Table VIII. Comparison of Atomic Ionization Energies (eV) for the Process $Ln^{2+} \rightarrow Ln^{3+} + e^-$ with f Orbital Ionization Energies (eV) of $Ln(C_5Me_5)_2$

	Ln^{2+}			
			$Ln(C_5Me_5)_2$	
	TSOE	exptl[a]	TSOE[b]	exptl
Yb	25.3	25.2	5.9	6.65[c]
Eu	25.1[d]	24.9	5.6[d]	6.42[c]
(Yb–Eu)	0.2	0.3	0.3	0.2

[a] References 42 and 43. [b] Estimated values; see Table VII. [c] Spin–orbit average using the results of the fit. [d] Spin-polarized calculated.

therefore, attribute the lack of structure to the highly ionic nature of this complex, revealed by the calculations. The onset of the ring ionizations lies considerably lower than those given above (Sm, 6.3 eV; Eu, 6.3 eV; Yb, 6.5 eV), reinforcing the view that the rings of the lanthanide complexes are more negatively charged as indicated by the calculations.

Concomitant with the type of ionic behavior found by both calculation and experiment is a rather corelike behavior of the 4f electrons. A stringent test of the validity of our calculation procedure for the f ionizations is to calculate the IE of the corresponding Ln^{2+} ions. In Table VIII we compare experimental data for the processes Yb^{2+} ($f^{14} \rightarrow f^{13}$)[42] and Eu^{2+} ($f^7 \rightarrow f^6$), the latter value being obtained from a Born–Haber procedure,[43] and the appropriate TSOE from atomic $X\alpha$ calculations, to calculated and spin–orbit averaged IEs of the bis(pentamethylcyclopentadienyl) sandwich compounds. Calculated and experimental atomic ionization energies agree very well, as do the values for the complexes. This adds weight to the assignment of the Eu f band to the low-energy shoulder at 6.3 eV.

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Registry No. $Sm(C_5Me_5)_2$, 90866-66-3; $Eu(C_5Me_5)_2$, 101200-04-8; $Yb(C_5Me_5)_2$, 75764-11-3; $Eu(C_5H_5)_2$, 1271-25-6; $Yb(C_5H_5)_2$, 1271-31-4.

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Decomposition Mechanism and Kinetics of *n*-Butylsilane

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The thermal decomposition kinetics of *n*-butylsilane have been studied at 4800 torr between 1085 and 1250 K. Overall rate constants below 1150 K compare closely to those of other monoalkylsilanes but become increasingly larger at higher temperatures. The dominant primary dissociation processes are 1,1- and 1,2-H_2 eliminations (in the ratio of 2.1 ± 0.6, respectively); C–C bond fissions also contribute at the higher temperatures. Silylene chain reactions as well as short free-radical chains occur in the uninhibited reaction. The dominant reaction intermediate, *n*-butylsilylene, decomposes to a variety of olefin products and also isomerizes to silacyclopentane via an intramolecular silylene insertion into C–H bonds of the end methyl group. Observation of this product supports the consecutive step mechanism for the decompositions of alkylsilylenes (R > Me), i.e., intramolecular silylene insertion into C–H bonds to produce silacyclic compounds followed by their subsequent decompositions to various olefins and silylenes (or silenes).

Introduction

The shock-induced decompositions of monoalkylsilanes[1-4] (1085–1250 K) occur mainly by two primary dissociation channels, 1,1-H_2 elimination and 1,2-H_2 elimination (reactions 1 and 2), with the former being the more

$$RCH_2SiH_3 \xrightarrow{1} RCH_2\ddot{Si}H + H_2$$

$$RCH_2SiH_3 \xrightarrow{2} RCH{=}SiH_2 + H_2$$

important by factors of 2–5. A third primary process, namely, alkane elimination, has also been observed for methylsilane (reaction 3)[1] and vinylsilane[4] (reaction 4), but curiously not for ethylsilane[2] and propylsilane.[3]

