ORGANOMETALLICS

Volume 5, Number 8, August 1986

Kinetics of the Thermal Decomposition of Ethynylsilane

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Received October 23, 1985

The kinetics and products of the thermal decomposition of ethynylsilane have been studied in a stirred flow reactor (5.8–8.5 torr, 590–784 K) and in a single-pulse shock tube (3200 torr, 1100–1225 K). The stirred-flow reaction is chain-induced and cannot be quenched by additions of usual free radical and silylene trapping agents; wall catalysis occurs at the lowest temperatures. The shock-tube reaction has a short-chain component which can be quenched by silylene trapping agents. Decomposition rate constants under butadiene inhibition given by $k = 10^{14.85}e^{-61200 \pm 5200 \text{cal}/RT}$ s^{-1} are interpreted in terms of four competing reaction channels. Three channels involve intramolecular reactions via silirane (to form ethylene, acetylene, and vinylsilylene) and the fourth is the usual 1,1-H_2 elimination.

Introduction

Acetylene and its derivatives are well-known silylene traps.[1-6] In the gas phase, silylene trapping by acetylene leads to numerous products under high concentration conditions[7] but only to ethynylsilane (ES) under low concentration conditions.[8] [Products observed under high concentration conditions for $:SiH_2 + C_2H_2$ are ethynylvinylsilane, vinylsilane, ethylene, and ethynyldivinylsilane.] The mechanism of Scheme I is consistent with these observations.

Scheme I is based on a similar scheme proposed by Barton to explain rearrangements of methylvinylsilylene[9] and (trimethylsilyl)vinylsilylene.[10] It is also consistent with our results on the thermal reaction of silane with acetylene.[4,7] Most trapping studies have been made under relatively low concentration conditions where subsequent reactions of vinylsilylene (i.e., the favored silacyclopropene decomposition product)[7] are relatively slow; hence only ES is observed. It has generally been assumed that ES is a stable product; however, recent observations have led us to question this assumption. Thus in the shock-induced decomposition of ethylsilane[11] and vinylsilane[12] (1150–1250 K) carried out in excess acetylene, no ethynylsilane product was observed even though the short silylene chains common to both shock-induced reactions were completely eliminated. Also, in the static system trapping of silylene by acetylene (650–700 K), yields of ethynylsilane plotted vs. time increased to maxima and then decreased.[7] The inference of both these observations is that ethynylsilane is less stable than its precursors (i.e., silane and mono-

Scheme I

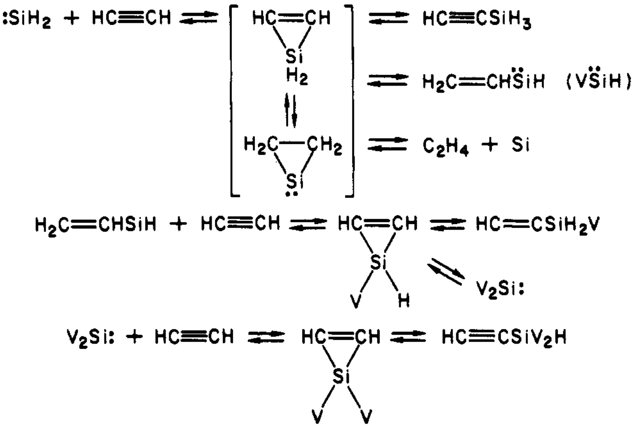

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Table I. Product Yield Data of the Ethynylsilane Decomposition under Stirred-Flow Conditions

	reactn[a]		yields, %				
T, K	mixture	% reactn	C_2H_2	C_2H_4	C_3H_6[b]	CH_4	runs
606–629	A	0–10	0.14	0.00	0.00	0.05	4
589–679	A	10–20	0.21	0.03	0.00	0.05	8
649–695	A	20–30	0.20	0.06	0.00	0.05	3
727–739	A	30–50	0.19	0.12	0.00	0.10	3
713	B	30–50		0.08	0.00	0.00	1
713	C	30–50		0.08		0.00	1
722–746	E[c]	30–50	0.21	0.13		0.10	3
749–774	A	50–60	0.14	0.16	0.01	0.13	8
746	B	50–60		0.10	0.00	0.09	1
737	C	50–60		0.13		0.00	1
722	D	50–60	0.08	0.13		0.10	1
781–784	A	60–80	0.13	0.18	0.02	0.13	2
758–784	B	60–80		0.20	0.00	0.13	3
774	C	60–80		0.28		0.19	1
745–773	D	60–80	0.08	0.28		0.10	1
768	E[c]	60–80	0.16	0.16		0.12	1

