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Mechanism of the Thermal Decomposition of Ethylsilane

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Products and kinetics of the thermal decomposition of ethylsilane, under static system conditions, are reported. Both neat and propylene-inhibited reactions follow silylene chain mechanisms. Modeling fits to product yield and reactant loss data establish approximate values for the rate constants of the ethylsilylene decomposition to ethylene and silylene ($k_2 \approx 2 \times 10^6$ s^{-1}) and the ethylsilylene isomerization to vinylsilane ($k_8 \approx 5 \times 10^2$ s^{-1}), both at 723 K. RRKM and thermochemical analyses of these results yield values for the high-pressure activation energy of the ethylsilylene decomposition ($EtSiH \xrightarrow{2} C_2H_4 + SiH_2$) of $E_2 = 25.0$ kcal/mol and a heat of formation for ethylsilylene of $\Delta H_f(EtSiH) = 47.7 \pm 2.5$ kcal/mol. An enthalpy group additivity for the methylene group in organosilanes and organosilylenes of $\Delta H_f[C-(H_2)(C)(Si)] = -1.3 \pm 2$ kcal/mol is deduced as well as the activation energy of the isomerization of ethylsilylene to vinylsilane ($EtSiH \xrightarrow{8} CH_2{=}CHSiH_3$) of $E_8 = 35.6 \pm 2$ kcal/mol.

Introduction

An earlier investigation in these laboratories of the thermally induced decomposition of $EtSiH_3$ (ES)[1] by the comparative-rate single-pulse shock-tube method (CR-SPST, $T = 1165 \pm 80$ K, $P_{total} \approx 3200$ Torr, $P_{ES} \approx 6$ Torr) showed that the ES decomposition is initiated by a 1,1-H_2 elimination process yielding ethylsilylene (EtSiH) and that the ethylsilylene so produced decomposes to C_2H_4 and SiH_2 with an activation energy of less than 30 kcal. Rate constants for the ES decomposition in excess acetylene (for maximum inhibition of silylene chains) were consistent with Arrhenius parameters of $\log A(s^{-1}) = 15.14 \pm 0.08$ and $E = 64.77 \pm 0.94$ kcal/mol, while rate constants for the ES decomposition without a silylene scavenger were only 20−65% higher. Thus silylene−initiated chains do not contribute significantly to the overall decomposition of ES under CR-SPST conditions, i.e., high temperatures (1160 ± 80 K), high total pressures (≈3200 Torr), short reaction times (≈300 μs), and relatively low reactant pressures (≈6 Torr).

In this paper we report results on the ethylsilane decomposition under standard, static reactor conditions: relatively low temperatures (720 ± 30 K), moderate total and reactant pressures (180 and 22 Torr, respectively), and long reaction times (300−1200 s). Under these conditions chain reactions in the decomposition of ES are far more likely. In fact, our results show that chain reactions dominate the static ES reaction decomposition.

Experimental Section

The apparatus and operation procedures used in this study have been described previously.[2] The ES decomposition was studied over a 53 K range (695−748 K) using reactant mixtures of ethylsilane and tetramethylsilane (TMS). The latter served as an internal analytical GC standard and as a third-body bath gas. ES pressures were held constant at 22 Torr, while total pressures varied from 114 to 531 Torr. The ES decomposition was also studied at 693 K in the presence of excess propylene using a reactant mixture which was about 10 propylene/1 ES/1 TMS. Reactant loss and product formations were followed by aliquot sampling in time followed by analysis using FID and/or TCD gas chromatography. Separation and analysis of the more volatile and less volatile products were achieved using column switching between a 20 ft SE-30 column and a 5 ft Poropak R column. Product identifications were made by comparisons of GC retention times with those of known samples and also by GC−MS cracking patterns.

Results

The only significant, GC measurable products of the ES/TMS static system decomposition were C_2H_4 and SiH_4. Small amounts of heavier products believed from their retention times to be ethyldisilane, vinylsilane, and diethyldisilane were also detected, but only the peaks attributed to ethyldisilane were under some conditions large enough to integrate. Representative product yield and reactant loss data are given in Table 1. ES losses were all significantly higher than those expected for a reaction governed solely by its primary dissociation. Thus, for example, the shock-tube Arrhenius parameters for the primary dissociation of ES predict a reactant loss of less than 2.2% in 600 s at 723 K, 20 times less than observed.