Table I. Monoalkylsilane Decomposition Kinetic Parameters

compd	log *A*	*E*, kcal	k_H/k_D	$\phi_{1,1}/\phi_{1,2}$	$k_{1145°C}$, s^{-1}
CH_3SiH_3[1]	15.29[a]	65 015 ± 3000[a]	1.1	4.7	757
$CH_3CH_2SiH_3$[2]	15.14	64 769 ± 940	1.23	2.2	597
$CH_2{=}CHSiH_3$[4]	14.95	63 268 ± 1259	1.29		746
$CH_3CH_2CH_2SiH_3$[3]	15.26	65 300 ± 1950		3.0	624

[a] High-pressure parameters obtained via RKKM fall-off corrections.

$$CH_3SiH_3 \xrightarrow{3} CH_4 + \ddot{Si}H_2$$

$$CH_2{=}CHSiH_3 \xrightarrow{4} C_2H_4 + {:}SiH_2$$

The kinetics of the monoalkylsilane decompositions show many similarities. Thus, the overall Arrhenius pa-

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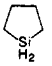
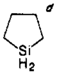
Table II. n-Butylsilane Decomposition Product Yields (%)

A. [n-$BuSiH_3$] = [C_2H_6] = [Xe] = 0.10%; Toluene = 3.00%; 96.7% Ar

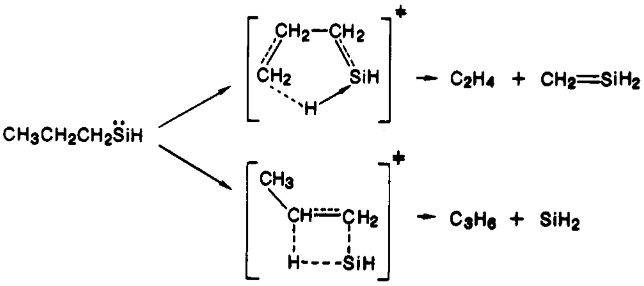
% decomp	CH_4	C_2H_4	C_3H_6	1-C_4H_8	2-C_4H_8		runs
19–30	0.12 ± 0.03	0.17 ± 0.03	0.12 ± 0.03	0.27 ± 0.04	0.13 ± 0.01	0.30 ± 0.03[a]	5
30–45	0.17 ± 0.01	0.25 ± 0.01	0.19 ± 0.01	0.34 ± 0.01	0.15 ± 0.01	0.34 ± 0.01	3
45–60	0.19 ± 0.01	0.27 ± 0.01	0.18 ± 0.02	0.36 ± 0.02	0.17 ± 0.02	0.37 ± 0.12	3
60–75	0.19 ± 0.01	0.26 ± 0.01	0.17 ± 0.02	0.32[b]	0.15[b]	0.32 ± 0.06[a]	3
75–90	0.29 ± 0.06	0.37 ± 0.04	0.19 ± 0.01	0.31 ± 0.03	0.17 ± 0.01	0.73 ± 0.10[e]	3

B. [n-$BuSiH_3$] = [C_2H_6] = [Δ] = 0.10%; Benzene = 3.00%; 96.7% Ar

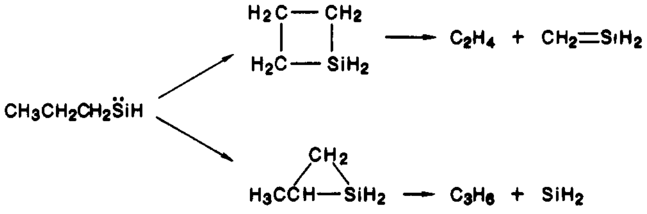
% decomp	CH_4	C_2H_4	C_3H_6[c]	1-C_4H_8	2-C_4H_8	 [d]	runs
30–45	0.14 ± 0.03	0.50 ± 0.08		0.29 ± 0.03	0.08 ± 0.01		5
45–60	0.18 ± 0.02	0.62 ± 0.10		0.38 ± 0.09	0.12 ± 0.03		2
60–75	0.20 ± 0.02	0.70 ± 0.03		0.39 ± 0.05	0.12 ± 0.03		4
75–90	0.27 ± 2	0.91 ± 0.01		0.44 ± 0.02	0.19 ± 0.06		2

[a] Silacyclopentane analyzed on only two of the five runs between 19 and 30% and two of three runs between 60 and 65%. [b] Butenes analyzed only for one of the three runs (60–75%) and three of five runs (19–30%). [c] Cyclopropane gives C_3H_6; therefore, propylene yields could not be accurately evaluated. [d] The benzene peak overlaped with that of silacyclopentane in our GC analysis. [e] These apparent very high yields may be an artifact caused by coelution of other reaction products (see *d* above).