[a] Reaction mixture compositions (in argon): A (1.0% ES), B (0.53% ES, 7.87; C_2H_2), C (0.50% ES, 7.44% C_2H_2, 7.44% C_3H_6), D (0.50% ES, 7.50% C_3H_6), E (0.49% ES, 7.36% C_3H_6, 7.36% C_4H_6). [b] C_3H_6 = propylene. [c] In 1,3-butadiene (C_4H_6) average yields of sila-3-cyclopentene were 0.10.

alkylsilanes) under conditions where the latter decompose. A study of the ethynylsilane thermal decomposition kinetics, therefore, seemed in order. In this paper we report kinetic and product study results on the thermal decomposition of ethynylsilane under both stirred-flow and single-pulse shock-tube reaction conditions.

Experimental Section

Ethynylsilane[4] was synthesized by passing a mixture of 1 part disilane to 2 parts acetylene through a heated cell at 470 K with residence times sufficient for better than 99% decomposition of the disilane. The reaction products were collected in a cold trap at liquid N_2 temperatures and then separated by preparative GC methods with a 6 ft × $^1/_4$ in. Porapak N column at 120 °C. The separated product was identified by IR and MS as ethynylsilane. Subsequent GLC analysis gave a purity estimate of 99.5%, with acetylene as the major contaminant. Product analyses were made by GC (Varian FID-MODEL 3700 and a Hewlett-Packard integrator, Model 3390A) on a 4 ft × $^1/_8$ in. Porapak N column.

In the stirred-flow studies, quite dilute reaction mixtures (less than 1% ES in Argon) were passed through a 64.0 cm^3 quartz reactor (V_{reactor}) at flow rates, reaction pressures, and residence times (t_{res}) ranging from 0.5 to 4.0 nmol/s, 5.8–8.5 torr, and 38–288 s, respectively. Rate constants of ES stirred-flow decomposition were calculated from the stirred-flow rate expression[13]

$$k\ (\mathrm{s}^{-1}) = [(\text{mol of ES})_{\mathrm{in}} - (\text{mol of ES})_{\mathrm{out}}]/[\mathrm{ES}]_{\mathrm{out}}V_{\mathrm{reactor}}[t_{\mathrm{res}}]$$

In the shock-tube studies, reaction mixtures were similarly dilute, but reaction pressures were about 3200 torr and residence times were about 300 μs. Details of the system and method have previously been described.[14,15]

Results

Stirred-Flow Studies. Kinetic and product yield results for the decomposition of ES are given in Figure 1 and Table I, respectively. A strong curvature in the Arrhenius plot of the neat ES reaction (curve A) is apparent. For the two distinct regions one obtained $k_{\mathrm{ES}} = 10^{3.28}e^{-17710\mathrm{cal}/RT}$ s^{-1} (590–700 K) and $k_{\mathrm{ES}} = 10^{9.08}e^{-36874/RT}$ s^{-1} (725–784 K). The extremely low *A* factor of reaction in the lower temperature regime strongly suggests wall catalysis. This is supported by the observation that generally slower reaction rates were found in runs where special measures were taken to condition the reactor walls. [Steady-state-flow conditions were maintained for more than an hour before product collection in runs (Figure 1). This was more than 6 times larger than the conditioning times of other runs.] Wall catalysis is also consistent with the ES yield variations in time observed in the static system acetylene trapping of silylene study.[7]

