Decomposition Kinetics and Thermochemistry of Butyl- and Pentylsilylenes

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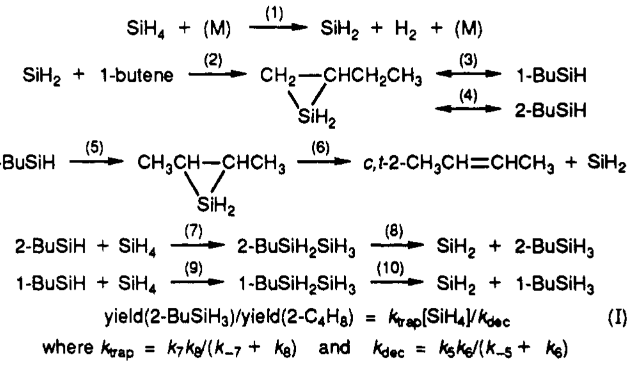
Reaction kinetics of alkylsilylenes (R = butyl, pentyl, and methylpentyl) and silacyclopropane intermediates produced by silylene additions to 1-butene, 1- and 2-pentene, 2-methyl-1-pentene, and 4-methyl-1-pentene are reported. Observations are consistent with a homogeneous, Barton[2]-type mechanism, which describes alkylsilylene isomerization and decomposition in terms of silacyclopropane (SCP) intermediates. Modeling studies on this basis conclude that SCP-forming and -opening reactions are at least an order of magnitude faster than SCP decompositions to olefins and SiH_2. All reactions are pressure dependent at 400 Torr. Decomposition versus trapping comparative rate data at 410 Torr, based on butylsilylene- and pentylsilylene-trapping reactions with silane of 4.8×10^9 M^{-1} s^{-1} and 3.1×10^9 M^{-1} s^{-1}, respectively, give limiting high-pressure Arrhenius parameters for the butyl- and pentylsilylene decompositions of $\log A_\infty = 15.5 \pm 0.1$, $E_\infty = 22.5 \pm 0.3$ kcal. The activation energies are consistent with the decomposition reaction thermochemistries ($\Delta H_{dec} = 26.6 \pm 3.4$ kcal, $\Delta E_{dec} = 25.3 \pm 3.4$ kcal), and A factors indicate surprisingly loose transition states for both alkysilylene decompositions as well as their reverse silylene/olefin additions. A loose silylene/olefin addition complex is suggested for the transition state as the thermochemistry of decomposition precludes the intermediacy of biradicals. Generic high-pressure Arrhenius parameters (A, s^{-1}: E, kcal) are deduced for silacyclopropane ring-opening (o), -closing (c), and -decomposition (d) reactions: $\log A_c = 12.3$, $E_c = 10.4$; $\log A_o = 14.0$, $E_o = 14.7 + \Delta E$; $\log A_d = 16.9$, $E_d = 26.1 + \Delta E$, where ΔE = (49.6 − SCP strain energy). The low SCP ring-closing activation energy indicates zero ring strain development in the transition state and is consistent with a reanalysis of prior estimates of the activation energy of the $SiH_2 + CH_4$ strain free, C–H bond insertion reaction.

Introduction

In a prior paper[1] we proposed a "Barton-type"[2] mechanism (Scheme I) to describe the reactions occurring in the pyrolysis of silane/1-butene mixtures. The focus of that study was to determine the decomposition kinetics of 2-butylsilylene, an intermediate produced in the SiH_2 addition process (reactions 2, 4). Analysis of yield data by the rate equation (I), produced a surprisingly low decomposition activation energy: $E_{dec} = 10.7 \pm 1.6$ kcal,[1] based on $E_{trap} = 0$. Since estimates[1] of the decomposition enthalpy were much higher (i.e., $\Delta H_{5,6} \geq 23$ kcal), the mechanism, kinetics, and thermodynamics could only be reconciled if $k_6 \gg k_5$ and reaction 5 were rate-limiting. Analysis on this basis was possible, but it produced two other questionable assignments: $E_5 = 10.5 \pm 2.6$ kcal and $A_6 = 10^{17.9\pm0.5}$ s^{-1}. The former is low when compared to a prior estimate of 17 kcal[3] (from the kinetics and thermochemistry of the $MeSiH_3 \rightarrow CH_4 + SiH_2$ reaction[3]), and the latter is high for any reaction. The possibility that free radicals, rather than silylenes, were responsible for the observations was considered. This possibility, Scheme II, was tentatively dismissed on the basis of two observations: 2-butene products of an SiD_4/1-butene reaction were singly *and* doubly deuterated (only single deuteration is predicted by Scheme II), and methane and ethane were not found in the products (silylbutyl radicals would be expected to decompose to these products at reaction temperatures). Thus free radical participation seemed unlikely, but the possibility of some other mechanistic interpretation remained. Pressure falloff effects in the 2-butylsilylene decomposition presented a second potential problem with the earlier study.[1] This was not initially considered because of the size of butylsilylene, but in view of how the study was conducted (i.e., product yield versus silane data were obtained by changing the total pressure of a fixed reactant composition mixture) and on the basis of rough RRKM falloff calculations, it became evident that falloff in the butylsilylene decomposition could well have influenced the data. Therefore, in order to resolve the experimental and interpretive ambiguities surrounding this system, additional investigations of silylene/olefin reactions, some under conditions of high and constant total pressure, were made. These are reported here.

Scheme I. Mechanism of the Silane/1-Butene Reaction



Scheme II. Mechanism of Free Radical Induced Olefin Isomerization

$$R^\bullet + CH_2{=}CHCH_2CH_3 \xrightarrow{(11)} RH + (CH_2{=}CH\dot{C}HCH_3 \Longleftrightarrow {}^\bullet CH_2CH{=}CHCH_3)$$

$${}^\bullet CH_2CH{=}CHCH_3 + SiH_4 \xrightarrow{(12)} SiH_3^\bullet + CH_3CH{=}CHCH_3$$

$$SiH_3^\bullet + CH_2{=}CHCH_2CH_3 \xrightarrow{(13a)} {}^\bullet CH_2CH(SiH_3)CH_2CH_3$$

$$\xrightarrow{(13b)} {}^\bullet CH(C_2H_5)(SiH_3CH_2)$$

$${}^\bullet CH_2CH(SiH_3)CH_2CH_3 + SiH_4 \xrightarrow{(14a)} CH_3CH(SiH_3)CH_2CH_3 + SiH_3^\bullet$$

$$\xrightarrow{(14b)} CH_2(C_2H_5)(SiH_3CH_2) + SiH_3^\bullet$$

Experimental Section

The reactants, silane and 1-butene (Matheson, 99.9% purity) and 1-pentene, 2-pentene, 2- and 4-methyl-1-pentene, and 2-methyl-2 pentene (Aldrich, 99% purity), were used as received

(1) Dickinson, A. P.; Nares, K. E.; Ring, M. A.; O'Neal, H. E. *Organometallics* **1987**, *6*, 2596.
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(3) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey, D., Jr. *Int. J. Chem. Kinet.* **1984**, *16*, 31.

