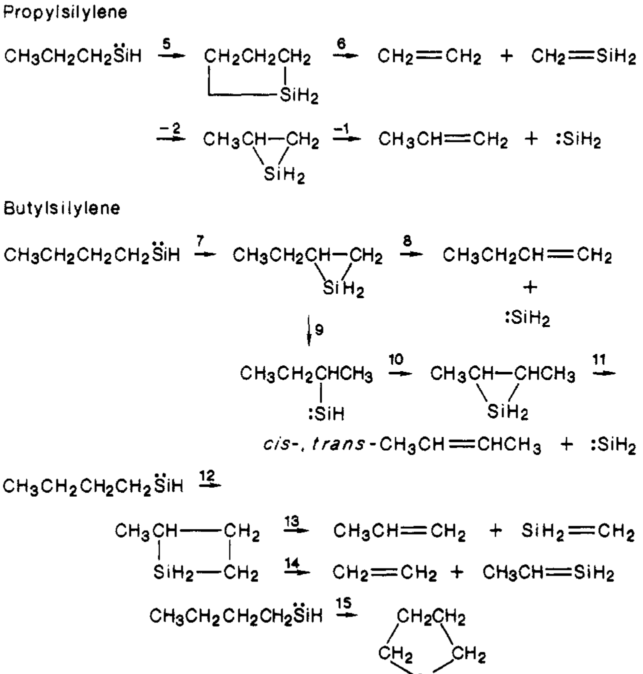
From the product yields of the *n*-butylsilylene decomposition, the relative rates of these intramolecular insertion processes were estimated to be (T_{mean} = 1170 K): $k_{\text{3-center}}/k_{\text{4-center}}/k_{\text{5-center}} = 1.08/0.32/1.0$.

Studies on the decompositions of long-chain alkylsilylenes at lower temperatures suggest that the intramolecular four- and five-membered ring forming reactions of

Scheme I



Scheme II



silylenes (reactions 5, 12, 15) may have significantly higher activation energies than their three-membered ring forming counterparts. Thus deuteriated propylsilylene and methylbutylsilylene (PrS̈iD and *n*-BuS̈iMe, generated respectively by flash vacuum pyrolysis of $PrSiD_2SiMe_3$[7] and $Me_3SiSi(OMe)(Me)Bu$[7] at 980 K produced only the three-membered cyclization products (i.e. propylene but not ethylene from PrS̈iD and 1- and 2-butenes but not propylene or methylsilacyclopentane from BuS̈iMe). Also

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(1) Rogers, D. S.; Walker, K. L.; Ring, M. A.; O'Neal, H. E. *Organometallics*, in press.

(2) Ring, M. A.; O'Neal, H. E.; Rickborn, S. F.; Sawrey, B. A. *Organometallics* **1983**, *2*, 1891.

(3) Rickborn, S. F.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1984**, *16*, 289.

(4) Rickborn, S. F.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1984**, *16*, 1371.

(5) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey, D., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 801.

(6) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1987**, *6*, 720.

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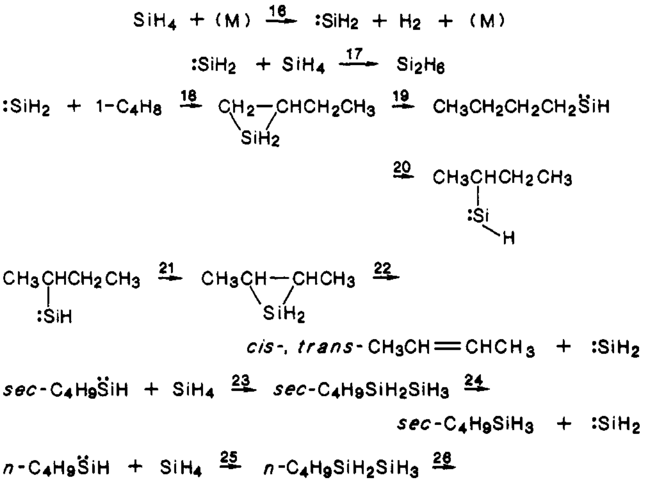
Scheme III



significant was the 60% deuteriation found in the propylene product of the PrS̈iD decomposition. This indicates that H–D exchange (via three-membered-ring formation at 980 K) occurs prior to and competes with the silacyclopropane decomposition.

