The H/$(CH_3)_3SiH/C_2H_4$ Reaction System and the Addition of $(CH_3)_3Si$ to Ethene. An End-Product Study

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Me_3Si and C_2H_5 radicals have been generated by the reaction of H atoms with mixtures of Me_3SiH and C_2H_4 and the subsequent reactions studied by end-product analysis. The primary radicals undergo self- and cross-combination and disproportionation reactions. The Me_3Si radical also adds to the C_2H_4, generating another radical, $Me_3SiCH_2CH_2$. This radical in turn undergoes a variety of self- and cross-combination as well as disproportionation reactions with all the radicals present. A number of relative rate constants were extracted from the data. In particular the ratio $k(H + Me_3SiH)/k(H+C_2H_4)$ was found to be in good agreement with recent absolute determinations of these two rate constants. For the addition reaction we obtained the relative rate constant $k(Me_3Si + C_2H_4)/k^{1/2}(2Me_3Si) = (8.7 \pm 0.2) \times 10^{-10}$ $cm^{3/2}$ $s^{-1/2}$ at room temperature. From studies in the temperature range 300−470 K the following values of the Arrhenius parameters for the addition reaction were obtained: $11.6 \leq E_a/kJ\ mol^{-1} \leq 14.1$ and $7.1 \times 10^{-13} \leq A/cm^3\ s^{-1} \leq 1.9 \times 10^{-12}$. In addition, it was found that alkyl and silyl radicals closely obey the geometric mean rule and that disproportionation reactions between alkyl and silyl radicals are of only minor importance. The reactivity of the silyl radical is much higher than that of the alkyl radical in adding to C_2H_4, and this can be explained in terms of polar effects.

Introduction

Radical addition to a double bond is an important method for the creation of a new chemical bond. A large number of studies have been carried out to unravel the factors which influence the rates of this type of reaction, and these are documented in review articles.[1,2]

More recently, new insights have been gained from experiment as well as from theory. In particular Fischer and his group[3] have reported a large number of absolute rate constants, and in some cases also Arrhenius parameters, measured by a modulated photolysis−ESR technique for the addition of various carbon-centered radicals to a large number of substituted olefins in the liquid phase.

Post-Hartree−Fock (HF) theoretical models have been used to calculate comparatively reliable barrier heights for this open-shell problem. Wong and Radom[4] have listed relevant theoretical and experimental work with pertinent references and have assessed the different computational methods applied. The outcome of the experiments and computations can be rationalized within the framework of simple models such as the frontier molecular orbital (FMO)[5] and the state correlation diagram (SCD)[6] models.

Systematic studies similar to those of Fischer and coworkers for other than carbon-centered radicals are not known, but in the case of silyl radicals absolute rate constants for the triethylsilyl radical addition to a number of olefins in the liquid phase have been reported.[7] Choo and Gaspar[8] determined an absolute rate constant as well as Arrhenius parameters for the trimethylsilyl radical addition to ethene, also in the liquid phase.

The investigation of gas-phase reactions has been limited to the addition of SiH_3 to ethene and propene.[9] Under their experimental conditions the authors could obtain a measurable rate constant only for propene, and the question was raised as to whether the measured rate constant for propene was really due to an addition reaction or was due to the abstraction of an allylic hydrogen atom. In a similar case,[10] an end-product study of the reaction of the triethylsilyl radical with tetrachloroethene revealed that abstraction dominated over addition. In contrast to this, a theoretical study by Bottoni[11] showed that in the SiH_3/C_3H_6 system abstraction is burdened by a much higher activation energy than that for simple addition. Furthermore, it was found that alkyl substitution enhances the reactivity of the olefin toward SiH_3 by a factor of 3−5, depending on the computational method used.