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Table I. 1-Butene + Silane Reaction Product Yield versus SiH_4 Data[a-c]

temp, K	$10^4[SiH_4]$, M	10^2[2-$BSiH_3$/2-B]	k_{exp},[c] M^{-1}	k_{dec},[d] s^{-1}
639.3	0.00	0.00	179 ± 9	2.68×10^7
	6.77	15.6		
	11.8	26.1		
	21.8	47.6		
	32.9	62.5		
	42.9	77.5		
650.3	0.00	0.00	149 ± 7	3.22×10^7
	6.66	12.3		
	11.8	21.7		
	22.4	39.6		
	33.3	53.1		
	44.4	66.5		
670.3	0.00	0.00	103 ± 3	4.66×10^7
	6.46	7.27		
	11.2	14.1		
	22.0	25.0		
	32.3	34.7		
	42.8	44.3		
690.8	0.00	0.00	70.4 ± 2	6.82×10^7
	6.27	4.63		
	10.9	8.75		
	21.4	16.5		
	31.1	21.8		
	41.3	29.4		

[a] All studies were at the same 408-Torr total pressure. [b] Line slopes = $k_{exp} = k_{trap}/k_{dec}$, see eq I and text. [c] $E_{exp} = -16.1 \pm 1.0$ kcal; log $A_{exp} = -3.25 \pm 0.30$; P_T = 408 Torr. [d] $E_{dec} = 16.1 \pm 1.0$ kcal; log $A_{dec} = 12.93 \pm 0.3$ at 408 Torr. These values are based on $k_{trap} = 4.8 \times 10^9\ M^{-1}\ s^{-1}$.

after usual vacuum line degassing and distillation. Two cylindrical quartz reaction cells, volumes of 185 and 250 cm^3, and a third quartz tubing packed reactor (factor of 10 S/V increase), were used in the studies. All were housed in resistively heated ovens with temperature control to ±0.2 K. Analyses were made by GLC using thermal conductivity detection (Carle Instruments Model 8500 GC) and/or flame ionization detection (Varian 1400 GC), with digital peak integration (Hewlett-Packard 3390A). A variety of columns were used under both isothermal and temperature-programmed conditions: 24 ft × 1/8 in. 20% squalene on Supelcoport, 20 ft × 1/8 in. 15% squalene on chromosorb P, and 20 ft × 1/8 in. 15% SE-30 Supelcoport. Product identifications were made by GLC retention time comparisons with authentic samples and by GC–MS (Finnigan 3000) when authentic samples were not available. Reactant mixtures of the olefin of interest, a silylene source (SiH_4 or Si_2H_6), and a GC analytical standard (Me_4Si, TMS) were prepared manometrically and stored in well-stirred Pyrex mixing vessels. All reactant mixtures were stable in time, as evidenced by repeated GC chromatographs. Silane/olefin reactions were studied in the 640–690 K range and reaction progress was followed in the batch mode, or by analyses on aliquots withdrawn sequentially over time.

Results

Silane/1-Butene Reactions. Five reactant mixtures with olefin/silane ratios of about 2 and silane concentrations ranging from 6.27×10^{-4} to 44.4×10^{-4} M were used. TMS was added as needed to bring total pressures to 408 ± 5 Torr. Reactions were limited to silane conversions under 6%, which corresponded to olefin isomerizations above 50%. Products were as before,[1] *cis*- and *trans*-2-butene, 1- and 2-butylsilane, and disilane. Yield data relative to eq I and rate constants derived from the appropriate plots of yield ratios versus $[SiH_4]$ shown in Figure 1, are given in Table I.

Silane/1-Pentene Reactions. Silane/1-pentene reactions were studied under the same total pressure, temperature, silane concentration, and conversion conditions as employed in the silane/1-butene studies. The products (*cis*- and *trans*-2-pentene and 1-, 2-, and 3-pentylsilanes) were those expected by the Barton mechanism (Scheme III). Yield data pertinent to the competitive trapping and decomposition of the 2- and 3-pentylsilylenes, according to the comparative rate equation (II), are given in Table II. Plots of the data are shown in Figure 2. Equation

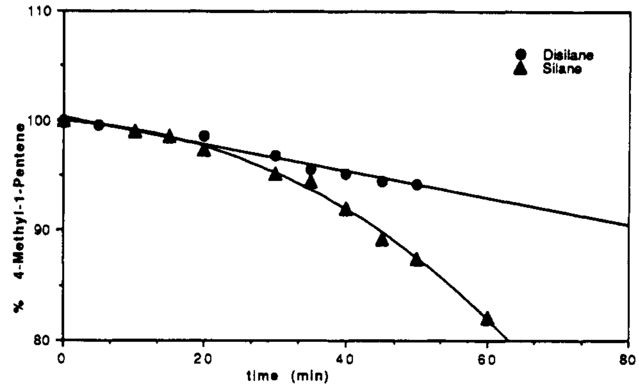
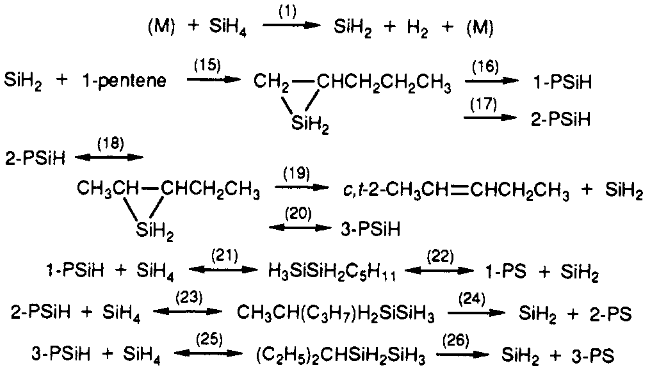


Figure 1. 4-Methyl-1-pentene versus time in silane and disilane-initiated pyrolyses. Silane decomposition at T = 639 K; 2% SiH_4 conversions occurs at about t = 30 min. Disilane decomposition at T = 583 K.

Scheme III. Mechanism of the SiH_4/1-Pentene Reaction



1-PSiH = n-$C_5H_{11}SiH$; 2-PSiH = $CH_3CH(SiH)C_3H_7$; 3-PSiH = $(C_2H_5)_2CHSiH$; 1-PS = n-$C_5H_{11}SiH_3$; 2-PS = $CH_3CH(C_3H_7)SiH_3$; 3-PS = $(C_2H_5)_2CHSiH_3$

$$\text{yield(2PS + 3PS)/yield(2-pentene)} = 0.93k_{trap}[SiH_4]/k_{dec} \quad \text{(II)}$$

$k_{dec} = k_{18}k_{19}/k_{-18}$; $k_{trap} = k_{23}F_T$; $F_T = k_{24}/(k_{-23} + k_{24})$

Table II. 1-Pentene + SiH_4 Reaction Product Yield versus SiH_4 Data[a-c]

temp, K	10^4[SiH4], M	10^2[(2PS + 3PS)/2-P]	k_{exp}, M^{-1}	k_{dec},[d] s^{-1}
648.7	0.00	0.00	98.8 ± 3.3	2.93×10^7
	7.68	9.89		
	12.4	12.5		
	18.8	20.7		
	31.5	32.9		
	43.4	43.0		
669.7	0.00	0.00	69.1 ± 3.2	4.19×10^7
	7.44	4.19		
	12.0	8.01		
	18.0	13.2		
	30.2	18.9		
	42.0	29.5		
691.1	0.00	0.00	43.3 ± 0.5	6.68×10^7
	7.21	2.79		
	11.6	4.83		
	17.4	7.63		
	29.5	12.6		
	40.9	17.6		

[a] All studies were at 410 Torr total pressure. [b] 2PS = 2-pentylsilane, 3PS = 3-pentylsilane, 2-P = 2-pentene. [c] Slope = $k_{exp} = 1.4k_{trap}/1.5k_{dec}$, see text; $E_{exp} = -17.3 \pm 1.6$ kcal, log A_{exp} (M^{-1}) = -3.83 ± 0.51. [d] At 410 Torr, log $A_{dec} = 13.29 \pm 0.5$, $E_{dec} = 17.3 \pm 1.6$ kcal; based on $k_{trap} = 3.1 \times 10^9\ M^{-1}\ s^{-1}$.