The objective of the present study was to generate a long-chain silylene by a method other than direct pyrolysis and then to study its elementary reaction pathways and kinetics. The intention was to obtain kinetic data for intramolecular cyclization reactions of long-chain silylenes.

Experimental Section

Silylene, generated by the pyrolysis of silane at temperatures between 643 and 689 K, was reacted with 1-butene (as in Scheme I) to produce *n*-butyl- and *sec*-butylsilylenes. Several reaction mixtures were employed with compositions roughly given by 85% silane, 13% 1-butene, and 2% tetramethylsilane. The latter served as an internal GLC standard. Reactions were carried out in a 150-mL quartz reactor immersed in a resistively heated air oven whose temperature was controlled to ±0.1 °C during any given run by a Bayley 124 controller. Product analyses were made on a $^1/_8$ in. × 24 ft stainless-steel column packed with 20% squalene on Supercoport operated at ambient temperatures with a Carle Instrument's TC chromatograph (Model 8500) in conjunction with a Hewlett-Packard 3380-A digital integrator. Products were identified on the basis of GLC retention time comparisons with authentic samples.

Results

Products of the pyrolysis of silane in the presence of 1-butene (temperature range 643.4–689.1 K, pressure range 30–202 torr) were disilane, *n*-butylsilane, *sec*-butylsilane, and *cis*- and *trans*-2-butene. Relative product yields of the butylsilanes and 2-butenes were essentially constant with percent conversion, total pressure, and temperature [(n-BuSiH$_3$/*sec*-BuSiH$_3$) ≈ 0.237 ± 0.003 and (*cis*-2-butene/*trans*-2-butene) ≈ 1.65 ± 0.05] although there appeared to be a slight downward trend in the latter ratio with increasing temperature. Scheme III is the proposed mechanism of reaction.

Note that ethylene, silacyclobutane, and silacyclopentane were not observed products and that there was no evidence for butylsilylene four- and five-membered-ring cyclizations under the relatively low-temperature conditions of these studies. This is in agreement with the flash pyrolysis results.[7]

Products of reaction can also be explained by a free radical mechanism. Thus addition of •SiH$_3$ radical to the π bond of 1-butene, followed by H-abstraction of the product radical (from silane), would lead to the butylsilane products observed. Also, H-abstraction from the allylic position in 1-butene, followed by π-bond migration and elimination of the adduct radical, is a possible route to the observed 1-butene isomerizations to cis- and trans-2-butene. However, it has already been shown that free radicals are not involved in the reactions of the silane decomposition when carried out in the presence of 1-butene and 1-pentene.[8] Thus, as pointed out previously, at silane pyrolysis temperatures, decompositions of the silyl radical–butene adducts (expected as intermediate products in the free radical production of butylsilanes) must compete with their H-abstraction reactions. Thus these radical adducts, if formed, must also lead to the productions of methane and ethane. Since neither product was observed in this or the former study,[8] one must conclude that the products of this study are not produced by free radical reactions.

Table I. SiD$_4$-Induced Isotopic Labeling in Product Butenes[a,b]

species	1-butene		*cis*-2-butene		*trans*-2-butene	
m/e[c]	normal	product	normal	product	normal	product
58	<1	10–14	1	15	1	20–15
57	9	24	3	28	5	33
56	100	22–50	60	26	50	30
43	3–15	40–70	7	30–50	2–11	50
42	20	78–100	10	80–90	8	90
41	5–100	100–78	100	100	100	100

[a] Analyses were made on a Finnigan 3000 GC–MS. [b] Relative signal heights of the mass spectra with the largest signal assigned a value of 100. [c] The m/e parent peak of a butene is 56; m/e 41 corresponds to the loss of one methyl group.

The possibility of surface catalysis, particularly toward the 1-butene isomerization reactions, was also checked. Thus parallel pyrolyses of the SiH$_4$–1-butene reaction mixture (83% SiH$_4$/14% 1-C$_4$H$_8$/3% TMS) were made at 466.4 K in an unpacked and packed reactor (S/V ≈ 10). The percent isomerizations, measured in terms of the yield ratios (*cis*- + *trans*-2-butene)/($\sum$butenes), were found to be the same within experimental error for the two reactors.