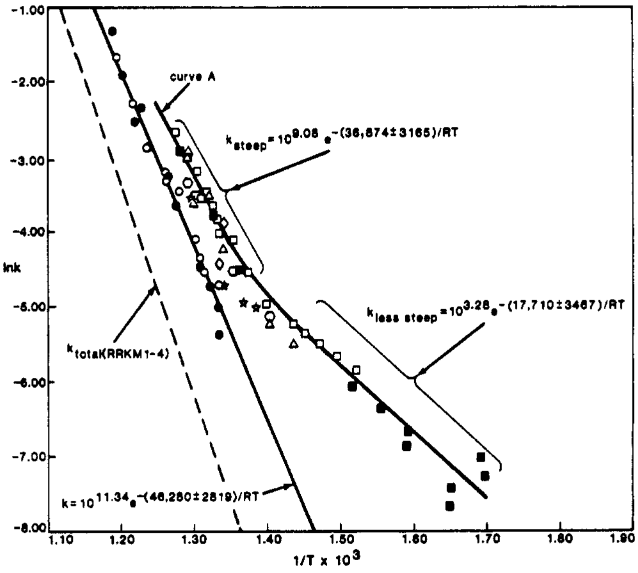

Figure 1. Arrhenius plot for ethynylsilane decomposition via a stirred-flow system (all mixtures in argon): □, mixture A (1.0% ES); ■, mixture A with extra wall conditioning; △, mixture B (0.053% ES, 7.87% C_2H_2); ○, mixture C (0.50% ES, 7.44% C_3H_6, 7.44% C_2H_2); ◇, mixture D (0.50% ES, 7.50% C_3H_6); ☆, mixture E (0.49% ES, 7.36% C_3H_6, 7.36% C_4H_6); ●, mixture I (0.10% ES, 0.1% c-C_3H_6, 9.0% C_4H_6); ○, mixture J (0.48% ES, 7.20% C_4H_6). The activation energies have units of (cal/mol) and the rate constants have units of s^{-1}.

The higher temperature regime *A* factor, while considerably higher and in the range found for many chain-induced homogeneous reactions, is still far too low to apply to any homogeneous unimolecular reaction of ES.

To see if the unimolecular primary dissociation reactions of ES could be isolated and measured under stirred-flow conditions, the ES pyrolysis was studied in the presence of various trapping agents (propylene, acetylene, and 1,3-butadiene). Propylene and acetylene had only minor effects on reaction rates (Figure 1), on products (Table I),

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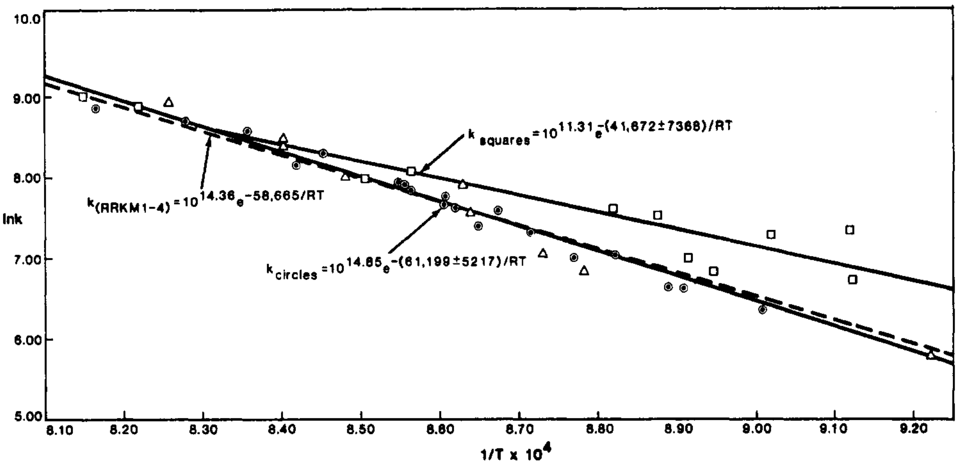
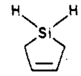


Figure 2. Arrhenius plot for ethynylsilane decomposition via a shock-tube system (all mixtures in argon): □, mixture F (0.10% ES, 10% c-C_3H_6); △, mixture G (0.093% ES, 0.099% c-C_3H_6, 2.85% C_2H_2); (⊙), mixture H (0.10% ES, 10% c-C_3H_6, 3.00% C_4H_6). The activation energies have units of (cal/mol) and the rate constants have units of s^{-1}.