Table III. Migration of the Double Bond in the 2-Methyl-1-pentene Pyrolysis in 80.7% Silane at 669.8 K, P_T = 130 Torr[a,b]

time, min	% 2-methyl-1-pentene		% 2-methyl-2-pentene		% 4-methyl-2-pentene		% 4-methyl-1-pentene		% $MePSiH_3$ silane	
	obsd	calcd[a]	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
0.0	100.0		0.0		0.0		0.0		0.0	
2.0	99.6		0.4		0.0		0.0		0.0	
4.0	98.6		1.2		0.2		0.0		0.1	
6.0	96.3	95.4	2.4	3.0	0.8	0.9	0.2	0.2	0.3	0.6
8.0	94.0		3.6		1.6		0.3		0.6	
12.0	88.5	89.6	6.7	6.6	2.9	2.0	1.0	0.4	2.0	1.4
18.0	73.6		13.5		6.1		1.4		5.6	
25.0	61.8	78.1 (68.3)	20.5	13.5 (19.0)	9.0	4.4 (6.6)	2.1	0.9 (1.4)	6.8	3.1 (4.6)
30.0	55.3		23.3		10.2		2.4		9.1	
40.0	46.0	66.6 (51.3)	28.0	20.0 (27.4)	12.7	7.0 (11.2)	2.9	1.4 (2.4)	10.5	5.1 (7.8)
55.0	37.8	54.8 (40.8)	34.0	24.8 (31.2)	17.0	9.5 (14.6)	3.7	2.0 (3.1)	8.5	7.0 (10.5)

[a] Calculated values not in parentheses were obtained with $k_1 = k_{P\&W}$.[5a] This initiation should be valid up to the 3% silane conversion or to about 12 min. Values in parentheses were obtained by setting $k_1 = k_{P\&W} + k_{wall}$[5b] starting at 12 min. This is roughly when the silane second stage begins. Values in parentheses past 12 min then should be and are closer to the observations. [b] $k_c = k_o = 3.29 \times 10^8$, $k_d = 3.29 \times 10^7$, $k_{48} = 5.7 \times 10^8$, $k_{-48} = 1.7 \times 10^6$, $k_{49} = 3.3 \times 10^5$ s^{-1}; $k_a = 6.0 \times 10^{10}$ and $k_T = 2.0 \times 10^9$ M^{-1} s^{-1}. k_c, k_o, k_d, and k_a are generic rate constants of reactions to and from silacyclopropane intermediates (see text).

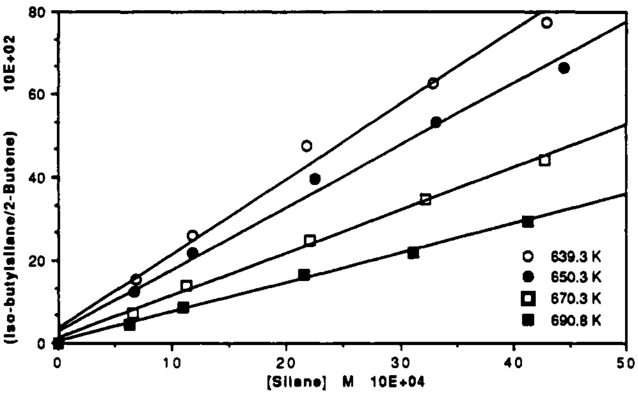


Figure 2. Plots of isobutylsilane/2-butene yield ratios versus silane (constant pressure, P_T = 408 Torr).

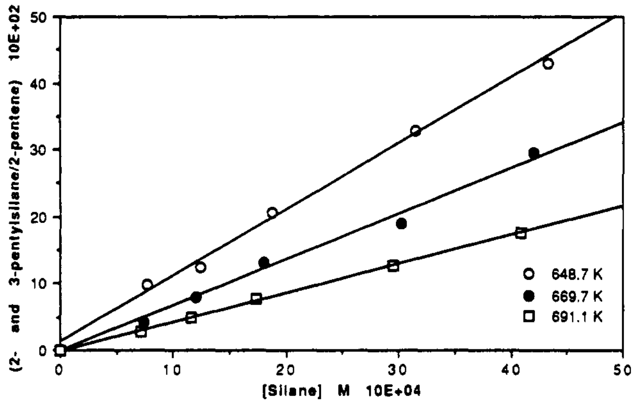


Figure 3. Plots of 2- and 3-pentylsilane/2-pentene yield ratios versus silane (constant pressure, P_T = 410 Torr).

II is based on several reasonable assumptions: that the concentrations of the 2- and 3-pentylsilylenes are in the same ratio as those of their corresponding pentylsilane product yields (i.e., 2-PS/3-PS = 2.5), that $k_{-20} = 2k_{18}$, that $k_{20} = k_{-18}$, and that the pentylsilylene-trapping rate constants with silane are equal.

In both 1-olefin/SiH_4 studies there was a strong preference for 1-alkylsilane product. Thus in 1-butene/SiH_4 reactions, 1-$BuSiH_3$/2-$BuSiH_3$ ≈ 3.7 at all conversions, and, correspondingly, in 1-pentene/SiH_4 reactions, 1-$PSiH_3$/(2-$PSiH_3$ + 3-$PSiH_3$) ≈ 2.2. In addition, olefin/$RSiH_3$ yield ratios were about 2.4 times larger in the 1-pentene system than in the 1-butene system at comparable silane concentrations. A similar increase in olefin/$RSiH_3$ ratios occurred in silane/2-methyl-1-pentene reactions,

Table IV. Silane + Pentene Pyrolysis Yields (675 K, P_T = 50 Torr)

t, s	% pentene isomerized obsd	calcd[a]	calcd[b]	1PS/2PS obsd	calcd[a,b]	2PS/3PS obsd	calcd[a,b]
			SiH_4 + 1-Pentene				
450	14.6	12.3	22.6	3.27	2.58	2.39	2.63
900	37.4	27.4	41.8	2.90	2.56	2.59	2.55
1260	52.3	37.3	52.8	3.08	2.52	2.63	2.49
			SiH_4 + 2-Pentene				
450	4.0	2.69	5.57	2.48	2.08	2.00	1.82
900	8.2	6.06	9.43	2.57	2.10	2.34	1.84
1260	10.7	8.29	11.0	2.26	2.11	2.47	1.86

[a] Calculated by using $k_1 = k_{P\&W}$[5a] = 4.1×10^{-5} s^{-1}. [a] Calculated by using $k_1 = k_{P\&W} + k_{wall}$[5b] = 15.3×10^{-5} s^{-1} starting at time 0. The second stage of reaction, at about 3% silane conversion, starts at about 12 min. [c] $k_c = k_o = 1.86 \times 10^8$, $k_d = 1.86 \times 10^7$, $k_{48} = 3.4 \times 10^8$, $k_{-48} = 8.4 \times 10^5$, $k_{49} = 2.4 \times 10^5$ s^{-1}; $k_T = 3.1 \times 10^9$, $k_a = 6.0 \times 10^{10}$ M^{-1} s^{-1}. k_c, k_o, k_d, and k_a are generic rate constants of reactions to and from silacyclopropane intermediates (see text).

and, by the mechanism, these observations suggest slower RSiH trapping versus SCP formation–decomposition with increasing R group size, i.e., a "steric factor" effect in RSiH + SiH_4 trapping reactions. Because of falloff, faster SCP decomposition with SCP size is also possible.