In excess propylene (olefins are recognized trapping agents for silylenes[3] and for free radicals[4]) the decomposition of ES resulted in increased yields of C_2H_4, decreased yields of SiH_4, and the formation of two new products: *n*-propylsilane and *sec*-propylsilane. Product yield and ES loss rate data for this reaction are shown in Table 2. Contrary to expectation, ES loss rates in excess propylene increased; for example, at 693 K with a 1200 s reaction time the ES loss in propylene was almost double that observed with no propylene: 24% as opposed to 13.5%.

Reaction Analysis and Modeling

Our results show that the ES decomposition under static reaction conditions is about 20 times faster than the projected rate of its primary decomposition step (reaction 1): therefore, a chain process must be operative. The propylsilane products of the "propylene-inhibited" reaction also point to a chain process (noninhibiting) propagated by intermediate/propylene reactions. On the basis of current information concerning organosilane decompositions, the reaction intermediates involved

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TABLE 1: Product Yield[a] and Reactant Loss Data[a] of the Ethylsilane Decomposition under Static System Conditions[b]

$T = 695$ K

	reaction time (s)		
	600	900	1200
% reaction,			
exptl	4.7 ± 0.93	9.7 ± 1.0	13.5 ± 0.8
calc (*)[e]	2.7(3.5)	6.3(7.5)	11.5(12.7)
$Y(C_2H_4)$,			
exptl	0.74 ± 0.16	0.61 ± 0.07	0.64 ± 0.06
calc (*)	0.81(0.75)	0.81(0.77)	0.81(0.78)
$Y(SiH_4)$,			
exptl	0.54 ± 0.10	0.46 ± 0.05	0.46 ± 0.04
calc (*)	0.68(0.62)	0.69(0.65)	0.69(0.65)
$Y(EtSi_2H_5)$,			
exptl	*c*	*c*	*c*
calc (*)	0.10(0.09)	0.08(0.08)	0.08(0.07)
$Y(VSiH_3)$,			
calc	0.0001	0.0001	0.0002

$T = 723$ K

	reaction time (s)			
	300	600	900	1200
% reaction,				
exptl	23.7 ± 0.8	40.7 ± 0.8	52.3 ± 1.3	58.6 ± 1.2
calc (*)	18.3(19.8)	44.3(42.0)	56.4(53.5)	65.8(62.5)
$Y(C_2H_4)$,				
exptl	0.64 ± 0.04	0.64 ± 0.04	0.59 ± 0.03	0.46 ± 0.02
calc (*)	0.82(0.79)	0.70(0.65)	0.58(0.55)	0.51(0.46)
$Y(SiH_4)$,				
exptl	0.42 ± 0.03	0.35 ± 0.03	0.28 ± 0.03	0.19 ± 0.02
calc (*)	0.68(0.64)	0.45(0.41)	0.27(0.25)	0.18(0.17)
$Y(EtSi_2H_5)$,				
exptl	*c*	0.08 ± 0.02	*c*	0.08[d]
(**)[f]	0.10**	0.17**	0.22**	0.24**
calc (*)	0.08(0.07)	0.09(0.08)	0.08(0.06)	0.06(0.05)
$Y(VSiH_3)$,				
exptl	trace	trace	0.003 ± 0.001	0.004 ± 0.001
calc	0.0003	0.001	0.002	0.004**

$T = 748$ K

	reaction time (s)	
	300	600
% reaction,		
exptl	71.1 ± 1.8	84.3 ± 2.0
calc (*)	67.3(64.2)	87.6(84.7)
$Y(C_2H_4)$,		
exptl	0.64 ± 0.03	0.61 ± 0.03
calc (*)	0.57(0.53)	0.44(0.42)
$Y(SiH_4)$,		
exptl	0.24 ± 0.02	0.15 ± 0.01
calc	0.22	0.06
$Y(EtSi_2H_5)$,		
exptl	0.02 ± 0.01	0.02[d]
calc (*)	0.067(0.05)	0.02(0.016)
$Y(VSiH_3)$,		
exptl	trace	0.001 ± 0.0005
calc (*)	0.006(0.016)	0.014(0.024)

[a] % decomposition = $[([ES]_0 - [ES]_t)/[ES]_0] \times 100$; yield(X) = mol X_{formed}/mol $ES_{reacted}$ = mol X/(mol ES_0 − mol ES_t). [b] Total pressure = 179 Torr (22 Torr ES + 157 Torr TMS); 3 runs were made at each temperature and each time condition except at the 600, 900, and 1200 s conditions at $T = 723$ K, where the number of runs made were 5, 4, and 4, respectively. Exptl = experimentally observed values. [c] No data taken. [d] Yields based on just one observation. [e] Modeling results using lower Arrhenius parameter limits to set k_1: see text. [f] Modeling yields obtained with $k_{u1} = k_{u2} = 0$.