Table II. Product Yield Data of the Ethynylsilane Decomposition under Shock-Tube Conditions

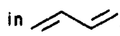
	reaction(a)		yields,[c] %				
T, K	mixture	% reactn	C_2H_2	C_2H_4		H_2	runs
	F	0–20	0.43	0.09		0.33	2
1100–1125	G	0–20		0.13		nm[b]	
	H	0–20	0.70	0.25	0.00	nm	2
	F	20–40	0.46	0.06		0.32	3
1125–1150	G	20–40		0.15		nm	
	H	20–40	0.40	0.25	0.14	nm	2
	F	40–60	0.54	0.11		0.44	2
1150–1175	G	40–60		0.17		nm	
	H	40–60	0.52	0.17	0.17	nm	3
	F	60–80	0.56	0.12		0.60	
1175–1200	G	60–80		0.20		nm	
	H	60–80	0.63	0.13	0.16	nm	1
	F	80–95	0.65	0.16		0.79	2
1200–1250	G	80–95		0.22		nm	
	H	80–95			0.08	nm	

[a] Reaction mixture compositions (in argon): F (0.10% ES, 0.10% cyclopropane (c-C_3H_6)), G (0.093% ES, 0.099% c-C_3H_6, 2.85% C_2H_2), H (0.10% ES, 0.10% c-C_3H_6, 3.0% C_4H_6). [b] nm = not measured. [c] 1,3-Butadiene (C_4H_6) alone produces both C_2H_2 and C_2H_4. The yields given are those obtained after corrections for this "background" source. Corrections were large and not meaningful at $T > 1200$ K.

or on rate constant Arrhenius parameters (Table IIIB). However, butadiene suppressed rates by factors of 2–3 and substantially raised the ES loss Arrhenius parameters (i.e., in 7.4% C_4H_6, $k_{ES} = 10^{11.3}e^{-46000\pm3000\text{cal}/RT}$ s^{-1}). Experimental scatter was also reduced. The A factor under butadiene inhibition, however, is still to low for a unimolecular gas-phase reaction. Therefore, the ES stirred-flow decomposition in the higher temperature regime is probably mainly a chain reaction, even in the presence of added butadiene.

From the product data for the stirred flow reaction (Table I), we see that the yields observed in any given conversion range are essentially the same. This suggests no significant change in reaction mechanism with added trapping agents, including butadiene. Little information concerning mechanism can be deduced from the product yields since mass balances are so poor and yields are so low. The very low yields of silicon containing products is consistent with Scheme I in that silylenes are the major products of that scheme and silylenes under stirred-flow conditions tend to polymerize[15] rather than react to form observable silicon-containing products. The production of silacyclopentane in runs with added butadiene also supports the role for silylene in the chain reaction(s). Other points of interest are that yields of the major product, acetylene, are roughly conversion independent, while yields of the minor product, ethylene, increase strongly with increasing temperature.

Shock-Tube Studies. Kinetic results for the decomposition of ES in argon and in the presence of acetylene and butadiene (acting as silylene quenching agents) are shown in Figure 2 and Table IIIC. Both acetylene and butadiene quench the shock-induced reaction, and the resulting Arrhenius parameters are in the range of those found for the primary processes of other monoalkylsilanes:

k(ES in , 1100–1225 K) $= 10^{14.85}e^{-61200\pm5200/RT}$ s^{-1}

Product yield data are given in Table II. As in the stirred-flow reaction, the major products are acetylene and ethylene with similar temperature dependencies but with much higher yields. Mass balances (for C) are also much better. It is also clear from Figure 2 that reaction rates for the uninhibited ES decomposition approach those of the inhibited reaction at the higher temperatures. Thus chain lengths are short and approach zero with increasing temperature.