Silane/2-Pentene Reactions. When silane/2-pentene mixtures were pyrolyzed under silane/1-pentene reaction conditions (P_{total} = 50 Torr, T = 675 K, see data in Table III), olefin isomerization rates were four to five times slower but the relative distribution of pentylsilane products was nearly the same. Thus for SiH_4/1-pentene 1PS/2PS/3PS = 7.8/2.5/1 at all conversions, and for SiH_4/2-pentene 1PS/2PS/3PS = 5.5/2.3/1. This preference for 1-alkylsilane products, regardless of the starting olefin, can only mean that SCP decompositions are slow compared to their opening and forming reactions. Just the opposite condition had to be assumed to rationalize the results of the former study.[1]

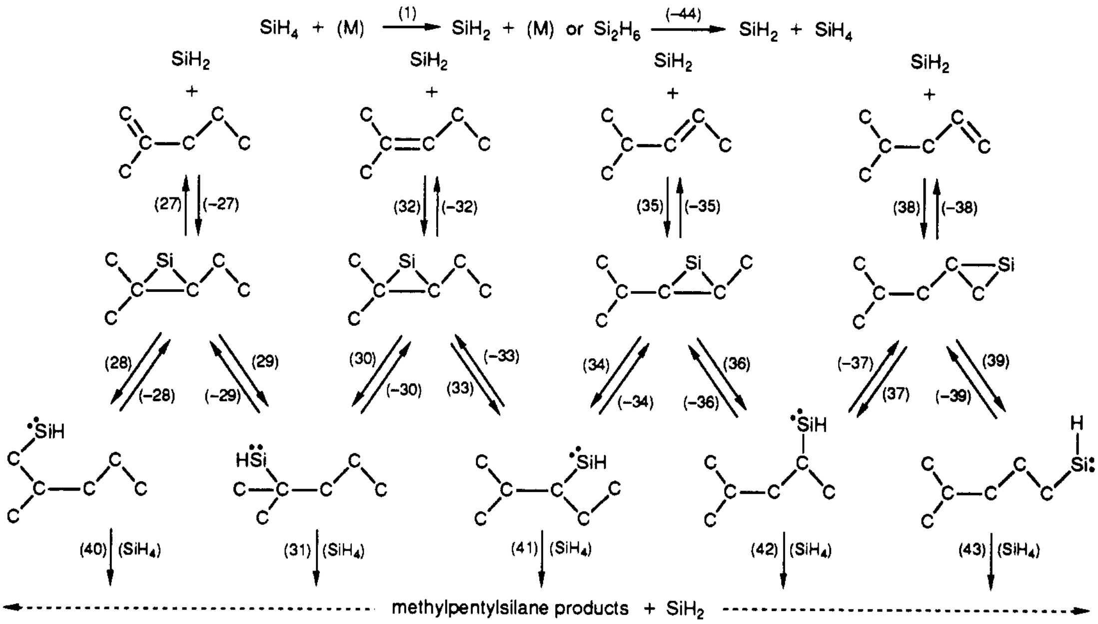
Methyl-1-pentene/SiH_4 Studies. Silane/2-methyl-1-pentene and silane/4-methyl-1-pentene reactions were studied in the 640–670 K range at 30–130-Torr total pressures. Results are given in Tables IV and V. As in the prior studies, products (i.e., disilane, four methylpentene isomers, five methylpentylsilanes, and traces of light hydrocarbons from olefin decompositions) are consistent with the Barton mechanism (Scheme IV). Most significant are the olefin yield developments in time. These show a stepwise, down the chain increase from either starting olefin position, which, by the mechanism, indicates

Table V. 4-Methyl-1-pentene + Si_2H_6 (T = 583 K, P_T = 130 Torr)

	% 4-Me-1-P		% 4-Me-2-P		% 2-Me-2-P		% 2-Me-1-P		% $MePSiH_3$	
t, s	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
600	98.9	97.9	0.7	0.9	0.4	0.7	0.0	0.5	0	0.1
1800	96.8	93.5	1.5	2.6	1.2	2.0	0.3	1.4	0.2	0.4
2400	95.2	91.2	1.9	3.5	1.8	2.6	0.5	1.8	0.8	0.9
3000	94.2	88.8	2.2	4.4	2.2	3.3	0.6	2.3	0.8	1.3

[a] $k_c = 1.48 \times 10^8$, $k_o = 1.07 \times 10^8$, $k_d = 4.25 \times 10^6$, $k_{48} = 4.6 \times 10^8$, $k_{-48} = 3.6 \times 10^5$, $k_{49} = 4.2 \times 10^4$ s^{-1}; $k_a = 6 \times 10^{10}$, $k_T = 2.0 \times 10^9$ M^{-1} s^{-1}. k_c, k_o, k_d, and k_a are generic rate constants of reactions to and from silacyclopropane intermediates (see text).

Scheme IV. Mechanism of Methylpentene/Silane Reactions



sequential migration of the silylene position via successive SCP ring-closing and ring-opening reactions.

Methylpentylsilane yields were too low to be separately quantified, but the data could be used in a semiquantitative manner through reaction modeling (see later) to determine relative rate constants of the competing ring-opening, -closing, and -decomposition reactions.

A most important general observation relative to all silane/olefin reactions was that no large-ring silacyclic products (e.g., silacyclobutanes, silacyclopentanes, and silyacyclohexanes) were detected in any of the reaction systems.

Mechanistic Investigations. The 1-butene/silane and 2-methyl-1-pentene/silane systems were investigated in packed reactors with order of magnitude S/V ratio increases. No olefin isomerization rate accelerations were observed, hence, in accord with initial study[1] conclusions, silane/olefin thermal reactions are homogeneous.

Two additional tests for free radical participation were made and both were negative: (1) silane/1-butene and silane/2-methyl-1-pentene reactions in the presence of toluene-d_8 were not rate inhibited and did not produce deuterated products and (2) neat reactant olefins were pyrolyzed under reaction conditions and no significant[4] decomposition or isomerization was observed.

Several studies were made to test the importance of silylenes to the observed olefin isomerization; all confirmed their importance. Thus silane/1-butene mixtures "reacted" at 598 K (a temperature where silane is "stable")[5] produced no olefin or alkysilane products, while disilane/1-butene mixtures reacted for the same time at 598 K (disilane[6] decomposes 600 times faster than silane at this temperature) exhibited olefin isomerization and butylsilane formation rates comparable to those of the disilane decomposition. In addition, 1-butene/silane and the 4-methyl-1-pentene/silane reactions, studied over silane conversion between 0 and 15%, showed rate accelerations at about 2% silane conversion. These accelerations correlate with the well-known[5] second-stage rate accelerations of the silane decomposition. Such rate accelerations did not occur in reactions initiated by disilane (see Figure 1). Finally, 1,1,2,2-tetramethyldisilane (a Me_2Si source[7]) reacted with 1-butene produced no olefin isomerization or butylsilane formation. This is consistent with the Barton[2] mechanism, as dimethylsilylene additions to olefins produce SCP's with no Si–H bonds, hence H-migration ring opening reactions, which lead to olefin isomerization, are not possible. All these observations show a clear correlation of olefin/silane reaction rates and pathways with silylene (SiH_2) concentration levels and provide additional support for the Barton mechanism.

Alkylsilylene Decomposition Kinetics and Thermochemistries. The experimental rate constants of the 2-butylsilylene reactions, $k_{exp} = k_{trap}/k_{dec}$, obtained from the Table I data and Figure 1 plots, give 408-Torr pressure Arrhenius parameters ($E_{exp} = -16.1 \pm 0.91$ kcal, log A_{exp}

(4) Highest isomerization yields were found in the neat 2-methyl-1-pentene reaction, and these were less than 3% of those with silane present. Isomerizations in neat pyrolses of the smaller olefins were less than 1% of that with silane present.

(5) (a) Purnell, J. H.; Walsh, R. *Proc. R. Soc. London* **1966**, *A293*, 543. (b) White, R. T.; Espino-Rios, R. L.; Rogers, D. S.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1985**, *17*, 1029.

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Table VI. 4-Methyl-1-pentene + SiH_4 (T = 639 K, P_T = 130 Torr)[a,b]

	% 4-Me-1-P		% 4-Me-2-P		% 2-Me-2-P		% 2-Me-1-P	
t, s	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
1200	97.3	97.3 (92.8)	1.3	1.5 (3.2)	0.9	0.6 (1.7)	0.5	0.3 (1.5)
2400	92.0	93.0 (82.5)	3.6	3.1 (7.5)	3.1	1.7 (4.1)	1.3	0.9 (2.4)
3600	82.1	88.2 (72.1)	7.3	5.3 (11.5)	7.3	2.9 (6.6)	3.2	1.7 (3.9)

[a] Values not in parentheses are with $k_1 = k_{P\&W}{}^{5a} = 6.55 \times 10^{-6}$ s^{-1}. Values in parentheses are with $k_1 = k_{P\&W} + k_{wall}{}^{5b} = 2.04 \times 10^{-5}$ s^{-1} starting at time 0. Since the second stage does not begin until after 2000 s, unbracketed values should (and do) fit the observations up to 2400 s. [b] $k_c = 2.54 \times 10^8$, $k_o = 2.08 \times 10^8$, $k_d = 1.59 \times 10^7$, $k_{48} = 5.3 \times 10^8$, $k_{-48} = 1.1 \times 10^6$, $k_{49} = 1.7 \times 10^5$ s^{-1}; $k_a = 6.0 \times 10^{10}$, $k_T = 2.0 \times 10^9$ M^{-1} s^{-1}. k_c, k_o, k_d, and k_a are generic rate constants of reactions to and from silacyclopropane intermediates (see text).