SCHEME 1: Chain Mechanisms of the Ethylsilane Decomposition

A: The Pure Ethylsilane Decomposition Reaction

$$EtSiH_3 \xrightarrow{1} EtSiH + H_2$$

$$EtSiH + (M) \xrightleftharpoons[-2]{2} C_2H_4 + SiH_2 + (M)$$

$$SiH_2 + EtSiH_3 \xrightleftharpoons[-3]{3} EtSi_2H_5 \xrightleftharpoons[-4]{4} SiH_4 + EtSiH$$

$$SiH_4 + (M) \xrightarrow{5} SiH_2 + H_2 + (M)$$

$$SiH_2 + SiH_4 \xrightleftharpoons[-6]{6} Si_2H_6$$

$$EtSiH + EtSiH_3 \xrightleftharpoons[-7]{7} EtSiH_2SiH_2Et$$

$$EtSiH + (M) \xrightarrow{8} C_2H_3SiH_3 + (M)$$

$$C_2H_3SiH_3 \xrightarrow{9} C_2H_4 + SiH_2$$

$$EtSi_2H_5 \xrightarrow{u1} \text{“products”}$$

$$EtSiH_2SiH_2Et \xrightarrow{u2} \text{“products”}$$

B: Additional Reactions in the Presence of Added Propylene

$$EtSiH + H_2C{=}CHCH_3 \xrightleftharpoons[-10]{10} Et(Pr)Si: \xrightarrow{11} C_2H_4 + PrSiH$$

$$PrSiH + EtSiH_3 \xrightleftharpoons[-12]{12} PrSiH_2SiH_2Et \xrightleftharpoons[-13]{13} EtSiH + PrSiH_3$$

$$PrSiH \xrightarrow{14} CH_2{=}C(CH_3)SiH_3$$

$$EtSiH + H_2C{=}CHCH_3 \xrightarrow{15} CH_2{=}C(CH_3)SiH_2Et \text{ or } MeCH{=}CHSiH_2Et$$

$$PrSiH + H_2C{=}CHCH_3 \xrightleftharpoons[-16]{16} Pr_2Si:$$

$$PrSiH + H_2C{=}CHCH_3 \xrightarrow{17} CH_2{=}C(CH_3)SiH_2Pr \text{ or } MeCH{=}CHSiH_2Pr$$

$$Et(Pr)Si + H_2C{=}CHCH_3 \xrightarrow{18} CH_2{=}C(CH_3)SiH(Et)Pr \text{ or } MeCH{=}CHSiHEtPr$$

$$Pr_2Si + H_2C{=}CHCH_3 \xrightarrow{19} CH_2{=}C(CH_3)SiHPr_2 \text{ or } MeCH{=}CHSiHPr_2$$

$$PrSiH \xrightleftharpoons[-20]{20} SiH_2 + H_2C{=}CHCH_3$$

$$SiH_2 + PrSiH_3 \xrightleftharpoons[-21]{21} PrSi_2H_5 \xrightleftharpoons[-22]{22} SiH_4 + PrSiH$$

$$PrSiH_3 \xrightarrow{23} PrSiH + H_2$$

$$Pr_2Si + SiH_4 \xrightleftharpoons[-24]{24} Pr_2SiHSiH_3 \xrightarrow{25} Pr_2SiH_2 + SiH_2$$

$$Et(Pr)Si + SiH_4 \xrightleftharpoons[-26]{26} Et(Pr)SiHSiH_3 \xrightarrow{27} Et(Pr)SiH_2 + SiH_4$$

$$Pr_2SiHSiH_3 \xrightarrow{u3} \text{“products”}$$

$$Et(Pr)SiHSiH_3 \xrightarrow{u4} \text{“products”}$$

$$PrSiH_2SiH_2Et \xrightarrow{u5} \text{“products”}$$

$$PrSi_2H_5 \xrightarrow{u6} \text{“products”}$$

are silylenes. Hence, for the ES static system decomposition, we propose the silylene carried chain mechanism of Scheme 1A. The Scheme 1A reactions are all known processes (or are analogues of known processes). The possible exceptions to this are the reactions (denoted by u*i*) of the "heavy" alkyl-substituted disilane products. Early modeling without these u*i* reactions showed that while major product yield and reactant