Finally, as an additional test of mechanism, studies of the silylene–1-butene reaction using SiD$_4$ as reactant were made to see if deuterium incorporation into the butene reactant and products would occur. According to Scheme III, single D incorporation in the 2-butene products is required (via reaction 20) *and double incorporation of D is possible* (*via reactions –20 and 20 prior to decomposition*). If 2-butene formation proceeded catalytically on the walls, it is likely that no D incorporation would result, and if 2-butene formation occurred as a result of a radical mechanism (e.g. $R^\bullet$ + 1-butene $\rightarrow$ RH + CH$_2$=CHCHCH$_3$ $\rightarrow$ CH$_2$CH=CHCH$_3$ $\xrightarrow{SiD_4}$ DCH$_2$CH=CHCH$_3$ + $^\bullet$SiD$_3$), only monodeuteriation would result. Experimentally, after about 18% silane conversion, the final 2-butene products as well as the 1-butene reactant were all highly deuteriated, and the greatest enhancement occurred at the m/e 58 and 43 peaks (*indicating double D incorporation*). The results are shown in Table I. While the data were not very reproducible, the general trend is clear: both double and single deuterium incorporation occurs in all butenes. This observation, along with the previously cited arguments and observations, provides strong support for the proposed homogeneous gas-phase mechanism outlined in Scheme III.

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[8] Erwin, J. W.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1985**, *17*, 1067.

Table II. Initial Product Yield Data: Disilane vs 2-Butene plus Butylsilane Formation

T = 643.4 K, p = 30 Torr[a,c]			T = 674.2 K, p = 30 Torr[a,d]		
% isom[b]	% DS	% isom/ % DS[e,f]	% isom[b]	% DS	% isom/ % DS[e,f]
0.75	0.34	2.05	0.89	0.38	2.18
0.95	0.50	1.74	1.14	0.52	1.98
1.19	0.58	1.82	1.57	0.56	2.52
1.31	0.64	1.80	1.98	0.72	2.40
1.53	0.68	1.96	1.35	0.66	1.80
1.58	0.78	1.75	1.69	0.72	2.04
2.18	0.74	2.54			
2.19	0.80	2.35			

Average (% isom/% DS)$_{corr}$ = 2.06 ≈ k_{18}/k_{17}

[a] Reaction mixture was 84.7% SiH_4, 13.01% 1-butene, and 2.12% tetramethylsilane. [b] % isom = yields (2-butene + isobutylsilane)/[1-butene]. % DS = yield (disilane)/[SiH_4]. [c] Reaction times ranged from 22 to 39 min. [d] Reaction times ranged from 3.2 to 5.5 min. [e] The % isom/% DS ratios have been corrected for the disilane decomposition back reaction noting that $(DS/SiH_4)_{equil} \approx 0.028$. [f] From eq I, % isom/% DS ≈ k_{18}/k_{17} in the absence of the back reaction −17.

According to Scheme III, silylene trapping by silane to form disilane (reaction 17) competes with silylene trapping by 1-butene (reaction 18), the latter being responsible for alkylsilane formation as well as for 1-butene isomerization to 2-butene. Kinetic data relative to this competition are given in Table II. In the early stages of reaction (i.e. at conversions where the back-reaction decomposition of disilane is not significant), the relative rate of silylene trapping by 1-butene and by silane is given by eq I.

$$\text{yield }(2\text{-}C_4H_8 + BuSiH_3)/\text{yield }(Si_2H_6) = k_{18}(1\text{-}C_4H_8)_0/k_{17}(SiH_4)_0 \quad \text{(I)}$$

The steady-state value for the ratio (Si_2H_6/SiH_4) in the silane decomposition between 648 and 703 K is about 0.028,[9] and therefore even at the low conversions employed in the studies reported in Table II, the back reaction −17 is not entirely negligible. However, corrections for this back reaction can be easily made, and the product yield ratios (shown in columns III and VI of Table II) for the two competing processes have been so corrected. The average of these corrected ratios then provides a measure of the rate constant ratio for silylene trapping by 1-butene and silane under our reaction conditions: $k_{18}/k_{17} \approx 2.1$. This value compares favorably with the corresponding rate constant ratio of unity recently reported for the competing trapping reactions of silylene by ethylene and silane.[10] With the recent absolute rate constant measurement at 300 K for reaction 17 of $k_{17} = 6.6 \times 10^{10}$ M^{-1} s^{-1} [10] and with the reasonable assumption of zero activation energy for both processes, one obtains a rate constant for 1-butene trapping of silylene of $k_{18} \approx 10^{11.1}$ M^{-1} s^{-1}.