(M^{-1}) = −3.22 ± 0.30) that are appreciably higher than those obtained in the original study.[1] This illustrates the importance of pressure falloff in the isobutylsilylene decomposition and reflects the effect of the higher and constant total pressure of this study.

A similar treatment of the 1-pentene/SiH_4 reaction data and k_{exp} rate constants (Table II, Figure 2) give 410-Torr Arrhenius parameters for the isopentylsilylene reactions of E_{exp} = −17.3 ± 1.6 kcal and log A_{exp} (M^{-1}) = −3.83 ± 0.51.

In order to extract silylene decomposition rate constant values from the experimental constants, information on alkylsilylene-trapping rate constants is needed. This is not available. However, absolute rate constant versus temperature measurements by Walsh[8] on the analogous MeSiH + SiH_4 reaction suggest a rate constant at 670 K of $k_{trap} = 9 \times 10^{9\pm0.3}$ M^{-1} s^{-1}. Adopting the upper limit and dividing the factor of 2.4 decrease in $RSiH_3$/olefin yields with each C atom increase in R equally between a RSiH decomposition falloff effect and a trapping steric factor effect give trapping rate constants of $k_{trap,BuSiH} = 4.8 \times 10^9$ M^{-1} s^{-1} and $k_{trap,PSiH} = 3.1 \times 10^9$ M^{-1} s^{-1} at 670 K. With these values and the assumption of zero activation energy for silylene trapping, one calculates the alkysilene decomposition rate constants shown in the last columns of Tables I and II. Their corresponding Arrhenius parameters at 410 Torr are, for 2-BuSiH, log A_{dec} = 12.9 ± 0.3, E_{dec} = 16.1 ± 0.8 kcal and, for iso-PSiH, log A_{dec} = 13.3 ± 0.5, E_{dec} = 17.3 ± 1.6 kcal.

Analysis via Generic Rate Constants. Since alkylsilylene decomposition is a consecutive step process, the above rate constants are composites of other elementary rate constants. From the steady state, and in generic notation, $k_{dec} = k_ck_d/(k_o + k_d) = (k_ck_d/k_o)(1 + k_d/k_o)^{-1}$, where the subscripts c, o, and d stand respectively for closing of RSiH to SCP, opening of SCP to RSiH, and decomposition of SCP. Similarly, the equilibrium constant of an alkylsilylene decomposition can be represented as k_ck_d/k_ak_o, where k_a is the rate constant for silylene addition to the olefin product. Modeling of the olefin/silane systems (see later) indicates that $k_o/k_d \approx 10$; therefore, $k_ck_d/k_o = k_{cdo} = k_{dec}(1 + k_d/k_o) \approx 1.1k_{dec}$.

RRKM Calculations. Alkysilylene decomposition RRKM falloff calculations were made on the 2-butylsilylene and the 2- and 3-pentylsilylene k_{cdo} values. If one assumes zero activation energy and equal efficiencies for all butene reactions with SiH_2 (i.e., $k_a = k_{-6} = k_{-2} = A_{trap} = 10^{11.1}$ M^{-1} s^{-1}),[1] then with $\Delta S_{5,6} \approx 30.1$ eu,[9] one estimates for the butylsilylene decomposition a high-pressure A factor of $(A_cA_d/A_o)_\infty = 10^{15.5}$ s^{-1}; i.e., the decomposition and its inverse silylene/olefin addition take place via a very loose transition state. The same A factor should apply to the pentylsilylene decompositions, barring steric factor effects. RRKM calculations[10] made with this A factor (see input data of Table VII) yield the following Arrhenius parameters: for isobutylsilylene, log $k_{cdo,408}$ = 13.32–17,

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Table VII. RRKM Input for the BuSiH and PSiH Decompositions

2-Butylsilylene Decomposition:[a] $A_\infty = A_{cdo} = 10^{15.47}$ s^{-1}
$k_{cdo} = 5.27 \times 10^7$ s^{-1}, 670.3 K, P_T = 408 Torr; 25% SiH_4, β_c = 0.61, σ = 5.1 Å; 75% 1-butene + TMS, β_c = 0.92, σ = 6.0 Å
reactant frequencies (cm^{-1}): 9–3100, 2130, 7–1450, 2–1200, 2–1110, 2–1100, 2–1050, 3–900, 1–800, 690, 650, 2–420, 2–300, 250, 2–235, 230, 180
transition-state frequencies (cm^{-1}): 8–3100, 2–2130, 3–1460, 3–1450, 2–1110, 1100, 4–1060, 2–920, 905, 425, 420, 2–385, 235, 230, 135, 2–130, 100

Isopentylsilylene Decomposition:[a] $A_\infty = A_{cdo} = 10^{15.47}$ s^{-1}
$k_{cdo} = 4.84 \times 10^7$ s^{-1}, 669.7 K, P_T = 410 Torr; 25% SiH_4, β_c = 0.61, σ = 5.1 Å; 75% 1-pentene + TMS, β_c = 0.92, σ = 6.2 Å,
reactant frequencies (cm^{-1}): 2-butylsilylene frequencies + 2–3100, 1450, 2–1100, 900, 800, 420, 230
transition-state frequencies (cm^{-1}): 2-butylsilylene transition-state frequencies + 2–3100, 1450, 2–1100, 900, 800, 420, 230

RRKM Summary
2-butylsilylene: $M \to \infty$, 25% SiH_4, P_T = 408 Torr
log A_∞ = 15.47, E_∞ = 22.24 kcal; log A = 13.32, E = 17.16 kcal, k/k_∞ = 0.33
isopentylsilylene: $M \to \infty$, 42.8% SiH_4, P_T = 410 Torr
log A_∞ = 15.47, E_∞ = 22.81 kcal; log A = 13.68, E = 18.37 kcal, k/k_∞ = 0.46

[a] It has been shown[10] that falloff is not very dependent on the exact frequencies chosen for reactant and transition state, as long as they are consistent with the high-pressure A factor. The frequencies given are just reasonable guesses.