Scheme I. Concerted H-Atom Transfers



Scheme II. Consecutive Step Process

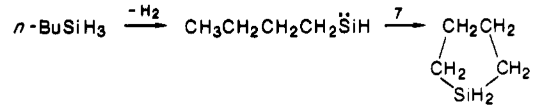


rameters of their decompositions are essentially identical (within the errors) as are their rate constants at mean reaction temperatures and their deuterium isotope effects. This is evident from the data of Table I. In addition, alkylsilylenes (with R > Me) produced directly in reaction 1 and indirectly after silene isomerization in reaction 2 decompose in subsequent secondary reactions to olefins and silylenes; e.g., ethylsilylene[2] forms ethylene, vinylsilylene[4] forms acetylene, and propylsilylene[3] forms ethylene and propylene (reactions 5 and 6).

$$n\text{-Pr}\ddot{\text{S}}\text{iH} \xrightarrow{5} C_2H_4 + SiH_2{=}CH_2 \text{ or } CH_3\ddot{\text{S}}\text{iH}$$

$$n\text{-Pr}\ddot{\text{S}}\text{iH} \xrightarrow{6} C_3H_6 + {:}SiH_2$$

The mechanisms of reactions like (5) and (6) are of particular interest. Do these reactions occur by concerted H-atom transfers (as in Scheme I), or do they occur by consecutive step processes initiated by intramolecular silylene insertions into C–H bonds to form silacyclic intermediates (as in Scheme II)? The present study on the chemistry and kinetics of the pyrolysis of n-butylsilane was undertaken mainly to answer this question. Thus, while 2-methylsilacyclopropane[5] and silacyclobutane[6] (the intermediates and possible Scheme II products of the n-propylsilane decomposition) are now known to be too unstable to subsequent decomposition to detect as reaction products under shock-tube reaction conditions, silacyclopentane (an expected Scheme II product of the n-butylsilane decomposition, see reaction) should be quite stable



and, hence, be an observable product. Observation of silacyclopentane, then, would provide support for the consecutive step mechanism of olefin formation in alkylsilylene decomposition.

Experimental Section

The single-pulse shock tube, accompanying equipment, and experimental method have been previously described.[7] Product analyses were made by gas–liquid chromatography with a Varian 1400 flame-ionization detector equipped with a Hewlett-Packard 3390A digital integrator. PoraPak N and OV-101 packed columns were used. Analyses for HD and D_2 were made with a Hitachi Perkin-Elmer RMU-6E mass spectrometer. The identification of silacyclopentane was based on a mass spectrum with m/e 86 and 85 peaks similar in ratio to the m/e 84 and 83 peaks of silacyclopentene and a GLC retention time on the OV-101 column that was nearly identical with that of silacyclopentene (as would be expected).

Results

Several reaction mixtures of normal or deuteriated n-butylsilane in argon containing various analytical standards (Xe for mass spectroscopy; C_2H_6 for gas chromatography), a comparative rate standard (cyclopropane), and various trapping agents (toluene for free radicals and butadiene for silylenes) were prepared and reacted. Product yield data and initial reaction mixture compositions are given in Table II. The major products were hydrogen, methane,

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Table III. Rate Constants of Decomposition of *n*-Butylsilane

A. Rate Constants in the Presence of Benzene[a]

T,[b] K	% decomp	$k_{n\text{-BuSiH}_3}$, s^{-1}	k_{PrSiH_3},[d] s^{-1}
1140	36.1	1600	550
1146	32.6	1360	639
1147	32.9	1450	656
1147	44.1	2080	656
1155	48.9	2400	800
1156	43.2	1980	820
1157	50.2	2210	840
1168	61.0	3190	1098
1170	62.7	3520	1152
1170	61.8	3260	1152
1172	62.4	3160	1208
1195	77.2	4770	2073
1211	86.6	6480	2981