TABLE 2: Yield and ES Loss Results (Experimental and Calculated) for the Ethylsilane Decomposition under Propylene Inhibition (T = 693 K, Time = 1200 s)[a]

$Y(C_2H_4)$	$Y(SiH_4)$	$Y(PrSiH_3)$[b]	$Y(EDS)$[c]	% ES loss	comments
0.90 ± 0.05	0.10 ± 0.02	0.48 ± 0.06		24.0 ± 2.0	exptl[d]
0.90	0.16	0.56	0.026	18.3	calc[e]
0.90	0.13	0.56	0.025	24.8	calc[e]*
0.94	*0.28*	0.58	0.028	20.2	calc[f]
0.90	0.16	0.56	0.026	18.3	calc[g]
0.91	0.15	0.57	0.029	22.5	calc[h]

[a] Propylene/ES/TMS = 10/1/1; P_{total} = 180 Torr. [b] $Y(n\text{-}PrSiH_3) = 0.41$; $Y(i\text{-}PrSiH_3) = 0.07$. The propylsilane isomers were not distinguished in the modeling. [c] EDS stands for ethyldisilane; not observed experimentally. [d] Experimental data are averages of 4 runs. [e] Modeling obtained from Table 3 rate constants. *Modeling using the lower Arrhenius parameter limits of log A_1 = 14.87, E_1 = 63 340 calc. [f] Modeling with Table 3 rate constant assignments except for $k_{24} = k_{26} = 1.7 \times 10^8$ M^{-1} s^{-1}, set by analogy with observations on the $Me_2Si + SiH_4 \rightarrow Me_2SiHSiH_3$ reaction: see text. [g] Modeling with Table 3 rate constants except that $k_{u3} = k_{u4} = k_{u5} = k_{u6} = 0$. [h] Modeling with Table 3 rate constants except that all $k_{ui} = 0$.

loss data could be successfully modeled, predicted yields of the alkyl-substituted disilanes (in particular, ethyldisilane) were always well above observed levels (see the double-starred values of Table 1). Thus, some additional "unspecified" kind of reaction of the heavy disilanes was needed to reconcile the proposed chain mechanism with the experimental data. There are two known minor reaction channels of polysilanes that are u*i* possibilities: 1,1-hydrogen elimination and wall capture. For the former, on the basis of disilane decomposition data,[5] Moffat et al.[6] proposed kinetics of $k_{H2} = 10^{15.81}e^{-56510\text{cal}/RT}$ s^{-1} (i.e., $k_{H2} = 5.3 \times 10^{-2}$ s^{-1} at 723 K), while for the latter, on the basis of trisilane decomposition data,[7,8] Ring et al. proposed kinetics of $k_w \approx 10^{13.32}e^{-46270\text{cal}/RT}$ s^{-1} (i.e. $k_w \approx 0.22$ s^{-1} at 723 K). Although heterogeneous effects are negligible in the pure disilane static system decomposition,[7] wall capture remains a possibility for disilanes having ethyl (or larger) alkyl group substitutions. Thus, in certain physical properties, such as boiling point and vapor pressure, no change occurs with the replacement of a silyl group by an ethyl group. Our approach to identifying the nature of the u*i* reactions was to establish values of their rate constants and rate constant parameters via reaction modeling.

Modeling of the Pure ES Decomposition (Scheme 1A). Initial modeling of the pure ethylsilane decomposition showed that ethylsilane conversion and product yield calculations were most sensitive to four reactions: reaction 1 (initiation), reaction 2 (chain length control), reaction 8 (vinylsilane yield), and reaction u1 (ethyldisilane yield). Since the rate constants of the other "not so critical" reactions were known or could be estimated with reasonable accuracy, we used modeling at the 723 K condition to establish values for three of these rate constants. The first modeling was directed at establishing a value for k_8 through fits of the vinylsilane yields. In these 723 K fits, $k_1 = 3.6 \times 10^{-5}$ s^{-1} (from the CR-SPST Arrhenius parameters), $k_2 = 1 \times 10^7$ s^{-1} (by analogy with similar alkylsilylene decompositions[3]), and $k_u = 0.22$ s^{-1} (arbitrarily set equal to the trisilane[8] wall capture rate constant). Rough estimates for k_2 and k_u were acceptable here because vinylsilane yields were not very sensitive to these rate constants. Reasonable fits were realized with $k_8 \approx 5 \times 10^2$ M^{-1} s^{-1}. Significantly higher values (i.e., factor of 10) predicted vinylsilane yields in the observable range (i.e., $Y(VSiH_3) \geq 1\%$), while significantly lower values predicted vinylsilane yields too small to detect (i.e., less than 0.1%). Next, fits of the ethyldisilane yields via variations in the k_{ui} rate constants were made to establish $k_{ui} \approx 4 \times 10^{-3}$ s^{-1}. This is slower than the rate constant estimates of either of the suspected reaction channels (40 times slower than wall capture and 10 times slower than 1,1-H_2 elimination), but is not unreasonable in light of the possible errors of those estimates. An improved value of $k_2 \approx 2 \times 10^6$ s^{-1} (723 K) was then determined by fitting the reactant percent conversion data. This is also slower than the preliminary estimate (factor of 6.7), but is within the estimate and modeling errors.