Table VIII. RRKM Calculated Arrhenius Parameters

Generic Rate Constants

k_d
$k_{d(50 Torr)} = 10^{12.58}e^{-16380 cal/RT}$ s^{-1} — $E_{d,\infty}$ = 26 080 cal
$k_{d(130 Torr)} = 10^{13.20}e^{-17570 cal/RT}$ s^{-1} — $A_{d,\infty} = 10^{16.85}$ s^{-1}
$k_{d(410 Torr)} = 10^{13.95}e^{-19070 cal/RT}$ s^{-1}

k_o
$k_{o(50 Torr)} = 10^{10.55}e^{-7270/RT}$ s^{-1} — $E_{o,\infty}$ = 14 650 cal
$k_{o(130 Torr)} = 10^{11.20}e^{-8438/RT}$ s^{-1} — $A_{o,\infty} = 10^{13.96}$ s^{-1}
$k_{o=410 Torr)} = 10^{11.98}e^{-9963/RT}$ s^{-1}

k_c
$k_{c(50 Torr)} = 10^{10.12}e^{-5685/RT}$ s^{-1} — $E_{c,\infty}$ = 10 370 cal
$k_{c(130 Torr)} = 10^{10.68}e^{-6845/RT}$ s^{-1} — $A_{c,\infty} = 10^{12.34}$ s^{-1}
$k_{c(410 Torr)} = 10^{11.41}e^{-8215/RT}$ s^{-1}

Silylsilylene and Disilene Reaction Rate Constants[a]

$SiH_3SiH \xrightarrow{(48)} Si_2H_4$; $Si_2H_4 \xleftarrow{(-48)} SiH_3SiH$; $Si_2H_4 \xrightarrow{(49)} Si_2H_2 + H_2$
$k_{48(50 Torr)} = 10^{8.84}e^{-959/RT}$ s^{-1} — E_∞ = 5570 cal
$k_{48(130 Torr)} = 10^{9.32}e^{-1730/RT}$ s^{-1} — $A_\infty = 10^{12.74}$ s^{-1}
$k_{48(410 Torr)} = 10^{9.85}e^{-2352/RT}$ s^{-1}
$k_{-48(50 Torr)} = 10^{9.84}e^{-12100/RT}$ s^{-1} — E_∞ = 19 390 cal
$k_{-48(130 Torr)} = 10^{10.40}e^{-12708/RT}$ s^{-1} — $A_\infty = 10^{13.42}$ s^{-1}
$k_{-48(410 Torr)} = 10^{10.98}e^{-13244/RT}$ s^{-1}
$k_{49(50 Torr)} = 10^{11.15}e^{-17800/RT}$ s^{-1} — E_∞ = 20 190 cal
$k_{49(130 Torr)} = 10^{11.52}e^{-18396/RT}$ s^{-1} — $A_\infty = 10^{12.36}$ s^{-1}
$k_{50(410 Torr)} = 10^{11.84}e^{-19120/RT}$ s^{-1}

[a] The kinetics of these processes are not established. Arrhenius parameters for reaction 48 are based on observations of Walsh,[23] while the Arrhenius parameters of reactions −48 and 49 are based on our recent modeling studies of the silane decomposition.[17]

160 cal/θ s^{-1}, $(k_{408}/k_{\infty})_{670\,K} = 0.33$, and $\log k_{cdo,\infty} = 15.47$–22, 240 cal/$\theta$ s^{-1}; for the isopentylsilylenes, $\log k_{cdo,410} = 13.68$–18, 370 cal/θ s^{-1}, $(k_{410}/k_{\infty})_{670\,K} = 0.46$, and $\log k_{cdo,\infty} = 15.47$–22, 810 cal/$\theta$ s^{-1}, where $\theta = 2.3RT$. Falloff calculations on the generic rate constants (k_c, k_d, k_o, see Table VIII) give an activation energy for the $(1 + k_d/k_o)$ factor of about 0.8 kcal at 410 Torr. Therefore the calculated and observed activation energies for both systems at 408 Torr are in excellent agreement: e.g., for the isobutylsilylene decomposition, $E_{dec} = E_{cdo,410} - 0.8 = 16.4$ kcal, which compares well with the experimental value of 16.1 kcal (assuming $E_{trap} = 0$).

Correlation of Decomposition Kinetics and Thermochemistries. The RRKM high-pressure activation energies of the butyl- and pentylsilylene decompositions are in the range $E_{dec,M\to\infty} = 22.5 \pm 0.3$ kcal, and these agree, within the errors, with their decomposition energies of $\Delta E_{dec(670\,K)} = 25.3 \pm 3.4$ kcal (see the decomposition thermochemistry below).

reaction:	2-butylSiH	⟶	c,t-2-C_4H_8[12]	+	SiH_2	(5, 6)
ΔH_f, kcal/mol	34.6 ± 2.8		−2.7		64 ± 2	
$C_{p,298}$, eu/mol	26.6		20.1		8.2	
$C_{p,500}$, eu/mol	40.3		30.4		8.9	
$C_{p,800}$, eu/mol	54.3		41.3		10.2	

These agreements are consistent with the assigned values of zero for the activation energies of silylene additions to olefins and support our present data analysis.

Regarding the thermochemistry, the above heat of formation for 2-butylsilylene is higher than our earlier estimate.[1] This is a consequence of "new" methylsilylene and isopropylsilane heats of formation data; i.e., ΔH_f(MeSiH) = 48 ± 2 kcal/mol[11] and $\Delta H_f(iPrSiH_3) = -15.5 \pm 0.3$ kcal/mol, where the isopropylsilane heat of formation (which yields a new group additivity value of $\Delta H_f[C-(H)(C_2)(Si)] = 1.7 \pm 0.2$ kcal mol) is an average of values calculated by Benson's EECBA method[13] and Allinger's MM2 method.[14]

It is important to emphasize again the significance of the close to collision levels of the silylene/olefin addition reactions and the high A factors of the alkylsilene decompositions. Both signify very "loose" transition states for the decomposition and addition reactions. On this basis, we suggested earlier[1] the possibility of biradical formation. However, present thermochemistry places the biradical at an energy level more than 12 kcal above that of the silylene/olefin products, i.e., $\Delta H_f(MeCH(SiH_2)\dot{C}HMe) \approx 73.6$ kcal/mol. Therefore, the transition state of alkylsilylene decomposition (or silylene/olefin addition) must be some kind of long-range complex in which the silylene is relatively free to rotate (or rock) against the olefin.

Reaction Modeling. There are essentially five classes of reactions participating in the silylene/olefin reactions, the four already discussed and the alkylsilylene trapping reactions (rate constants k_T). Reactions of a given class should have similar rate constants, although some variations are required by the product thermochemistries. Thus the relative stabilities of the methylpentene/SiH_4 reaction products are, by group additivity estimates,[12] 2-methyl-2-pentene/2-methyl-1-pentene/4-methyl-2-pentene/4-methyl-1-pentene = 20/5.6/4.4/1. The rate constants of Scheme IV must reflect this. Yield data are clearly not sufficient to set values for all the individual rate constants of the reaction schemes; however, rough modeling fits of the yield and rate data can provide important semiquantitative information on relative rate constants of the five reaction classes. With this objective, we modeled the following reactions: (1) SiH_4/1- and 2-pentene (Table IV for conditions and data), (2) SiH_4/2-methyl-1-pentene (Table III for conditions and data), (3) Si_2H_6/4-methyl-1-pentene (Table V for conditions and data), and (4) SiH_4/4-methyl-1-pentene (Table VI for conditions and data).

Rate Constant Assignments. Rate constant assignments were made in terms of their generic values. Silylene additions to pentenes were assigned rate constants of $k_a = 6 \times 10^{10}$ M^{-1} s^{-1}. This reflects a small steric factor effect relative to the SiH_2/1-butene rate constant previously established[8] as $10^{11.1}$ M^{-1} s^{-1}. The pentylsilylene- and methylpentylsilylene-trapping reactions were assigned values of $k_{T(PSiH)} = 3.1 \times 10^9$ M^{-1} s^{-1} and $k_{T(MPSiH)} = 2.0 \times 10^9$ M^{-1} s^{-1}, reflecting the 1.5/C steric factor reduction cited earlier. The generic alkylsilene ring-closing rate constant was assigned a value of $k_c = k_{dec}(1 + k_o/k_d) = 4.9 \times 10^8$ s^{-1} at 670 K and 410 Torr. This follows from the pentylsilylene-decomposition rate constant (Table II) and a $k_o/k_d = 10$. The latter was based on preliminary modeling of the 1- and 2-pentene/silane reactions (see Table IV) and follows from the fact that the strong preference for 1-alkylsilane products could not be duplicated with k_o/k_d values less than 10. Also, values of k_o/k_d much greater than 10 produced unrealistically low activation energies for the ring-closing reaction.