$\log k_{n\text{-BuSiH}_3} = 14.60 \pm 2.01 - 59558 \pm 10810 \text{ cal}/\theta$

B. Rate Constants of n-BuSiH$_3$ Decomposition in Excess Butadiene[c]

T,[b] K	% decomp	$k_{n\text{-BuSiH}_3}$, s^{-1}	k_{PrSiH_3},[d] s^{-1}
1065	1.72	57.5	72.2
1118	7.11	254	313
1131	13.2	457	437
1134	13.9	507	472
1132	15.8	555	449
1164	29.7	1100	996
1173	38.6	1480	1237
1204	69.8	3520	2546
1227	85.7	5890	4246

$\log k_{n\text{-BuSiH}_3} = 17.12 \pm 0.74 - 74864 \pm 2890 \text{ cal}/\theta$

[a] Reaction mixture composition: [n-BuSiH$_3$] = [C_2H_6] = [c-C_3H_6] = 0.10%; 3.00% C_6H_6; 96.7% Ar. [b] From cyclopropane (comparative rate standard) decomposition kinetics. [c] Reaction mixture composition: [n-BuSiH$_3$] = [C_2H_6] = [c-C_3H_6] = 0.10; 3.50% C_4H_6; 96.2% Ar. [d] Calculated from the observed Arrhenius parameter for propylsilane decomposition under butadiene and toluene inhibition.

ethylene, propylene, 1-butene, *cis*- and *trans*-2-butene, and silacyclopentane.

Rate data for the n-butylsilane decomposition, obtained vs. the kinetics of the comparative rate standard cyclopropane ($\log k(\text{c-}C_3H_6) = 14.56\text{–}62350 \text{ cal}/2.303RT$, 4800 torr, and 1050–1250 K[3,8]) were obtained in the presence of benzene (i.e., no inhibition of chains) and in the presence of excess butadiene (i.e., inhibition of silylene chains) at temperatures between 1065 and 1227 K and pressures of about 4800 torr. The first-order rate constants obtained are given in Table III along with rate constants (calculated) for propylsilane[3] (the most analogous system) under similar temperature and inhibition conditions for comparative purposes. For the gas-phase reaction in the presence of benzene, the Arrhenius parameters obtained for decomposition were $\log A$ (in benzene) = 14.60 ± 2.01 and E (in benzene) = 59558 ± 10810 cal, in fair agreement with other RSiH$_3$ results. However, errors were very large (indicative of reaction complexities), and rate constants were almost three times larger than those obtained for other analogous systems. For the gas-phase decomposition in excess butadiene, the rate constant data give $\log A$ (in C_4H_6) = 17.12 ± 0.74 and E (in C_4H_6) = 74864 ± 3890 cal, where the errors correspond to the 95% confidence limit. Here the rate constants of decomposition are not much different from those of analogous systems, but the Arrhenius parameters are much too high to be attributable solely to the usual primary dissociation processes.

Discussion

Kinetics. The rate constant of decomposition for n-BuSiH$_3$ in butadiene at the mean reaction temperature of 1145 K is essentially identical with the average of other monoalkylsilanes at this temperature (i.e., $\langle k \rangle \simeq 680\ s^{-1}$; see Table I). Without butadiene, reaction rate constants are almost 3 times larger. The uninhibited reaction, therefore, is subject to silylene chains like reactions 8–10.

$$:\text{SiH}_2 + n\text{-BuSiH}_3 \overset{8}{\rightleftarrows} n\text{-BuSiH}_2\text{SiH}_3$$

$$n\text{-BuSiH}_2\text{SiH}_3 \xrightarrow{9} n\text{-Bu}\ddot{\text{Si}}\text{H} + \text{SiH}_4$$

$$n\text{-Bu}\ddot{\text{Si}}\text{H} \xrightarrow{10} 1\text{-}C_4H_8 + :\text{SiH}_2$$

