sequent attack on aromatic hydrocarbon. *Therefore, the k_T/k_B determined noncompetitively does not reflect the relative reactivity of toluene over benzene, and thus can not be used to test the Brown selectivity relationship.*

On the other hand, a k_T/k_B determined by competitive methods can be used.[11] Our preliminary results based upon three competitive runs indicate a $k_T/k_B = 2.5 \pm 0.1$, together with a toluene isomer product distribution of 45 ± 2% ortho, 6 ± 1% meta, and 49 ± 2% para. These values remained reasonably constant even after the addition of small amounts of H_2O. The isomer percentages are also in satisfactory agreement with values obtained by noncompetitive means: % ortho = 44 ± 3, % meta = 7 ± 1, and % para = 49 ± 3.

It is noteworthy that the toluene product isomer percentages are essentially constant and consistent from run to run, whether competitive or noncompetitive, at longer times as well as short times, and regardless of H_2O concentration. These facts also support the proposal of a common electrophilic species reacting with the aromatic hydrocarbon substrates.

Our competitive results appear to be an exception to the Brown selectivity relationship. Whether this is a fundamental discrepancy or an experimental artifact remains to be seen. Further work, particularly that dealing with mixing control, is underway in our laboratory.

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Kinetics of the Silane and Silylene Decompositions under Shock Tube Conditions

Sir:

We have studied the silane decomposition in a single pulse shock tube at temperatures between 1200 and 1300 K, and can conclude from our results (Tables I–III) that at shock temperatures the initiation reaction for the silane decomposition is the H_2 molecular elimination reaction (1) and not the bond fission process (2). These were the initiation reactions first

Table I. Hydrogen Products from Decompositions of Silane (1250 K)

% reactants in argon			hydrogen product ratios, $H_2:HD:D_2$
SiH₄	SiD₄	toluene	
1.00	1.00	0.00	2.94:2.50:1.00
	0.50	1.00	0.29:1.00
	0.10	1.00	0.94:1.00
	0.01	1.00	0.91:1.00

Table II. Rate Constants for SiH₄ Loss at 1250 K[a,b]

% SiH_4 in argon	ln [$(SiH_4)_0$/(SiH_4)]	$k \times 10^{-4}$ s⁻¹
1.00	1.36	1.13
0.10	1.66	1.38
0.01	1.46	1.22

[a] Residence times at shock temperatures were $T \simeq 120 \pm 5$ μs. [b] Silane concentrations before and after the shock were measured by mass spectroscopy relative to xenon as an internal standard at a concentration 3.13 times that of the SiH_4.

Table III. Preliminary Kinetic Data for Dissociation Reaction 1

no. of runs	τ, μs	T, K	$k \times 10^{-4}$ s⁻¹[a]
3	140 ± 5	1204	0.285 ± 0.032
5	120 ± 5	1250	1.056 ± 0.071
5	100 ± 5	1304	1.857 ± 0.153

[a] Errors shown are ±σ (1 standard deviation).

proposed as possibilities by Purnell and Walsh[1] on the basis of their thorough and pioneering study of the silane pyrolysis at temperatures between 653 and 703 K.

$$SiH_4 \rightarrow SiH_2 + H_2 \tag{1}$$

$$SiH_4 \rightarrow SiH_3\cdot + H\cdot \tag{2}$$
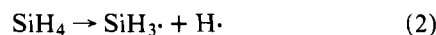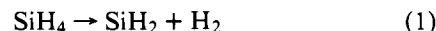
The first entry of Table I shows the hydrogen isotope product ratios generated in the copyrolysis of equimolar mixtures of SiH_4 and SiD_4 at 1250 K. Clearly hydrogen atom processes are as evident at shock temperatures as they were in lower temperature static studies.[2] Under single pulse shock conditions, with the possible exception of some very fast H-atom reactions, only homogeneous and unimolecular reactions are possible. The rate constant data of Table II support this expectation. Thus there is no apparent variation in the rate constants of dissociation with silane concentration. Hence there is no chain dissociation of silane in either the shock period or in the subsequent cool-down period. The rate constants observed then apply to the initial silane dissociation process. Further, since the observed rate constants are five orders of magnitude larger than the rate constant value expected for reaction 2 at 1250 K,[3] it is clear that the initiation reaction of the silane pyrolysis must be reaction 1.

In a start toward obtaining the Arrhenius parameters of reaction 1, a total of 13 pyrolyses covering the 1200–1300 K temperature range were made. Results (shown in Table III) are tentative and not particularly reliable since the temperatures noted were calibrated from the extent of cyclohexene dissociation in separate studies under similar shock conditions (i.e., an external method). The usual Arrhenius least-square analysis of the rate constant data give parameters of $A_1 = 10^{13.7 \pm 0.3}$ s⁻¹ and $E_1 = 56.1 \pm 1.7$ kcal/mol. However, transition-state considerations indicate that this A factor is certainly too low for the high pressure limiting reaction.[4] Strausz and Neudorfl[5] have recently studied the static system ($T \simeq$ 700 K) pyrolysis kinetics of CH_3SiH_3 and $(CH_3)_2SiH_2$ in

excess C_2H_4 (used as a free radical trap and chain suppressor) and have concluded that both dissociations are initiated by H_2 molecular elimination reactions like reaction 1. They also report Arrhenius parameters for H_2 elimination consistent with intrinsic activation entropies of, $\Delta S^{\ddagger} = 3.7 \pm 0.4$ eu/mol. Assuming this intrinsic activation entropy for the silylene molecular H_2 elimination reaction gives $A_1 = 10^{15.2}$ s^{-1}. We have performed RRKM pressure falloff calculations for a transition-state model consistent with this high pressure A factor and with a rate constant of $k_1 = 1.86 \times 10^4$ s^{-1} at 1304 K, $P = 3825$ Torr. The calculations indicate that reaction 1 is in its falloff region with $k/k_{\infty} = 0.32$ and give a high pressure activation energy of 61.7 kcal/mol and a critical activation energy of $E_0 = 59.1$ kcal/mol. We are presently refining our shock tube data using the internal standard comparative rate technique[6] and should soon be able to report firm values for the Arrhenius parameters of reaction 1.