Discussion

There are at least four plausible primary dissociation channels for ES. Three follow from Scheme I: ES can react intramolecularly through silirane and silirene in-

Table III. Arrhenius Parameter Summary

A. Monoalkylsilane Decompositions

compd	log A, s^{-1}	E,[a] cal	k (1158 K)	ref
CH_3SiH_3	14.35	60 690 ± 3000[b]		20
	15.20	64 780 ± 3000[c]	940	
$C_2H_5SiH_3$	15.14	64 769 ± 1433	822	11
n-$C_3H_7SiH_3$	15.30	65 300 ± 1950	944	21
$H_2C{=}CHSiH_3$	14.95	63 268 ± 1260[d]	1020	12

B. Stirred-Flow Kinetic Results

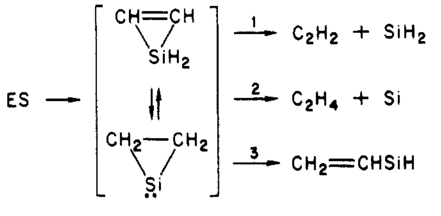
mixture[e]	log A, s^{-1}	E,[a] cal	% reactn	runs
B	7.92	33 045 ± 3640	28–80	
C	7.83	32 943 ± 2640	34–78	3
D	7.84	32 337 ± 4170	51–79	3
E	8.18	34 424 ± 8930	34–71	4
I[f]	11.86	48 197 ± 1833	32–91	12
J[f]	11.00	45 080 ± 3090	37–88	10

C. Shock-Tube Kinetic Results

mixture[e]	log A, s^{-1}	E,[a] cal	% reactn	runs
F	11.31	41 672 ± 7368	4–97	12
G	15.99	67 147 ± 10258	10–92	9
H	14.85	61 199 ± 5217	4–92	19

[a] Error limits correspond to the 95% confidence level. [b] Overall experimental parameters at reaction pressures of 4700 torr. [c] High-pressure parameters for the 1,1-H_2 elimination reaction channel. [d] An intramolecular elimination channel producing C_2H_4 may contribute significantly to this reaction. In other systems, hydrogen eliminations is dominant (i.e., from 85 to 100% of the overall decomposition). [e] Mixture compositions A–E and F–H are given in Tables I and II, respectively. [f] Mixture I: (0.10% ES, 0.1% c-C_3H_6, 9.0% C_4H_6 in Argon). mixture J: (0.48% ES, 7.20% C_4H_6 in Argon).

termediates to form acetylene, ethylene, and vinylsilylene (reactions 1–3, respectively). The fourth is reaction by the



major pathway common to other monoalkylsilanes, 1,1-H_2 elimination (reaction 4).

$$ES \xrightarrow{4} HC{\equiv}CSiH + H_2$$

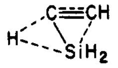
It is possible to estimate rate constants and Arrhenius parameters for reaction 1 since absolute rate constants for the reverse reaction are now available[8] and the reaction thermochemistry can be guessed within reasonable error limits. [ΔH°_f(ES) assumes equivalent enthalpies of hydrogenation for ES and C_2H_2; $\bar{S}^\circ$(ES) assumes equivalent intrinsic entropy changes for $C_2H_5SiH_3 \rightleftarrows$ ES and $C_3H_8 \rightleftarrows CH_3C{\equiv}CH$. $\Delta H^\circ_f(SiH_2)$ = 59.1 kcal/mol;[16] other estimates obtained from group additivities.[17,18]] Thus we have at 298 K

$$SiH_2 + C_2H_2 \rightleftarrows HC{\equiv}CSiH_3$$

$\bar{S}^\circ$, eu/mol:	49.2	48.0	65.9 ± 2	$\Delta S^\circ = -31.1$ eu
ΔH°_f, kcal/mol:	59.1	54.2	63.2 ± 4	$\Delta H^\circ = 50.1 \pm 4$ kcal

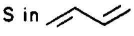
$$k_{-1}\ (298\ \mathrm{K}) = 10^{9.11}e^{-4326\pm2290\mathrm{cal}/RT}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

Converting reaction 1 parameters to the atmospheric standard state and combining with the reaction thermochemistry gives $k_1 = 10^{14.1}e^{-54426\pm6300\mathrm{cal}/RT}\ \mathrm{s}^{-1}$. [A parallel calculation utilizing a previous estimate of the transition-state entropy ($S^{\circ\ddagger}$ = 67.5 ± 2 eu/mol)[8] gives $\Delta S_1^\ddagger$ = 1.6 eu and $A_1 = 10^{13.6}\ \mathrm{s}^{-1}$, in satisfactory agreement with the above. The transition state can be represented as



Arrhenius parameters would be somewhat different at elevated temperatures, but the changes are small and compensating and for our purposes can be ignored.