At higher temperatures, butylsilane decomposition rate constants are increasingly larger than those of other monoalkylsilanes, and free-radical chain processes are undoubtedly the cause. Thus, yields of the products expected from free radical chain induced decompositions of the reactant (i.e., mainly ethylene and methane via reactions like (11)–(13) also increase with temperature. Butylsilane

$$\text{R}\cdot + n\text{-}C_4H_9\text{SiH}_3 \xrightarrow{11} \text{RH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\dot{\text{Si}}\text{H}_2$$

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\dot{\text{Si}}\text{H}_2 \xrightarrow{12} \text{CH}_2{=}\text{SiH}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\cdot$$

$$\text{CH}_3\text{CH}_2\text{CH}_2\cdot \xrightarrow{13} C_2H_4 + \cdot\text{CH}_3$$

has two relative weak C–C bonds; hence, bond fission reactions (reactions 14 and 15, with $E \simeq 80$ kcal and $\log A \simeq 17.0$)[8] can occur competitively with the usual hydrogen elimination processes. At 1145 K, the rate constant for

$$n\text{-BuSiH}_3 \xrightarrow{14} n\text{-Pr}\cdot + \cdot\text{CH}_2\text{SiH}_3$$

$$n\text{-BuSiH}_3 \xrightarrow{15} \text{CH}_3\text{CH}_2\cdot + \cdot\text{CH}_2\text{CH}_2\text{SiH}_3$$

C–C bond fission is estimated to be 107 s^{-1} or 16% of k(obsd). Thus, free radicals are undoubtedly produced, and this is probably the cause of the unreasonably high Arrhenius parameters observed. Propylsilane is potentially subject to the same kind of chain complications, yet its observed Arrhenius parameters of decomposition were "normal". This can be rationalized by the fact that propylsilane was studied in the presence of toluene as well as butadiene. The former (a good free-radical trap) apparently quenched the free-radical reactions leading to induced n-propylsilane decomposition. Unfortunately, toluene could not be employed in the present study because of its interference with the n-BuSiH$_3$ in GC analysis.

Primary Processes. Butane was not a reaction product. Therefore, as found for ethyl- and propylsilane, direct alkane elimination (analogous to reactions 3 and 4) does not occur in n-butylsilane. Bond fission, as previously stated, can account for 10–20% of the observed rate constant. The remaining 80–90% must be attributed to the usual 1,1- and 1,2-H_2 elimination reactions (reactions 16 and 17, respectively).

$$n\text{-}C_4H_9\text{SiH}_3 \xrightarrow{16} n\text{-}C_4H_9\ddot{\text{Si}}\text{H} + H_2$$

$$n\text{-}C_4H_9\text{SiH}_3 \xrightarrow{17} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}{=}\text{SiH} + H_2$$

If one assumes that the butylsilane decomposition at temperatures below 1145 K in the presence of excess butadiene is relatively free of chain processes (the correlation of rate constants with other maximally inhibited comparable systems supports this assumption), then the D_2/HD yield ratios for n-BuSiD$_3$ should be direct measures of the two hydrogen elimination primary processes. The data,

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[8] Benson, S. W.; O'Neal, H. E. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1970**, *NSRDS-NBS 21*, 233.

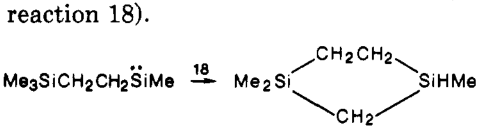
Table IV. Hydrogen Yields (%) from n-BuSiD$_3$ in Excess Butadiene[a]

% decomp	T, K	D_2	HD	D_2 + HD
16.6	1142	0.57	0.27	0.84
16.7	1142	0.70	0.33	1.03
18.8	1146	0.54	0.34	0.88
21.6	1152	0.52	0.25	0.77
27.8	1162	0.24	0.31	0.54
28.5	1163	0.62	0.29	0.91
53.7	1194	0.74	0.35	1.09[b]
61.7	1202	0.47	0.22	0.69
67.4	1208	0.42	0.21	0.63
81.5	1224	0.56	0.27	0.83[b]