Results for SiD_4 pyrolysis in the presence of excess toluene (Table I) conclusively show that the D atoms generated in the SiD_4 decompositions under shock conditions arise from the fast dissociation of SiD_2:

$$SiD_2 + (M) \rightarrow SiD + D + (M) \qquad (3)$$
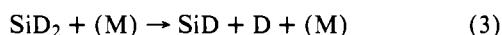
Thus under the conditions stated (i.e., large toluene excess) there was no significant change in reaction rates (hence no appreciable chain-induced SiD_4 decomposition), and all D atoms generated should be scavenged by toluene to give HD. The observation of significant amounts of HD and D_2 requires a molecular elimination reaction for D_2 production (reaction 1) and a D atom generation reaction. The latter process must be reaction 3 since reaction 2 is far too slow. Further, the nearly 1:1 D_2:HD ratios observed[7] suggest nearly complete dissociation of SiD_2 at shock temperatures. If the SiD_2 dissociation were not complete, one would expect a change in the ratio of hydrogen produced to silane consumed with increasing temperature. However, our stoichiometric data indicate that this ratio remains constant within experimental error from 1200 to 1300 K: $\Delta(H_2)/\Delta(SiH_4) = 1.85 \pm 0.10$. Therefore, the first two steps of the shock tube dissociation of silane are reactions 1 and 3, respectively.

Since no disilanes or higher silanes were found in the mass spectra of the products, the reaction stoichiometry is reasonably well represented by

$$SiH_4 \rightarrow 0.7Si + 0.3SiH + 1.85H_2$$
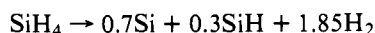
suggesting a significant amount of $SiH + H \rightarrow H_2 + Si$ in uninhibited shock pyrolyses.

An analysis of reactions 1 and 3 by the usual kinetics of consecutive reactions[8] provides a *lower* limit for k_3. Thus the stoichiometry establishes an upper limit for SiH_2 formation: (SiH_2 produced/SiH_4 initial) ≤ 0.15. With 80% SiH_4 dissociated, one then calculates $k_3/k_1 \leq 2.2$ at 1304 K. Also, assuming $A_3 \simeq 10^{14.0}$ s^{-1}, an *upper* limit of $E_3 \leq 56.0$ kcal/mol is obtained. This surprisingly low value leads to the interesting thermochemical values below, using $\overline{\Delta H_f^{\circ}}$ (SiH_4) = 8.2 kcal/mol,[9] $\overline{\Delta H_f^{\circ}}$ (Si_2H_6) = 17.0 kcal/mol,[9] $\overline{\Delta H_f^{\circ}}$($Si$) = 107.7 kcal/mol,[9] BDE(SiH_3–H) = 94 kcal/mol,[10] and for the reaction

$$Si_2H_6 \underset{b}{\overset{f}{\rightleftharpoons}} SiH_2 + SiH_4$$
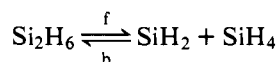
$E_f = 49.3$ kcal,[11] $E_b = X$. BDE(2): $SiH_3 \rightarrow SiH_2 + H$ ($\Delta H^{\circ} = 60.1 - X$, $\overline{\Delta H_f^{\circ}}(SiH_3) = 50.1$ kcal/mol, $\overline{\Delta H_f^{\circ}}(SiH_2) = (58.1 - X)$ kcal/mol). DBE(3): $SiH_2 \rightarrow SiH + H$ ($\Delta H^{\circ} = 56.0$ kcal, $\overline{\Delta H_f^{\circ}}(SiH) = (62.0 - X)$ kcal/mol). BDE(4): $SiH \rightarrow Si + H$ ($\Delta H^{\circ} = 97.8 + X$ kcal).

It is interesting to compare the RRKM-calculated value of the rate constant for reaction at the static pyrolysis conditions

of Purnell and Walsh,[1] with their observed rate constants. Thus at 653 K, with $[SiH_4] = 3.2 \times 10^{-3}$ M (i.e., ~100 Torr), the Purnell and Walsh results give for a first-order rate constant $k_{uni} = 10^{15.18 - (55.91/\theta)} \times [SiH_4]^{1/2} = 1.7 \times 10^{-5}$ s^{-1}. The RRKM-calculated value is $k_1 = 3.7 \times 10^{-7}$ s^{-1}, with $k/k_{\infty} \simeq 0.11$. The observed rate constant is therefore more than a factor of 40 larger than the initiation rate constant, k_1. This supports the view that the pyrolysis under static system conditions follows predominantly a chain mechanism.[2] We are presently refining our shock tube kinetic data, reexamining the reaction under static low temperature conditions, and completing the RRKM calculations on the reaction falloff properties.

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Stereospecific Total Synthesis of *dl*-Helenalin: A General Route to Helenanolides and Ambrosanolides

Sir:

Helenalin (**1**), a potent cytotoxic substance[1] isolated from *Helenium autumnale* over 65 years ago,[2] is representative of a group of pseudoguaianolides known as helenanolides,[3] which have as a characteristic feature a C-10 α-oriented methyl group. Despite early attempts at structure elucidation,[4,5] it was not until the early sixties that the relative and absolute configuration of **1** was established.[6,7]

We have reported[8] the facile and efficient synthesis of intermediate **3** in 25% overall yield from norbornadiene and