Modeling established that calculated product yields and reaction rates were independent of the k_c/k_o ratio. This means that no information about the relative stabilities of alkylsilylenes and their silacyclopropane isomers can be obtained through modeling. Therefore, calculations were made with $k_c/k_o = 1$ at 410 Torr and 670 K. This assignment ascribes comparable stabilities to alkylsilylenes and their silacyclopropane isomers and is consistent with our unpublished SCP ring strain estimate of 49.6 kcal/mol.[15] Gordon's[16] calculations at the SCF(HF/6-31G(d)//HF/631G(d) and MP2 (MP2/6-31)G(d)//HF/6-31G(d) gave SCP ring strains of 45.1 and 42.9 kcal/mol, respectively. These lower strain energies imply slightly higher activation energies for the ring opening and ring decomposition reactions (by 4–7 kcal) but do not substantially affect the treatment that follows. Values of k_c, k_o, and k_d for all the relevant reaction conditions were obtained from RRKM calculations (see Table VIII), using the above 410-Torr rate constants and thermochemical kinetic estimates[12] of the high-pressure Arrhenius parameters: $\log A_{c,\infty} \approx 12.3$, $\log A_{o,\infty} \approx 14.0$, $\log A_d \approx 16.9$, A in s^{-1}. Individual rate constants within the five reaction classes were then assigned. Ring-closing rate constants were set by their reaction path degeneracies (i.e., $k_c \times$ rpd/2), and ring-opening and ring-decomposition rate constants were set to be consistent with group additivity estimates[9,17] of the product RSiH and reactant olefin stabilities. In general, silacyclopropane rings producing the more stable olefin products were assumed to be more reactive toward ring decomposition and ring opening. These considerations produced the following assignments in the methylpentene/SiH_4 reactions: ring-closing reac-

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(16) Boatz, J. A.; Gordon, M. S. *J. Am. Chem. Soc.* **1989**, *93*, 3025.
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tions, $k_c = k_{-39} = k_{-34} = k_{-30} = k_{-36}$, $0.5k_c = k_{-33} = k_{-28}$, $1.5k_c = k_{-37}$, $3k_c = k_{-29}$; ring-opening reactions, $k_o = k_{34} = k_{30} = k_{36}$, $2k_o = k_{37} = k_{29} = k_{39}$, $0.5k_o = k_{33} = k_{28}$; ring-decomposition reactions, $k_d = k_{38}$, $k_{35} = 3.3k_d$, $k_{32} = 5k_d$, $k_{27} = 2.8k_d$. Corresponding 1-pentene/SiH_4 reaction assignments were $k_c = k_{18} = k_{-16}$, $2k_c = k_{-17} = k_{-20}$; $k_o = k_{-18} = k_{20}$, $2k_o = k_{17}$, $4k_o = k_{16}$; $3.3k_d = k_{19}$, and $k_d = k_{-15}$. Assignments of $4k_o$ to k_{16} (rather than $2k_o$) and of $5k_d$ to k_{32} (rather than $15k_d$) were subsequent adjustments needed to improve the modeling.

Since the generic ring-opening, -closing, and -decomposition rate constants are both temperature and pressure dependent, appropriate values for each system modeled (given in each table addenda) were obtained by RRKM[10] calculations. The latter are summarized in Table VIII. The other important reactions to the modeling are those controlling silylene steady-state levels: initiation reactions (silane and disilane decompositions, reactions 1 and −44, respectively) and silylene sink reactions (reactions 44–49). The latter were assumed to be the those of the silane decomposition.[17]

$$SiH_2 + SiH_4 \overset{(44)}{\leftrightarrow} Si_2H_6 \quad k_{44} = 6.0 \times 10^9\ M^{-1}\ s^{-1}\ ^{18} \quad k_{-44} = 10^{15.75}e^{-52200cal/RT}\ s^{-1}\ ^{6}$$

$$Si_2H_6 \overset{(45)}{\leftrightarrow} SiH_3SiH + H_2 \quad k_{45} = 10^{16.45}e^{-57800cal/RT}\ s^{-1}\ ^{6}$$

$$SiH_2 + Si_2H_6 \overset{(46)}{\leftrightarrow} Si_3H_8 \quad k_{46} = 2.4 \times 10^{11}\ M^{-1}\ s^{-1} \quad k_{-46} = 10^{15.7}e^{-53200cal/RT}\ s^{-1}\ ^{19}$$

$$Si_3H_8 \overset{(47)}{\leftrightarrow} SiH_4 + SiH_3SiH \quad k_{47} = 10^{15.41}e^{-51170cal/RT}\ s^{-1}\ ^{19} \quad k_{-47} = 6.0 \times 10^{11}\ M^{-1}\ s^{-1}$$

$$SiH_3SiH \overset{(48)}{\leftrightarrow} Si_2H_4 \quad k_{48}\ \text{(Table VIII and footnote)} \quad k_{-48}$$

$$Si_2H_4 \overset{(49)}{\leftrightarrow} Si_2H_2 + H_2 \quad k_{49}\ \text{(Table VIII and footnote)}$$

One modeling complication concerns the silane-decomposition rate acceleration, which occurs in the 3–6% conversion range. Up to this point, the decomposition rate constant for silane is the pseudo-first-order value determined by Purnell and Walsh:[5a] $k_1 = k_{P\&W} = 10^{15.18}e^{-55900cal/RT}M^{0.5}\ s^{-1}$; beyond this point the reaction accelerates (presumably because of a wall-initiated catalysis[5b] by either $(SiH_2)_x$ or $(SiH)_x$ on the walls) and the rate constant of this wall-enhanced process has been shown[5b] to fit $k_{1(wall)} = 10^{7.82}e^{-43800/RT}[SiH_4]^{-0.8}\ s^{-1}$. Because of this rate change, reactions initiated by the silane decomposition were modeled two ways: with $k_1 = k_{P\&W}$ and with $k_1 = k_{P\&W} + k_{wall}$. Calculated yields with $k_1 = k_{P\&W}$ should fit the experimental observations up to about 3% silane loss and be lower than observations at higher conversions. Calculated yields with $k_1 = k_{P\&W} + k_{wall}$ should be larger than the experimental values at low silane conversions but approach the observed yields at high silane conversions. This is the case (see Tables III–VI). Comparisons of the modeling yields and rates with the experimental observations (Tables III–VI) show agreements within a factor of 2. Considering the guesses required in setting individual rate constants and the large pressure and temperature ranges covered (50–410 Torr, 583–670 K), this agreement must be considered quite good. The main conclusions of the modeling are (1) that silacyclopropane ring-opening and ring-closing reactions are about an order of magnitude faster than their decompositions and (2) that the ring-closing reactions forming silacyclopropanes are unusually fast. RRKM calculations on the ring-closing reaction, assuming a tight transition state ($A_{c,\infty} = 10^{12.3}\ s^{-1}$), give an $E_{c,410} = 8.2$ kcal and an $E_{c,\infty} = 10.4$ kcal in the 670 K range. Surprisingly, this is essentially the same activation energy deduced from the earlier study[2] for SCP formation via an alkylsilylene, intramolecular C–H insertion reaction.