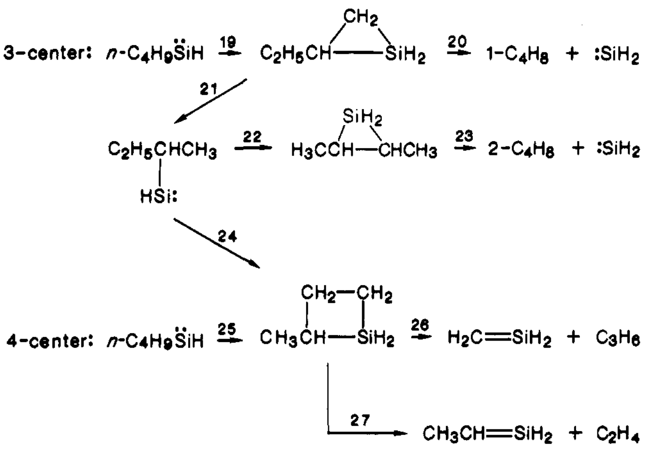
[a] Reaction mixture composition: 0.20% BuSiD$_3$, 0.10% C$_2$H$_6$, 0.10% Xe, 3.0% C$_4$H$_6$, and 96.6% Ar. [b] Suspect results. Values are too high? (See text.)

Table IV, covering a decomposition range from 16.6 to 81.5% give $D_2/HD \simeq k_{16}/k_{17} \simeq 2.1 \pm 0.6$, roughly conversion independent. This is similar to the value found for ethylsilane.[2] The rate constant comparisons of Table III suggest that as much as 40% of the reaction at the highest study temperatures is free-radical chain. Hydrogen produced in the chain should be mainly H$_2$ (there are many more abstractable H atoms than D atoms in the system and at high temperatures there is very little activation energy discrimination in abstraction reactions); therefore, little change in the D$_2$/HD ratios is expected (as observed). However, hydrogen yield sums (as monitored by D$_2$ and HD yields only) should decrease with increasing temperature. Thus, one would expect the D$_2$ + HD yield sums to vary from about 0.90 at 1065 K (i.e., 10% free-radical chain from C–C bond fission processes) to about 0.64 at 1227 K (about 40% free-radical chain producing H$_2$ only). The data of Table IV tend to support this expectation although errors in the absolute yields obscure the trend.

Secondary Reactions (Non Free Radicals). In the absence of free-radical reactions (i.e., reactions inhibited by toluene), the most important secondary reactions are those of n-butylsilylene. With the exception of the C–C bond fission reactions (14) and (15), every reaction involving n-butylsilane loss (e.g., reactions 16 and 17) or every reaction sequence involving reactant loss (e.g., reactions 8–10) produces n-butylsilylene. Thus, under toluene inhibition, essentially all observed products (see Table II) arise from the decomposition of this intermediate. (The exceptions are methane and some of the ethylene; see later.) Formation of silacyclopentane is perhaps the most significant observation of this paper. As previously noted, its presence in the products strongly supports the consecutive step mechanism for alkylsilylene decompositions (i.e., Scheme II and reaction 7). A similar reaction has been reported for methyl(2-(trimethylsilyl)ethyl)silylene[9] generated from the dichloride by reaction with Na/K at 300 C (i.e., reaction 18).



Its occurrence in the butylsilane pyrolysis strongly infers that other products are produced via competing intramolecular C–H insertion processes (i.e., 3-center and 4-center) with the subsequent decompositions of their product rings as in reactions 19–27. Note that 2-butene formation cannot be reasonably explained by a concerted reaction and that while 1-butene formation can be rationalized by