To extend the modeling to the other study temperatures, values for k_2 and k_8 at those temperatures had to be determined. This was done through RRKM calculations (that is, both reactions are in their pressure falloff regimes under study conditions) using high-pressure A-factor estimates of $A_{2,\infty} = 4.4 \times 10^{14}$ and $A_{8,\infty} = 10^{13.9}$, both in s^{-1}. The former follows from the back reaction kinetics and entropy (i.e., $A_{-2,\infty} = 1.0 \times 10^{11}$ M^{-1} s^{-1}, $E_{-2} = -0.73$ kcal/mol,[9] $\Delta S^\circ_{2,-2} = 25.0$ eu,[10,11] respectively), and the latter follows from a thermochemical kinetic estimate[10] of the reaction's intrinsic activation entropy and path degeneracy (i.e., $\Delta S_8^\ddagger(\text{intrinsic}) \approx -3.5$ cal/(deg·mol); rpd$_8$ = 12). Input and output data for the RRKM calculations are given in the Appendix.

With the critical rate constants k_2 and k_8 established (as above) and the other rate constants of Scheme 1A known or estimated (see Table 3), modeling fits of ES conversions for the pure ethylsilane reaction at 695 and 748 K were made using k_{ui} as adjustable parameters. Reasonable fits were obtained with $k_{ui} \approx 7.6 \times 10^{-4}$ s^{-1} (695 K) and $k_{ui} \approx 1.6 \times 10^{-2}$ s^{-1} (748 K). Coupled with the 723 K result, Arrhenius parameters of log $A_{ui}(\text{s}^{-1}) = 15.62$ and E_{ui} = 59 587 cal were obtained, which are clearly more like those for 1,1-H_2 elimination than they are for wall capture. However, if the u_i reactions are three-center H_2 eliminations, it's difficult to see how they can be sink reactions since H_2 eliminations form silylene products which react in ways that are not chain terminating (isomerization/decomposition to a silylene, Si−H insertion followed by decomposition to a silylene, etc.) Therefore, important aspects of the u*i* processes are not resolved by the present treatment.

Complete ES conversion and product yield modeling results for the pure ES decomposition, obtained with the rate constants of Table 3 and the mechanism of Scheme 1A, are shown with the data for comparisons in Table 1. Agreements are generally reasonable and, in most cases, within the true (larger than statistical) measurement errors.

One final important aspect of the modeling concerns the initiation reaction. The results given here were generated with k_1 values based on our CR-SPST Arrhenius parameters.[1] These were measured at temperatures more than 400 K higher than those employed in the present study; hence, the possibility of extrapolation errors is high. If the lower limits of the SPST Arrhenius parameters are used to set k_1, i.e., $k_1 = 10^{14.87}e^{-63340\text{cal}/RT}$ s^{-1}, modeling fits to product yields and reactant conversions are uniformly improved. This is particularly true at the lowest temperature of 695 K; see the starred values of Table 1.

Modeling of the ES/Propylene Reaction (Scheme 1A,B). To model the ES decomposition in the presence of propylene, the mechanism was expanded to include silylene intermediate reactions with propylene (to produce alkylsilylenes) and all subsequent reactions of the formed alkylsilylenes with reactant and products. While only 16 reactions were needed to model the pure ethylsilane decomposition, an additional 27 reactions were needed for the reaction in excess propylene. Fortunately, as in the pure ethylsilane decomposition, the additional reactions either are established processes with known kinetics or are reactions whose kinetics can be estimated by analogy. Assigned rate constant parameters for the reactions are given in Table 3,