Scheme III also indicates that unimolecular reaction of *sec*-butylsilylene (via reactions 21 and 22) to *cis*- and *trans*-2-butene competes with its bimolecular trapping by silane (via reactions 23 and 24) to form *sec*-butylsilane. Kinetic data relative to this competition are shown in Table III. A steady-state analysis of the Scheme III mechanism for the relative rates of formation of *sec*-$BuSiH_3$ and 2-butene gives eq II.

$$\text{yield }(sec\text{-}BuSiH_3)/\text{yield }(2\text{-}C_4H_8) = k_{23}f_{23}(1 + k_{-21}/k_{22})[SiH_4]/k_{21} \quad \text{(II)}$$

In the above, $f_{23} = k_{24}/(k_{24} + k_{-23})$. Thus plots of the LHS of eq II vs [SiH_4] should be linear and go through the origin. Figure 1 confirms this expectation. Silane conversions for the studies reported in Table III were held to under 5%; therefore, approximating the silane concentration in any run to the final silane concentration entails little error. Rate constants, $k_{exptl} = k_{23}f_{23}(1 + k_{-21}/k_{22})/k_{21}$, calculated on this basis from [LHS eq II]/[SiH_4] ratios of each run are shown in column 3 of Table III. An Arrhenius treatment of the weighted average values of these rate constants at the four temperatures gives log A_{exptl} (M^{-1}) = −1.64 ± 0.5 and E_{exptl} = −10.71 ± 1.6 kcal.

The activation energy can be identified with the temperature dependencies of the various individual rate constants and terms as follows: $E_{exptl} = E_{23} + E(f_{23}) + E(F) - E_{21}$, where $E(F)$ is the effective activation energy of the function $F = (1 + k_{-21}/k_{22})$. From the methyldisilane decomposition[11] kinetic results, $k_{24}/k_{-23} \approx 6$ and $(E_{24} - E_{-23}) \approx 0.9$ kcal; therefore $E(f_{23}) \approx 0$. In addition, $E(F)$ can be shown to be given by $(k_{-21}/k_{22})(E_{-21} - E_{22})/(1 + k_{-21}/k_{22})$.

Table III. Product Ratios (*sec*-$BuSiH_3$/2-Butene) vs Silane Pressure

10^2(*s*-BS/2-B)	P_{SiH_4}, Torr	10^3k_{exptl}, Torr^{-1}	no. of runs
(A) T = 643.4 K, 83.6% SiH_4 and 16.4% 1-Butene; k_{exptl} (M^{-1}) = 99.08			
6.89 ± 0.39	25.9 ± 1	2.66 ± 0.26	3
11.8 ± 0.7	44.2 ± 1	2.67 ± 0.22	7
19.5 ± 1.2	84.9 ± 1	2.30 ± 0.17	6
29.0 ± 2.1	126 ± 1	2.30 ± 0.19	10
wt av		2.47 ± 0.20	
(B) T = 657.6 K, 83.8% SiH_4 and 16.2% 1-Butene; k_{exptl} (M^{-1}) = 82.81			
5.13 ± 0.53	26.0 ± 1	1.97 ± 0.28	4
9.24 ± 0.47	43.2 ± 1	2.14 ± 0.16	4
16.4 ± 0.9	84.2 ± 1	1.95 ± 0.13	6
25.6 ± 2.6	127.3 ± 1	2.01 ± 0.23	7
wt av		2.02 ± 0.14	
(C) T = 674.9 K, 83.8% SiH_4 and 16.2% 1-Butene; k_{exptl} (M^{-1}) = 71.53			
4.35 ± 0.35	25.0 ± 1	1.74 ± 0.19	5
7.21 ± 0.06	41.5 ± 1	1.74 ± 0.06	4
14.4 ± 0.8	85.2 ± 1	1.69 ± 0.11	10
26.8 ± 2.5	168 ± 1	1.59 ± 0.16	7
wt av		1.70 ± 0.11	
(D) T = 689.1 K, 80.7% SiH_4 and 19.3% 1-Butene; k_{exptl} (M^{-1}) = 55.42			
3.43 ± 0.47	26.4 ± 1	1.30 ± 0.23	6
10.7 ± 0.5	81.5 ± 1	1.31 ± 0.07	4
19.6 ± 2.7	160.3 ± 2	1.22 ± 0.18	7
wt av		1.29 ± 0.13	