The estimated reaction 1 Arrhenius parameters are significantly lower than the experimental parameters of the inhibited ES decomposition; rate constants however are actually larger. Thus at the mean study temperature of 1158 K

k(ES in ) = 1985 s^{-1}

while k_1(estimated) = 6720 s^{-1} with about a factor of 30 uncertainty. It is clear, therefore, that reaction 1 (hence also the competing reactions 2 and 3) must be contributing primary dissociation processes in the homogeneous decomposition of ES (i.e., $k_1 \geq 6720/30\ s^{-1}$).

From the Arrhenius parameter summary for other monoalkylsilanes (Table IIIA), it is also clear that 1,1-H_2 elimination should also occur in the shock-induced ES decomposition. Thus the average $k_{1,1\text{-}H_2\,\mathrm{elim}} \simeq 930\ s^{-1}$ at 1158 K, with no apparent dependence on the nature of the alkyl group.

The product yield data of Table II are consistent with this four-channel primary dissociation process interpretation. Thus it is possible to make product yield (Y) and primary process efficiency (ϕ) identifications with the following assumptions: that vinylsilylene is removed from the system by polymerization processes, that silylene is trapped by butadiene as silacyclopentene with a 50% efficiency [this is the efficiency observed for the same reaction under similar conditions in the propylsilane decomposition study[18]], and that ethynylsilylene decomposes rapidly to acetylene and silicon ($HC{\equiv}CSiH \rightarrow C_2H_2 + Si$). Then one obtains

$$\phi_1 = Y(\mathrm{scp})/0.50 \qquad \phi_2 = Y(C_2H_4)$$

$$\phi_3 = 1 - (\phi_1 + \phi_2 + \phi_4) \qquad \phi_4 = Y(C_2H_2) - \phi_1$$

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Table IV. RRKM Calculations of Rate Constants of Contributing Reaction Channels in the Ethynylsilane Decomposition

	A. Reference Values—RRKM Input Data			
reaction	1	2	3	4
k(1158 K), s^{-1}	615	337	437	596
log A, sec^{-1}	13.79	15.62	14.06	15.08
	B. RRKM—Results			
E_∞, kcal	58.06	68.03	60.23	64.24
10^4k(750 K)[a]	5.26	0.254	2.16	1.06
10^2k(850 K)[a]	3.95	0.322	1.88	1.08
$10^{-2}k$(1100 K)[b]	1.66	0.786	1.11	1.51
$10^{-3}k$(1250 K)[b]	3.65	2.37	2.69	3.97

T, K	k_{total} (RRKM 1–4)	k_{exptl}
750	8.73×10^{-4}	50×10^{-4}
850	7.23×10^{-2}	37×10^{-2}
1100	5.07×10^{2}	4.8×10^{2}
1250	12.7×10^{3}	14.0×10^{3}

Overall, $k(1100\text{–}1250)_{calcd} = 10^{14.36}e^{-58665/RT}/s^{-1}$

[a] Stirred-flow pressure ≈ 8 torr. [b] Shock-tube total pressure ≈ 3176 torr.

Table V. Input Data

1158 K: $k_1 = 595\ s^{-1}$, $k_2 = 332\ s^{-1}$, $k_3 = 423\ s^{-1}$, $k_4 = 607\ s^{-1}$;
$A_1 = 6.2 \times 10^{13}\ s^{-1}$, $A_2 = 4.1 \times 10^{16}\ s^{-1}$, $A_3 = 1.1 \times 10^{14}\ s^{-1}$, $A_4 = 1.2 \times 10^{15}\ s^{-1}$

σ(ES-Ar) = 4.45 Å; σ(ES-heavy) = 5.35 Å

Reaction mixtures: stirred flow, 10% "heavy" molecules in argon, P_{Total} = 8.0 torr;
shock tube, 3.2% "heavy" molecules in argon, P_{Total} = 3200 torr