either concerted or consecutive step processes, the latter offers the simplest, most consistent, and, therefore, most reasonable explanation. If this interpretation is correct, then the relative rates at shock-tube reaction temperatures of the 3-center/4-center/5-center insertion reactions can be approximated from the product yields of Table II. For conversions under 75% (where free-radical product production is minimized) the data suggest that $k_{3\text{-center}}/k_{4\text{-center}}/k_{5\text{-center}} \sim 0.54/0.16/0.50$. This result is based on the assumption that $k_{19} = k_{22}$, $k_{20} = k_{23}$, and $k_{24} = k_{25}$ and that $[n\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}]/[i\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}] = Y(1\text{-C}_4\text{H}_8)/Y(2\text{-C}_4\text{H}_8) = 2.1$ and arises from the following: $k_{3\text{-center}}([n\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}] + [i\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}])/k_{4\text{-center}}([n\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}] + [i\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}])/k_{5\text{-center}}([n\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}][1.47])] = (Y(1\text{-C}_4\text{H}_8) + Y(2\text{-C}_4\text{H}_8) + 0.33Z)/(0.67Z)/(Y[\text{c-C}_5\text{H}_{10}] \times 1.47)$. The factor 1.47 is equal to $([n\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}] + [i\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}])/[n\text{-Bu}\ddot{\mathrm{S}}\mathrm{iH}]$, and $Z = [Y(\text{C}_3\text{H}_6) + Y(\text{C}_2\text{H}_4) - Y(\text{CH}_4)]$. It has also been assumed that methane arises from free-radical reactions as in reactions 11–13 and that ethylene is generated on a 1/1 basis with methane. This interpretation of the data suggests that the three intramolecular insertion reactions are competitive in this system.

Assuming an activation entropy decrease of about 3.5 eu for each internal rotational degree of freedom lost in the cyclization reactions gives $A_{3\text{-center}}/A_{4\text{-center}}/A_{5\text{-center}} \simeq 36/6/1$. Therefore, activation energy differences, using the above rate constant ratios, imply $(E_{3\text{-center}} - E_{4\text{-center}}) \simeq 1.4$ kcal and $(E_{3\text{-center}} - E_{5\text{-center}}) \simeq 8.4$ kcal.

$$\frac{k_3}{k_4} = \frac{0.54}{0.16} = 6e^{(E_4-E_3)/RT}$$

$$\frac{k_3}{k_5} = \frac{0.54}{0.50} = 36e^{(E_5-E_3)/RT}$$

It is also gratifying to note that the sum of the intramolecular insertion process yields is 1.04, which is close to unity as required (note that the 5-center process yield is 0.50/1.47).

The rather sharp increase in methane and ethylene yields at the highest conversions (75–90%) is indicative of free-radical processes that are not fully inhibited by toluene. This is as observed in prior studies[10] and follows from the fact that toluene can act as a radical source at temperatures above 1200 K under our shock-tube conditions. The reactions are

$$\text{PhCH}_3 \xrightarrow{27} \text{PhCH}_2\cdot + \text{H}\cdot$$

$$\text{H}\cdot + \text{PhCH}_3 \xrightarrow{28} \text{PhH} + \cdot\text{CH}_3$$

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[9] Gusel'nikov, L. E.; Polyakov, Y. P.; Volnina, E. A.; Nametkin, N. S. *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Wiley: New York, 1985; p 115.

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Organometallics **1987**, *6*, 724–727

Since benzene eluted with silacyclopentane on our GC columns, the above reaction can account for part (i.e., roughly one-third) of the apparent unexpectedly large yield increases of the latter at the highest study temperatures. The principal cause of this apparent increase, however, still remains a serious concern.

Secondary Free-Radical Reactions. Reaction rates in benzene were close to 3 times as fast as those under butadiene inhibition. Benzene is neither a free radical nor a silylene inhibitor; therefore, both silylene and free-radical chains can occur in the presence of benzene. Toluene should quench most of the free-radical-induced decomposition. Therefore, the differences in product yields observed in added benzene (Table IIB) and in added toluene (Table IIA) can be attributed mainly to free-radical processes. The yields of most of the products are about the same in the two studies; however, ethylene yields increase substantially. Ethylene, then, must be the major product of the free-radical-induced decomposition of *n*-butylsilane. This is reasonable on the basis of the expected products of the predicted Rice–Herzfeld type chains. Thus radical H abstraction from *n*-butylsilane can generate five different radicals whose possible decomposition pathways and rough statistical weights (based on reaction path degeneracies) are shown in reactions 28–33.