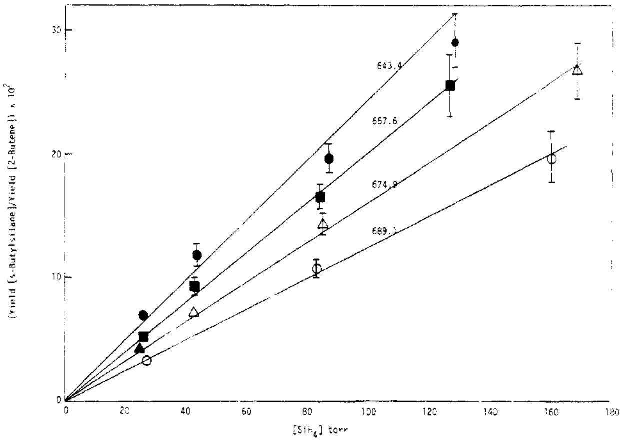

Figure 1. Experimental yield ratios as functions of silane concentration.

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(9) Purnell, J. H.; Walsh, R. *Proc. R. Soc. London, Ser.* **1966**, *293*, 543.

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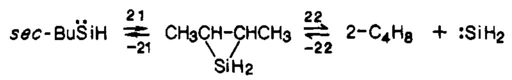
Scheme IV



sec-BuS̈iH $\underset{-21}{\overset{21}{\rightleftharpoons}}$ $CH_3CH-CHCH_3$ (SiH_2) $\underset{-22}{\overset{22}{\rightleftharpoons}}$ $2-C_4H_8$ + $:SiH_2$

$\Delta H°_{f,298}$	38.3	(37.3)^b	-2.7	64.3 kcal/mol
$\Delta S°_{f,298}$	91.8	84.2	72.7	49.2 eu/mol^a
$\Delta C_p°_{298}$	26.6	25.5	20.1	8.2 eu/mol^a
$\Delta C_p°_{500}$	40.3	40.4	30.4	8.9 eu/mol^a
$\Delta C_p°_{800}$	54.3	54.7	41.3	10.2 eu/mol^a

^{a}eu = cal/deg. ^{b}This is an estimated value that could have considerable error. The treatment which follows, however, does not depend on its accuracy.

Table IV. Arrhenius Terms Based on Assumed Values of k_{-21}/k_{22}

k_{-21}/k_{22}	$(E_{22} - E_{-21})$	$-E(F)$	(A_{22}/A_{-21})	F	$A(F)$
1	19.2	9.6	1.6×10^6	2	1.5×10^{-3}
1/2	14.4	4.8	9.9×10^4	1.5	4.1×10^{-2}
1/3	12.8	3.2	4.5×10^4	1.33	0.12
1/4	12.0	2.4	3.3×10^4	1.25	0.21
$\underline{1/5}$	$\underline{11.5}$	$\underline{1.9}$	$\underline{2.8 \times 10^4}$	$\underline{1.20}$	$\underline{0.29}$
1/6	11.2	1.6	2.3×10^4	1.17	0.35
1/8	10.8	1.2	2.5×10^4	1.13	0.45
1/10	10.6	0.95	2.9×10^4	1.10	0.54