T, K:	700	750	800	850	110	1150	1200	1250
$10^2\beta_{ES\text{-}heavy}$:	86	85	84	83	77	76	75	74
$10^2\beta_{ES\text{-}argon}$:	22	21	20	19	14	13	12	11

ES_w, cm^{-1}: 3000, 3 × 2130, 2000, 2 × 1100, 3 × 920, 685, 2 × 555

ES_w,* cm^{-1}: vibrationally adjusted to produce the above A_∞ values. These differ slightly from those deduced in the text; however, the results are not expected to be much influenced by these differences.

Collision efficiency estimates were obtained from equations developed by Troe.[24]

While hydrogen yields are difficult to interpret with confidence in these reactions (measurement errors are large and all the potential precursors are unknown), a fifth relationship involving hydrogen yields can be written. Thus with the assumption that hydrogen is formed only in reaction 4 and in silylene dimerization sink reactions (e.g., $SiH_2 + SiH_2 \rightleftarrows Si_2H_4 \rightarrow H_2 + Si_2H_2$), we have $Y(H_2) \simeq \phi_4 + (\phi_1 + \phi_3)/2$.

To apply the above relationships, it is necessary to use data for the reaction at high temperatures where induced chain decomposition is small. The most appropriate available data, then, are the product yields at the higher temperatures (i.e., 1175–1250 K). These data with some prejudice in favor of the inhibited systems give the following *approximate* yield values:

$$\phi_1 \simeq 0.15/0.50 = 0.30 \qquad k_1 = 596\ s^{-1}$$

$$\phi_2 \simeq 0.17 \qquad k_2 = 337\ s^{-1}$$

$$\phi_3 \simeq 0.23 \qquad k_3 = 457\ s^{-1}$$

$$\phi_4 \simeq 0.60 - 0.30 = 0.30 \qquad k_4 = 596\ s^{-1}$$

The hydrogen yield relationship provides a test of the above: $Y(H_2) = 0.30 + (0.30 + 0.23)/2 = 0.57$, in good agreement with the 0.60 experimental value. A second "check" follows from the assumption that k_4 for ES is as observed for other $RSiH_3$ compounds. Thus adjusting $k_{1,1\text{-}H_2\,elim} = 930\ s^{-1}$ (for $P \rightarrow \infty$) to the 3200-torr pressure condition of our shock-tube studies by RRKM methods (see Appendix 1) gives k_4 (1158 K, 3200 torr) = 596 s^{-1}, an embarrassingly good agreement with the deduced value. Thus both checks support the four primary process pathway interpretation of the ES reaction.

In the following, we estimate reasonable Arrhenius parameters to the four reaction channels and then calculate their contributions to the overall rate at several representative temperatures and total pressures of the stirred-flow and shock-tube systems. Comparisons of the calculated rate constants with the experimental values are then made.

The A factor estimates ($M \rightarrow \infty$) are

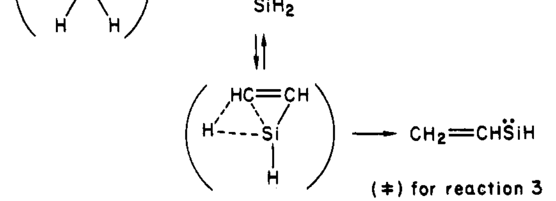
$$A_1 = 10^{13.8\pm0.3}\ s^{-1} \text{ (see text)}$$

$$A_2 = 10^{15.6}\ s^{-1} \text{ (see below)}$$

$$A_3 = 10^{14.1}\ s^{-1} \text{ (see below)}$$

$$A_4 = 10^{15.1}\ s^{-1} \text{ (by analogy with RSiH}_3\text{ data of Table III)}$$

The transition state for reaction 3 by difference method estimates, differs from that of reaction 1 by an optical center; hence $A_3 \simeq 2A_1$. [The reactions are