The above indicates that every 12 abstractions will produce roughly 11 ethylenes, four methanes, two propylenes, one 1-butene, and no 2-butenes. This correlates rather well with the observed yields of the two studies.

	stat wt
$\cdot CH_2CH_2CH_2CH_2SiH_3 \xrightarrow{29} 2C_2H_4 + \cdot SiH_3$	3
$CH_3\dot{C}HCH_2CH_2SiH_3 \xrightarrow{30} C_3H_6 + \cdot CH_2SiH_3$	2
$CH_3CH_2\dot{C}HCH_2SiH_3 \xrightarrow{31} 1\text{-}C_4H_8 + \cdot SiH_3$	1
$CH_3CH_2\dot{C}HCH_2SiH_3 \xrightarrow{32} CH_3\cdot + CH_2{=}CHCH_2SiH_3$	1
$CH_3CH_2CH_2\dot{C}HSiH_3 \xrightarrow{33} H\cdot + C_2H_4 + CH_2{=}CHSiH_3$	2
$CH_3CH_2CH_2CH_2\dot{S}iH_2 \xrightarrow{34} CH_3\cdot + C_2H_4 + CH_2{=}SiH_2$	3

Conclusions

The main primary dissociation processes for *n*-butylsilane are 1,1- and 1,2-hydrogen eliminations: $\phi_{1,1}/\phi_{1,2} \simeq 2$. At high temperatures, C–C bond rupture also occurs. Alkylsilylenes (R > Me) decompose readily to olefins, and the mechanism of their decompositions is stepwise through silacyclic species formed by intramolecular silylene insertions into C–H bonds. Such insertions, involving 3-, 4-, and 5-centered cyclic transitions states, are all competitive at shock-tube reaction temperatures (i.e., $T > 1065$ K).

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Registry No. *n*-BuSiH$_3$, 1600-29-9; silacyclopentane, 288-06-2.

Chemistry of Methylgallium(III) Compounds in Protic Solvents

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The chemical properties of as well as routes to the formation of methylgallium(III) compounds in aqueous acidic solutions and in other protic solvents have been investigated. Aqueous perchloric acid solutions of Me_2GaClO_4 at room temperature are surprisingly resistant to hydrolytic cleavage of the gallium–carbon bond. Only 14% of the available methyl groups of Me_2GaClO_4 when dissolved in 0.0171 M $HClO_4$ are converted to CH_4 after a 3-month time period. In contrast, Me_2GaClO_4 undergoes a significantly faster methyl-transfer reaction with $Ga(ClO_4)_3$ in aqueous $HClO_4$ solution to form $MeGa^{2+}$(aq) which in turn hydrolyzes to form Ga^{3+}(aq) and methane. Approximately 36% of the initially available methyl groups form CH_4 in 3 months. The dimethylgallium cation also methylates Hg^{2+}(aq) to form $MeGa^{2+}$(aq) and $MeHg^+$(aq) in aqueous solution, but Me_2Ga^+(aq) does not react with Al^{3+}(aq), Zn^{2+}(aq), or Na^+(aq). In a second series of experiments the methylation of gallium(III) by Me_2Co(BDM1,3pn) (BDM1,3pn = {*N*,*N*′-propane-1,3-diyl[bis(biacetyl monooxime imino)]}) was investigated in ethanol and acetone solutions by using UV titration and ^1H NMR data. The observed stoichiometry of the reaction requires 1 mol of $Ga(ClO_4)_3$ for every 2 mol of Me_2Co(BDM1,3pn). The identified products are Me_2Ga^+ and MeCo(BDM1,3pn)$^+$. In contrast, gallium(III) is not methylated by methylcobalamin in aqueous solution.

Introduction

Methylgallium compounds can exist in aqueous solution,[1] and these solutions are exceedingly toxic.[2,3] The inorganic derivatives of gallium are also poisonous.[3] However, relatively little is known about the hydrolytic stability, the chemical reactions, or the modes of formation of methylgallium compounds in aqueous solution. The hydrolysis of trimethylgallium is very rapid until the first methyl group has been removed, and then further hydrolysis becomes slow.[1,4,5] The removal of the second and third methyl groups has been described as being particularly slow.[1,4,5] For example, the reaction of a diethyl ether solution of Me_3GaOEt_2 with a slight excess of water gives Me_2GaOH, which in turn reacts readily with both aqueous

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