Therefore, the activation energy for three membered ring formation from *sec*-butylsilylene is

$$E_{21} = (E_{23} + E(F) + 10.7) \pm 1.6 \text{ kcal} \qquad \text{(IIIA)}$$

A second relationship for E_{21} is supplied by the thermochemistry[12] of the *sec*-butylsilylene decomposition (Scheme IV). For the *sec*-butylsilylene decomposition reaction at 670 K, one obtains $\Delta H° \approx 23.3$ kcal, $\Delta E° = 22.0$ kcal, and $\Delta S° \approx 29.6$ (cal/deg)/mol. Since $\Delta E° = (E_{21} + E_{22} - E_{-21} - E_{-22})$ and $E_{-22} \approx 0$, solving for E_{21} gives

$$E_{21} = 22.0 - (E_{22} - E_{-21}) \text{ kcal} \qquad \text{(IIIB)}$$

Equating eq IIIA and IIIB and setting $E_{23} = 1.7$ kcal[13] gives

$$(E_{22} - E_{-21}) = (9.6 - E(F)) \pm 1.6 \text{ kcal} \qquad \text{(IV)}$$

[Errors from the terms in parentheses in eq IV (which includes errors in E_{23} and in the reaction enthalpy $\Delta H°$) have not been included as there is no way currently to estimate these errors.] If $k_{-21} > k_{22}$, then $E(F) = -(E_{22} - E_{-21})$ and eq IV cannot be an equality. However, if eq IV *is* valid, it is possible to calculate values for $E(F)$, A_{-21}/A_{22}, and $(E_{22} - E_{-21})$ as a function of assigned values for k_{-21}/k_{22}. These are shown in Table IV. Since it would be difficult to believe an $(E_{22} - E_{-21})$ and an (A_{22}/A_{-21}) much greater than 10 kcal and 10^4, respectively, a best compromise for the various Table IV values appears to be $(E_{22} - E_{-21}) = 11.5 \pm 1$ kcal, $-E(F) = 1.9 \pm 1$ kcal, $(A_{22}/A_{-21}) = (3 \pm 1) \times 10^4$, $A(F) = 0.29 \pm 0.07$, and $k_{22}/k_{-21} = 0.2 \pm 0.1$. These choices are reasonably well-supported by the following A-factor analysis: According to eq I, $A_{\text{exptl}} = 10^{-1.64\pm0.5} = A_{23}A_{f_{23}}A_F/A_{21}$. With $A_{f_{23}} = 0.86$ and $A_{23} = 10^{10.8}$ M^{-1} s^{-1},[13] this gives $A_{21} = 10^{12.4\pm0.5}A_F$ s^{-1}, which agrees within the experimental errors with the thermochemical kinetic estimate of $A_{21} \approx 10^{12.2\pm0.3}$ s^{-1}.[14] Equation II and the present mechanistic treatment depend critically on the relative values of k_{22} and k_{-21} and their temperature dependencies. It is possible to estimate the Arrhenius parameters of these reactions through the kinetics and thermochemistries of their back reactions. The relative trapping efficiency of silane and 1-butene toward silylene is pertinent to this point as this efficiency (assuming zero activation energies for both trapping reactions) yields an approximate value of A_{-22}. Thus, assuming that reactions 18 and −22 are quantitatively analogous and accounting for the fact that the experimental rate constant for reaction 18 is based on silylene removal, we have $k_{18} \approx A_{18} \approx 10^{11.1}$ M^{-1} s^{-1} [13] $\approx k_{-21}/k_{22}A_{-22}$. Hence, with $k_{22}/k_{-21} \approx 5$, $A_{-22} \approx 10^{11.8}$ M^{-1} s^{-1}. From the thermochemistry of this reaction reaction ($\Delta S°_{22,-22} \approx 37.9 \pm 2$ (cal/deg)/mol[15,16] at 670 K), one then calculates $A_{22} \approx 10^{17.9\pm0.5}$ s^{-1}. Similarly, the experimentally deduced A_{21} and reaction entropy change ($\Delta S°_{-21,21} = 7.8 \pm 2$ (cal/deg)/mol[15,16]) gives $A_{-21} \approx A_F \times 10^{14.1\pm0.6}$ s^{-1}. Thus one estimates that $A_{22}/A_{-21} \approx 10^{3.7\pm0.5}/A_F$, which is in very good agreement with the row 5 (underlined) values of Table IV.