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Observations on Silylene into C–H Bond Insertion Reactions. The two studies that provide semiquantitative information on silylene insertions into C–H bonds are the present study (assuming the validity of the proposed mechanism and analysis) and a former study on the shock-induced decomposition of methylsilane.[3] The latter provides C–H insertion reaction information through its thermochemistry.

$$MeSiH_3 \xrightarrow{(50)} CH_4 + SiH_2$$

$$k_{50} \approx 227\ s^{-1}\ \text{at 1200 K;}^{3}\ \Delta H_{1200} = 51.5\ \text{kcal;} \quad \Delta S_{1200} = 30.8\ \text{eu}^{12}$$

If the insertion reaction is assigned a transition state consistent with the present treatment for ring closing (i.e., normal and tight), then $A_{50} \approx 10^{13.5}\ s^{-1}$ and $E_{50} = 61.2$ kcal at 1200 K. With the reaction enthalpy, this gives $E_{-50} = 12.1$ at 1200 K and translates to an activation energy of $E_{-50} \approx 10.0$ kcal at 670 K (M standard state), in good agreement with the value deduced from this study. The significantly higher silylene/C–H insertion activation energies of prior treatments[1,3] (i.e., $E_c \approx 16$–20 kcal) were due to differences in the estimated reaction thermochemistry and assumed A factor. Thus the silylene and methylsilylane heats of formation used previously[3] were 58 and −8.3 kcal/mol (rather than 64 and −7.4 kcal/mol[11]) and an A factor of $10^{14.5}\ s^{-1}$ (an order of magnitude higher value than the one used here) was assumed.[20] The near equivalence in activation energies of the strain-free SiH_2+CH_4 reaction and the RSiH intramolecular ring-closing reaction indicates an absence of strain in the transition state of the latter. This is contrary to our earlier assumptions[21] and goes far toward explaining why silacyclic rings larger than silacyclopropanes are not commonly observed.[22] Thus larger-ring-forming reactions have lower activation entropies (by about 3.5 eu per additional internal rotation lost in the transition state), and, contrary to conventional views on ring strain energy effects on ring-closing activation energies, they may also have sizable activation energies. Indeed observations of silacyclopentane in yields as high as 30% from the decomposition of *n*-butylsilylene at shock temperatures[21] (i.e., 1100–1200 K) and the absence of this same product in the present study (where yield observation limits were about 0.02) can only be rationalized by an activation energy difference between silacyclopentane and silacyclopropane ring formations of 10 kcal or more.

(20) It should be noted that the alkylsilylene/C–H studies under discussion (i.e., this work and ref 3) are mutually consistent regardless of the nature of the assumed transition states as long as they are either both "tight" or both "loose".
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Summary

Observations on olefin/SiH_4 reactions (olefin isomerization, alkylsilane formation) are consistent with Barton mechanisms involving silacyclopropane and alkylsilylene intermediates. SCP ring-forming and -opening reactions are at least an order of magnitude faster than their decompositions (to olefins and SiH_2). All reactions are pressure dependent at 400 Torr. On the basis of butylsilylene- and pentylsilylene-trapping reactions with silane of 4.8×10^9 M^{-1} s^{-1} and 3.1×10^9 M^{-1} s^{-1}, respectively, high-pressure Arrhenius parameters for the butyl- and pentysilylene decompositions of $\log A_\infty = 15.5 \pm 1$ and $E_\infty = 22.5 \pm 0.3$ kcal are derived. Activation energies are consistent with decomposition reaction thermochemistries ($\Delta H_{dec} = 26.6 \pm 3.4$ kcal, $\Delta E_{dec} = 25.3 \pm 3.4$ kcal), and A factors indicate surprisingly loose transition states for both alkysilylene decompositions and their reverse silylene/olefin additions. A loose silylene/olefin addition complex is suggested for the transition state, as the thermochemistry of decomposition precludes the intermediacy of biradicals. Generic high-pressure Arrhenius parameters (with A in s^{-1}, E in kcal) for the elementary reactions of silacyclopropane ring opening (o), closing (c), and decomposition (d) are $\log A_c = 12.3$, $E_c = 10.4$; $\log A_o = 14.0$, $E_o = 14.7 + \Delta E$; and $\log A_d = 16.9$, $E_d = 26.1 + \Delta E$, where ΔE = (49.6 – SCP strain energy).

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Registry No. Silane, 7803-62-5; 1-butene, 106-98-9; 1-pentene, 109-67-1; 4-methyl-1-pentene, 691-37-2; 2-pentene, 109-68-2; 2-methyl-2-pentene, 625-27-4; disilane, 1590-87-0; 2-butylsilylene, 110550-55-5; isopentylsilylene, 135710-28-0; silylene, 13825-90-6; 2-methyl-1-pentene, 763-29-1.

Organochromium π-Complexes. 3.[1,2] Preparation and Reactions of Bis(η^3-allyl)chromium(II) Complexes

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$Cr(PR_3)_2Cl_2$ (PR_3 = PMe_3, PMe_2Ph, PPh_2Me), $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$, and $[Cr(Pr^i_2PC_2H_4PPr^i_2)Cl_2]_2$ react with 2-propenylmagnesium chloride or 2-methyl-2-propenylmagnesium chloride to give thermolabile $(\eta^3\text{-allyl})_2Cr(PR_3)_2$ and $(\eta^3\text{-allyl})_2Cr(R_2PC_2H_4PR_2)$ compounds. In contrast, the final product of the reaction between $Cr(PMe_3)_2Cl_2$ and 2-butenylmagnesium chloride contains an η^2,η^2-bonded dimethyldiallyl group derived from the reductive coupling of two η^3-1-MeC_3H_4 fragments. $(\eta^3\text{-}C_3H_5)_2Cr(PMe_3)_2$ reacts with 2-butyne with alkyne insertion into an η^3-allyl group to give a compound containing both η^3-allyl and η^1,η^2-4-methyl-1,4-hexadienyl groups. The structures of these paramagnetic organochromium(II) compounds have been confirmed by X-ray structural determinations of three examples, viz. $(\eta^3\text{-}C_3H_5)_2Cr(PMe_2Ph)_2$ (**2**) (a = 8.894 (4) Å, b = 27.56 (1) Å, c = 9.355 (3) Å, β = 107.64 (3)°, space group $P2_1/n$, Z = 4), $(\eta^3\text{-}C_3H_5)_2Cr(Pr^i_2PC_2H_4PPr^i_2)$ (**6**) (a = 9.171 (1) Å, b = 15.936 (2) Å, c = 15.368 (1) Å, β = 102.22 (1)°, space group $P2_1/n$, Z = 4) and $(\eta^3\text{-}C_3H_5)(\eta^1,\eta^2\text{-4-methyl-1,4-hexadienyl})Cr(PMe_3)_2$ (**9**) (a = 9.299 (5) Å, b = 14.474 (8) Å, c = 13.916 (5) Å, space group $P2_12_12_1$, Z = 4).

Introduction

Although the organic compounds of chromium have not attained industrial importance as homogeneous catalysts, it has been known for over a quarter of a century that species containing the η^3-allyl group do have considerable activity. For example, $(\eta^3\text{-}C_3H_5)_3Cr$ attracted attention in the late 60's as a non-Ziegler catalyst for the polymerization of ethylene and butadiene while $[(\eta^3\text{-}C_3H_5)_2CrI]_2$ cyclotrimerizes butadiene to cyclododecatriene.[3-5] Subsequently, it was shown that η^3-allyl–chromium species catalyze the cyclotrimerization of alkynes[6] as well as the polymerization of acrylonitrile, methyl methacrylate, and substituted 1,3-dienes[7] while dozens of publications have been concerned with the catalytic activity of supported η^3-allyl–Cr catalysts.

Examples of *mononuclear* η^3-allyl complexes of chromium are, however, limited to those containing Cr(III) or Cr(I), e.g. $(\eta^3\text{-}C_3H_5)_3Cr$,[3] $Cp(\eta^3\text{-}C_3H_5)_2Cr$,[1] and $(\eta^3\text{-}C_3H_5)(\eta^4\text{-1-}EtC_4H_5)Cr(Me_2PC_2H_4PMe_2)$,[2] and as far as we are aware, no compounds of this type containing Cr(II) have been reported in the literature. Attempts to prepare such compounds by reacting the dinuclear species $(\eta^3\text{-}C_3H_5)_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2Cr_2$ with donor ligands were not successful.[8] On the other hand a few bis(aryl)- and bis(alkyl)–Cr(II) complexes, e.g. $(2,4,6\text{-}Me_3C_6H_2)_2Cr(PR_3)_2$,[9,10] $(Me_3CCH_2)_2Cr(Pr^i_2PC_2H_4PPr^i_2)$,[10] and $Me_2Cr(Me_2PC_2H_4PMe_2)_2$,[11,12] have been prepared by reacting

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