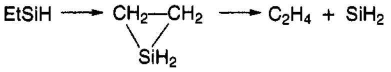
TABLE 3: Modeling Input for Scheme 1

reaction	log A^a	E^a	ref
$EtSiH_3 \xrightarrow{1} EtSiH + H_2$	15.14	64.77	1
$EtSiH + (M) \xrightarrow{2} C_2H_4 + SiH_2 + (M)$	12.27	20.17	3^b
$\xleftarrow{-2}$	10.48	0.0	9
$SiH_2 + EtSiH_3 \xrightarrow{3} EtSi_2H_5$	10.70	0.0	26
$\xleftarrow{-3}$	15.26	50.83	19
$EtSi_2H_5 \xrightarrow{4} SiH_4 + EtSiH$	13.66	48.44	19
$\xleftarrow{-4}$	9.90	0.0	12
$SiH_4 + (M) \xrightarrow{5} SiH_2 + H_2 + (M)$	12.76	51.53	20
$SiH_2 + SiH_4 \xrightarrow{6} Si_2H_6$	10.78	0.0	21
$\xleftarrow{-6}$	15.75	52.20	6
$EtSiH + EtSiH_3 \xrightarrow{7} EtSiH_2SiH_2Et$	9.78	0.0	12
$\xleftarrow{-7}$	14.30	47.90	22
$EtSiH + (M) \xrightarrow{8} VSiH_3{}^d$	9.41	20.00	*b*
$VSiH_3{}^d \xrightarrow{9} C_2H_4 + SiH_2$	14.48	62.52	23
$EtSi_2H_5 \xrightarrow{u1} ?$		see text	
$EtSiH_2SiH_2Et \xrightarrow{u2} ?$		see text	
$EtSiH + CH_2{=}CHCH_3 \xrightarrow{10} Et(Pr)Si$	10.48	0.0	9
$\xleftarrow{-10}$	7.60	0.0	3
$Et(Pr)Si \xrightarrow{11} C_2H_4 + PrSiH$	6.30	0.0	*c*
$PrSiH + EtSiH_3 \xrightarrow{12} PrSiH_2SiH_2Et$	9.60	0.0	12
$\xleftarrow{-12}$	14.30	47.9	22
$PrSiH_2SiH_2Et \xrightarrow{13} EtSiH + PrSiH_3$	14.30	47.9	22
$\xleftarrow{-13}$	9.60	0.0	12
$PrSiH + CH_2{=}CHCH_3 \xrightarrow{14} CH_2{=}C(Me)SiH_3$	9.41	20.0	*b*
$RSiH + CH_2{=}CHCH_3 \xrightarrow{15,17} \text{products}$	4.70	0.0	*e*
$R_2Si + CH_2{=}CHCH_3 \xrightarrow{18,19} \text{products}$	4.70	0.0	*f*
$PrSiH + CH_2{=}CHCH_3 \xrightarrow{16} Pr_2Si$	10.30	0.0	9
$\xleftarrow{-16}$	7.60	0.0	3
$PrSiH \xrightarrow{20} SiH_2 + CH_2{=}CHCH_3$	7.60	0.0	3
$\xleftarrow{-20}$	10.60	0.0	9
$SiH_2 + PrSiH_3 \xrightarrow{21} PrSi_2H_5$	10.70	0.0	26
$\xleftarrow{-21}$	15.26	50.83	19
$PrSi_2H_5 \xrightarrow{22} SiH_4 + PrSiH$	13.66	48.44	19
$\xleftarrow{-22}$	9.90	0.0	12
$PrSiH_3 \xrightarrow{23} PrSiH + H_2$	15.14	64.77	1
$Pr_2Si + SiH_4 \xrightarrow{24} Pr_2SiHSiH_3$	9.90	0.0	18
$\xleftarrow{-24}$	13.12	51.79	24
$Pr_2SiHSiH_3 \xrightarrow{25} Pr_2SiH_2 + SiH_2$	15.26	50.83	24
$Et(Pr)Si + SiH_4 \xrightarrow{26} Et(Pr)SiHSiH_3$	9.90	0.0	18
$\xleftarrow{-26}$	13.12	51.79	24
$Et(Pr)SiHSiH_3 \xrightarrow{27} Et(Pr)SiH_2 + SiH_2$	15.26	50.83	24

[a] *A* in units of s^{-1} or M^{-1} s^{-1}; *E* in units of kcal/mol. [b] RRKM falloff parameters for 180 Torr (see Appendix). [c] Determined by modeling fits; see text. [d] V = $CH_2{=}CH-$. [e] RSiH = EtSiH or PrSiH. [f] R_2Si = EtPrSi or Pr_2Si.