If the row 5 (Table IV) values are assumed, Arrhenius parameter estimates for the pertinent reactions of the *sec*-butylsilylene decomposition can be obtained by using the various relationships developed above. Thus one obtains: $A_{21} = 10^{11.9\pm0.6}$ s^{-1}, $E_{21} = 10.5 \pm 2.6$ kcal; $A_{-21} = 10^{13.6\pm0.7}$ s^{-1}, $E_{-21} = 11.6 \pm 2.6$ kcal; $A_{22} = 10^{17.9\pm0.5}$ s^{-1}, $E_{22} = 23.1 \pm 2.6$ kcal; $A_{-22} = 10^{11.8\pm0.5}$ M^{-1} s^{-1}. Even without considering all the error sources (see note in brackets following eq IV) errors are quite large; therefore, these Arrhenius parameters are more important qualitatively than quantitatively. In this sense, some very significant conclusions concerning the nature of the reactions involved can be drawn. Thus eq IIIA or IIIB yields an activation energy for *sec*-butylsilylene intramolecular C–H insertion of $E_{21} \approx 10.5$ kcal. This is considerably lower than previous estimates of about 19 kcal[17] (P standard state), which are based on the activation energy for silylene insertion into the C–H bond of methane. [Recent revisions in the heat of formation of silylene, now thought to be ~64.3 kcal/mol[18] rather than 58–60 kcal/mol, required a downward adjustment in this latter activation energy to about 16.6 kcal, M standard state.] However, since methyl substitution for H in a silylene appears to raise alkylsilane decomposition activation energies[2] [and therefore also the reverse H–H and C–H insertion activation energies] by 3–5 kcal, the estimated activation energy of an alkylsilylene insertion into the C–H of methane becomes about 20 kcal. On this basis, the lowest possible value for *sec*-butylsilylene intramolecular C–H insertion (as in reaction 21) is 11 kcal. [The 9-kcal reduction corresponds to the difference in bond energies of the C–H bonds reacted.[15]] Thus the E_{21} = 10.5 kcal value deduced here from the kinetics indicates little or no ring strain in the transition state for three-

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(12) Licciardi, G.; O'Neal, H. E.; Ring, M. A. to be submitted for publication.

(13) Walsh has found a significantly lower rate constant for the Me_2Si: insertion into the Si–H bond of silane than was found by Inoue for the corresponding SiH_2 insertion (i.e. 1.2×10^8 M^{-1} s^{-1} vs 6.6×10^{10} M^{-1} s^{-1}, respectively). Attributing the rate difference to an activation energy, Walsh has suggested for the former process Arrhenius parameters of $A = 4 \times 10^{10}$ M^{-1} s^{-1} and $E = 3.4$ kcal. Asuming that the reactivity of *sec*-butylsilylene toward silane is the same as that of methylsilylene and that MeS̈iH has an intermediate reactivity to that of SiH_2 and Me_2Si:, we have assigned Arrhenius parameters for reaction 23 of $A_{23} = 5 \times 10^{10}$ M^{-1} s^{-1} and $E_{23} = 1.7$ kcal. The error in E of this assignment could be as large as 3 kcal since the observed Me_2Si and SiH_2 rate constant difference could as easily be attributed solely to their A factors. Thus the true origins of the rate constant differences in silylenes according to substitution and the assumed rate similarities for the silylenes of similar alkyl substitution are clearly important problems which beg early solutions.

(14) Two internal rotations are restricted in the transition state of reaction 21; each restriction corresponds to an entropy loss of about 3.5 eu. The reaction path degeneracy of reaction is two (i.e., there are two possible C–H bonds which can react); hence the estimated A factor of reaction is $A_{21} \approx rpd(ekT/h)e^{\Delta S°/R} = 10^{12.3\pm0.3}$ s^{-1}.

(15) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

(16) O'Neal, H. E.; Ring, M. A. *J. Organomet. Chem.* 1981, *213*, 419.

(17) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey, D., Jr. *Int. J. Chem. Kinet.* 1984, *16*, 31.

(18) Martin, J. G.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* 1987, *19*, 715.

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membered-ring closing, even though the ring strain in the product ring must (on the basis of the known instability of silacyclopropanes) to be considerable.