The temperature dependence of ethylene vs. acetylene yields (Table II, mixture F) suggests $(E_2 - E_{ES}) \simeq$ 10–15 kcal. This would set $E_2 \simeq 71\text{–}76$ kcal and $\log A_2 \simeq 16\text{–}17$. These values seem too high, but recognizing the trend we have assumed for reaction 2 the compromise value of A_2 equals $10^{15.6}$ s^{-1}. With use of the above high-pressure A factors and the 1158 K rate constants, RRKM fall-off calculations were performed with the results shown in Table IV. The calculated Arrhenius parameters for the shock tube are lower than those observed but still lie within the error limits of the experimental data. As expected, the calculated Arrhenius parameters for the stirred-flow conditions are higher than those observed, and the rate constants are factors of 5–6 times lower. Thus the rate constant calculations for the ES primary processes are consistent with a chain component to the stirred-flow reaction as previously argued.

It is quite possible that the chain reaction decomposition of ES under stirred-flow conditions is not initiated by any of the four primary processes considered here but rather is due to the acetylene moiety reactivity. Thus we found, while conducting control experiments, that acetylene reacts at rates within a factor of 2 of those of ES when passed through the stirred-flow reaction under reaction conditions ($k_{\mathrm{HC{\equiv}CH}} \simeq 10^{6.6} \times e^{-29000\,\mathrm{cal}/RT}$ s^{-1}). The reaction is probably initiated by carbene formation ($\mathrm{HC{\equiv}CH} \rightarrow \mathrm{CH_2{=}C{:}}$); this kind of reaction has been observed at our reaction temperatures.[19] Initiation of the ES stirred-flow reaction in this manner would explain why acetylene was not an effective quenching agent under stirred-flow conditions but was effective under shock-tube conditions. Thus if reaction 1 were the initiation reaction in the stirred-flow pyrolysis, acetylene would have to act as a quenching agent. Since it did not, some other initiation process is suggested.

Conclusion

It is evident that the ES decomposition is a complex reaction. At low temperatures, as encountered in static and stirred-flow systems, wall catalysis is indicated. At moderate temperatures chain reactions which cannot be completely quenched contribute significantly to the overall reaction. The homogeneous gas-phase dissociation reactions at moderate temperatures, while in practice eclipsed by chain reactions of indeterminant nature, should proceed mainly through silirane and silirene intermediates and produce acetylene, ethylene and vinylsilylene (reactions 1–3). At shock tube reaction temperatures, H_2 elimination (reaction 4) as well as reactions 1–3 are the initiation processes. The shock-tube reaction has a small chain component which decreases in importance with increasing temperature. It can be quenched by standard silylene trapping agents.

Appendix I. RRKM Calculations

Calculations used RRKM theory[22] and the Beyer–Swinehart algorithm[23] for calculating state densities and sums (Table V). Collision efficiency estimates were obtained from equations developed by Troe.[24]

Acknowledgment. We are indebted to the Air Force Office of Scientific Research (AFSOR 83-0202) for financial support.

Registry No. ES, 1066-27-9.

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Analysis of Stereochemical Properties of Molecular Orbitals of (Trimethylsilyl)acetylenes by Penning Ionization Electron Spectroscopy

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Received December 3, 1985

The Penning ionization electron spectra (PIES) resulting from thermal collision of He* (2^3S) metastable atoms and He I ultraviolet photoelectron spectra (UPS) were measured for (trimethylsilyl)acetylene and bis(trimethylsilyl)acetylene. Comparison of the relative intensities of the observed bands in PIES provided information of the stereochemical properties of the individual molecular orbitals of these compounds. The π(C≡C) orbitals of the monosilylacetylene showed a large activity of PIES, whereas the activity of the corresponding orbitals of the disilylacetylene was relatively low. This finding can be explained in terms of the effective steric shielding of the orbital by the two trimethylsilyl groups.

Introduction

In the framework of one-electron approximation, molecular orbital calculations yield orbital energies and orbital wave functions of molecules. The squares of wave functions give spatial electron distributions of molecular orbitals. From chemical point of view, the knowledge of both energies and electron distributions of individual molecular orbitals is very important. In most cases, where Koopmans' theorem[1] can be applied, orbital energies are related to observed ionization potentials obtained by photoelectron

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0276-7333/86/2305-1526$01.50/0