and the modeling results for the ES/propylene reaction (with the experimental data for comparisons) are given in Table 2. Agreements with experiment are good. It's particularly interesting to note that if k_{24} and k_{26} are assigned values of 1.7×10^8 M^{-1} s^{-1} (by analogy with Me_2Si + SiH_4, the only dialkylsilylene/silane reaction whose kinetics have been determined[12]), the predicted yields of silane are too high. To fit the silane yields, higher values are needed, i.e., $k_{24} = k_{26} \geq 8 \times 10^9$ M^{-1} s^{-1}. These higher values are more in line with the silylene/Si−H insertion rate constants found for other less substituted silylenes, and this suggests that the Me_2Si/SiH_4 reaction could have anomalous kinetics.

If one accepts the rate constants established by the modeling, it's possible to extract some interesting kinetic and thermodynamic information. Consider first the ethylsilylene decomposition to ethylene and silylene (reaction 2; thermochemistry shown below).



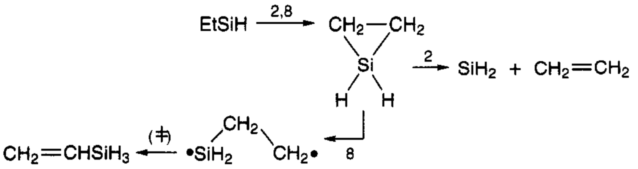
(2)

	EtSiH	C_2H_4	SiH_2	$\Delta X°$
$\Delta H_f°$ (kcal/mol)	(to establish)	12.5[10]	64 ± 1[13]	
S(cal/(deg·mol))	76.6[11]	52.4	49.2[11]	25.0
$C_p°(298)$	17.1	10.3	8.2	1.4
$C_p°(500)$	26.1	14.9	8.9	−1.3
$C_p°(800)$	33.0	20.0	10.2	−2.8

The RRKM calculations on this reaction, using our extracted $k_2 = 2.0 \times 10^6$ s^{-1} at 723 K (P = 150 Torr) and estimated $A_{2,\infty} = 4.4 \times 10^{14}$ s^{-1}, give a high-pressure activation energy of E_2 = 25.0 kcal/mol. Coupled with the back reaction result[9] (i.e., E_{-2} = −0.73 kcal/mol), this gives reaction enthalpies of $\Delta H_{2,-2} \approx 25.7$ kcal/mol (at 723 K) and $\Delta H_{2,-2} \approx 26.1$ kcal/mol (at 298 K). Thus, from the reaction thermochemistry, ΔH_f(EtSiH) = 50.4 ± 2.5 kcal/mol, where the error comes from uncertainties in the silylene heat of formation and in k_2. This can be compared to ΔH_f(ESiH) = 45 ± 2.4 kcal/mol obtained from heats of formation reported for ethylsilane, methylsilane, and methylsilylene (i.e., $\Delta H_f(EtSiH_3)$ = −10.0 ± 1 kcal/mol;[14] $\Delta H_f(MeSiH_3)$ = −7.0 ± 1 kcal/mol;[15] ΔH_f(MeSiH) = 48.0 ± 2 kcal/mol[13]) assuming the same difference between heats of formation of the $RSiH_3$ and RSiH species (R = Me and Et). The authors' preferred heats of formation (i.e., $\Delta H_f(EtSiH_3)$ = −9.5; $\Delta H_f(MeSiH_3)$ = −8.0; ΔH_f(MeSiH) = 49.0 all in kcal/mol) give a slightly higher heat of formation of ΔH_f(ESiH) = 47.5 kcal/mol. The lower ethylsilylene heats of formation, when used as the basis for heat of formation estimates of other larger alkylsilylenes, have resulted in estimated enthalpies of decomposition (to olefin and silylene) which are too high when compared to the experimentally measured activation energies.[3] Therefore, we favor a compromise ΔH_f(EtSiH) = 47.7 ± 2.5 kcal/mol. This establishes a $[C-(CH_2)-Si]$ group enthalpy additivity for alkylsilane and alkylsilylene heat of formation estimates of $\Delta H_f[C-(H)_2(C)(Si)] = -1.3 \pm 2.5$ kcal/mol.

Next consider the $k_8 \approx 5 \times 10^2$ s^{-1} (723 K) set by the modeling fits of the vinylsilane yields. This k_8 establishes a rough activation energy for the ethylsilylene → vinylsilane isomerization.