It is also interesting to note the implications of the surprisingly high Arrhenius parameters deduced for reaction 22 (i.e. the silacyclopropane dissociation to olefin and silylene). Past treatments have assumed this to be a concerted process with a "normal" A factor on the order of ekT/h. The present results are consistent only with a consecutive step process, probably involving biradical formation. The addition of silylene to butadiene[19] (forming 3- and 4-silacyclopentene) appears to proceed in a similar fashion so there is some support for this kind of high-entropy, loose transition-state process in silylene additions to (or eliminations from) olefins.

Summary

Intramolecular isomerizations of long-chain alkylsilylenes are very fast processes and at static temperatures proceed exclusively (when possible) via three-membered ring forming cyclizations. The silacyclopropane intermediates so formed decompose (to olefins and silylene) at rates which are several times faster than their isomerizations to alkylsilylenes. This is the case even though the decompositions have activation energies significantly higher (11–12 kcal) than the competing isomerizations. The unusually high activation entropies of decomposition, reflected in the high A factors of reaction (e.g. $A_{22} \approx 10^{17.9}$ s^{-1}), suggest a consecutive step mechanism probably involving biradical intermediates. Thus the reverse reactions and their analogues (i.e. silylene additions to olefin π systems) are high A-factor, biradical, consecutive step processes and not, as formerly believed, concerted single-step processes.

Acknowledgment. We are indebted to AFOSR for financial support of this work under Grant 83-0209.

Registry No. SiH_4, 7803-62-5; $CH_3CH_2CH{=}CH_2$, 106-98-9; SiH_2, 13825-90-6; SiD_4, 13537-07-0; $HSiCH(CH_3)CH_2CH_3$, 110550-55-5; *n*-$C_4H_9SiH_3$, 1600-29-9; *s*-$C_4H_9SiH_3$, 18165-84-9; *cis*-$CH_3CH{=}CHCH_3$, 590-18-1; *trans*-$CH_3CH{=}CHCH_3$, 624-64-6; 2,3-dimethylsilacyclopropane, 110550-56-6; disilane, 1590-87-0.

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Structure and Reactivity of (η^5-C_5H_5)Mn(CO)$_2$ in Room-Temperature Solution. Evidence for Formation of a Dinuclear Intermediate Detected by Flash Photolysis and Time-Resolved Infrared Spectroscopy

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Received May 28, 1987

UV laser flash photolysis (308 nm, 15 ns) with UV/vis monitoring and with time-resolved IR spectroscopy has been used to characterize two transient species formed by the photolysis of $CpMn(CO)_3$ (Cp = η^5-C_5H_5) in alkane solution. The first species has been identified as $CpMn(CO)_2S$ where S = cyclohexane or *n*-heptane, from both its kinetic behavior and its IR spectrum. $CpMn(CO)_2S$ reacts with CO, N_2, and PPh_3 with bimolecular rate constants similar to those previously published for the corresponding reactions of the group 6 metal pentacarbonyls. The second transient species $Cp_2Mn_2(CO)_5$ is formed by the reacton of $CpMn(CO)_2S$ with unphotolyzed $CpMn(CO)_3$. ^{13}CO enrichment and IR spectroscopy are used to establish that $Cp_2Mn_2(CO)_5$ has a single bridging CO group. The formation of $Cp_2Mn_2(CO)_5$ can be suppressed by reagents, e.g. PPh_3, added to the solution.

Introduction

A knowledge of the reactivity of coordinatively unsaturated organometallic complexes is of primary importance in understanding the mechanisms of many systems. Transition-metal carbonyl complexes are particularly suitable for mechanistic studies because their chemical and spectroscopic properties permit a wide range of techniques to be applied. The structures of many reaction intermediates have been established by IR spectroscopy of low-temperature matrices[2] or frozen hydrocarbon glasses.[3] Reaction pathways in solution have been followed by using a variety of transient spectroscopic techniques,[4] as well as by more conventional photochemical studies.

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[2] For a general reference to matrix isolation see, e.g.: Perutz, R. N. *Annu. Rep. Prog. Chem., Sect. C* 1985, 157.

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0276-7333/87/2306-2600$01.50/0