Mechanistically, reaction 8 is a multistep process, possibly proceeding by a biradical intermediate as shown below. Reaction 8 competes with reaction 2.



The RRKM calculation for reaction 8, based on $A_8 \approx 10^{13.9}$ s^{-1}, gave $E_{8,\infty} \approx 36.8$ kcal/mol. Thus $(E_8 - E_2)_\infty \approx 11.8$ cal/mol. This can be compared with a thermochemical kinetic estimate of the enthalpy difference between the two reaction transition states, namely, $(E_8 - E_2) \approx 9.4$ kcal/mol. Thus, $\Delta H_f(\ddagger)_8 = \Delta H_f(^{\bullet}CH_2CH_2SiH_2{}^{\bullet})^{16} + E_{1,2(\text{H migration})}{}^{17} = 74.4 + 10.8 = 85.2$ kcal/mol; and $\Delta H_f(\ddagger)_2 = \Delta H_f(C_2H_4) + \Delta H_f(SiH_2) + E_{-2} = 12.5 + 64 + (-0.7) = 75.8$ kcal/mol. Since the two calculations agree well within their errors (at least ±2 kcal/

mol for each), the above results set an activation energy for the ethylsilylene isomerization to vinylsilane of about $E_8 = 35.6 \pm 2$ kcal/mol.

Conclusions

While there are facets of the ethylsilane decomposition not completely understood, the general behavior of the decomposition, both neat and in the presence of propylene, can be quantitatively rationalized by the mechanism of Scheme 1 and the rate constants of Table 3. Only silylene intermediates are involved, and only reactions with precedents found in other silane and organosilane reactions are invoked. Reaction modeling establishes several thermochemical kinetic values of interest: a heat of formation for ethylsilylene of $\Delta H_f(C_2H_5SiH) = 47.5 \pm 2.5$ kcal/mol; a methylene enthalpy group additivity of $\Delta H_f[C-(H_2)(C)(Si)] = -1.5 \pm 2.5$ kcal/mol; and an activation energy for the ethylsilylene to vinylsilane isomerization of $E_8 = 35.6 \pm 2$ kcal/mol.

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Appendix: Input Parameters for RRKM Falloff Calculations[25]

$$C_2H_5SiH \xrightarrow{8} CH_2{=}CHSiH_3 \qquad (8)$$

Vibration frequencies consistent with $A_\infty = 10^{13.9}$ s^{-1} listed in wavenumbers and number (cm^{-1}, (#)). Reactant: 3000(5), 2130(1), 1450(4), 1200(4), 950(1), 800(1), 700(1), 690(2), 250(1) 225(1). Transition state: 3000(4), 2130(1), 1450(4), 1300(1), 1250(1), 1200(4), 950(1), 800(1), 690(2), 225(1). Conditions: $k_8 = 5 \times 10^2$ s^{-1} at 723 K, $P = 180$ Torr, rpd = 12. Collision characteristics: $\beta_c = 0.85$ (all T), $\sigma = 4.0$ A.

Output: $\Delta E_0^\ddagger = 36.6$ kcal/mol; $E_\infty = 36.8$ kcal/mol; $(k/k_\infty)_{180\text{Torr}} = 0.85$, 0.82, and 0.80 at 693, 723, and 748 K, respectively. At 180 Torr, $\log A = 13.57$, $E = 35.57$ kcal/mol.

$$C_2H_5SiH \xrightarrow{2} SiH_2 + C_2H_4 \qquad (2)$$

Vibrational frequencies consistent with $A_\infty = 4.5 \times 10^{14}$ s^{-1} listed in wavenumbers and number (cm^{-1}, (#)). Reactant: 3000(5), 2130(1), 1450(4), 1200(4), 950(1), 800(1), 700(1), 690(2), 250(1) 225(1). Transition state: 3000(4), 2130(1), 1450(4), 1200(4), 950(1), 800(1), 690(2), 250(1), 225(1), 175(1). Conditions: $k_8 = 1.5 \times 10^6$ s^{-1} at 723 K, $P = 180$ Torr, rpd = 3. Collision characteristics: $\beta_c = 0.85$ (all T), $\sigma = 4.0$ A.

Output: $\Delta E_0^\ddagger = 23.0$ kcal/mol; $E_\infty = 25.0$ kcal/mol; $(k/k_\infty)_{180\text{Torr}} = 0.16$, 0.14, and 0.12 at 693, 723, and 748 K, respectively. At 180 Torr, $\log A = 12.15$, $E = 19.46$ kcal/mol.

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