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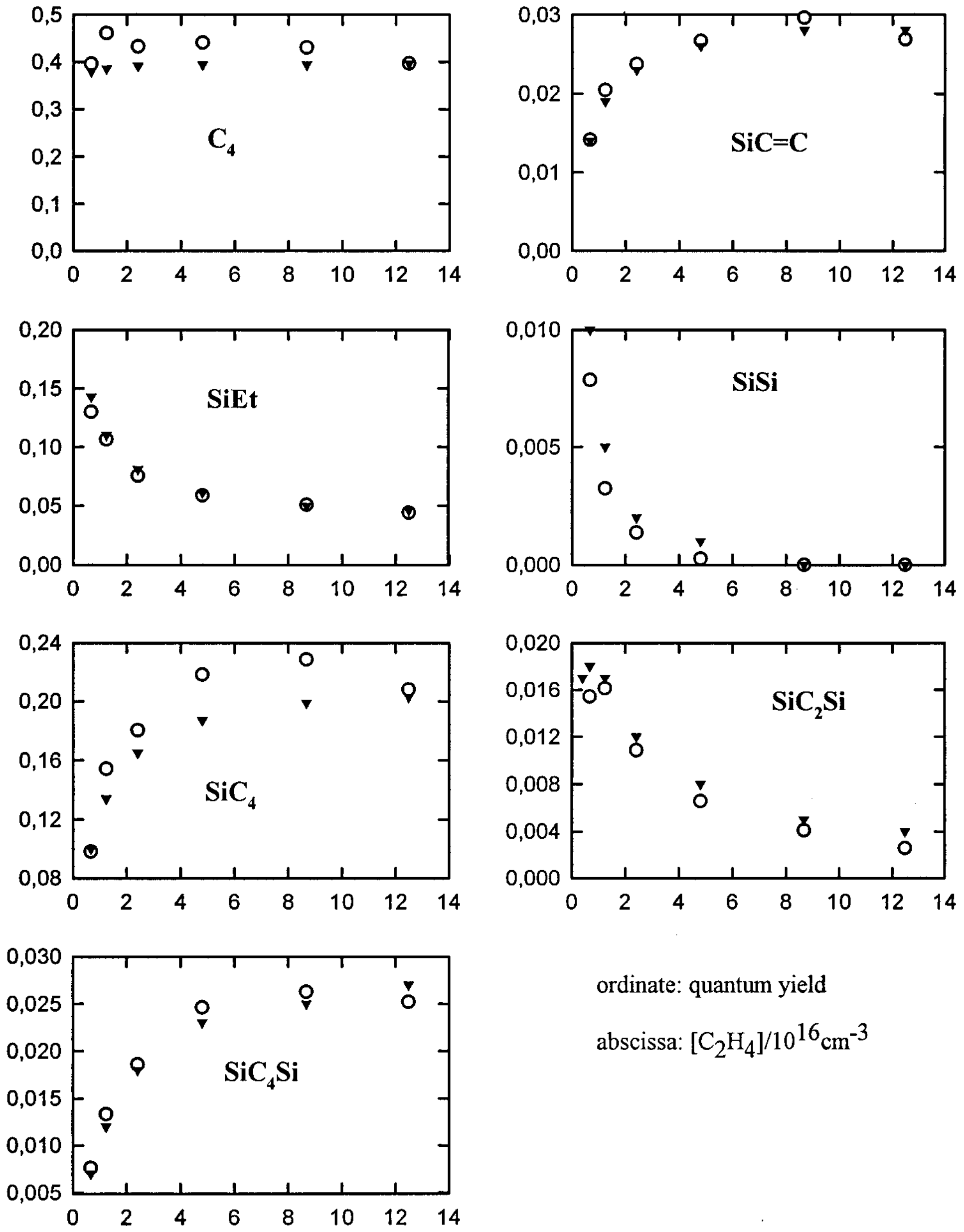

Figure 1. Dependence of the product quantum yields on ethene concentration for a constant reactant ratio [C$_2$H$_4$]/[Me$_3$SiH] = 1.02: (○) experimental values; (▼) calculated values.

The experimental results[8,9] are not in agreement with Bottoni's predictions[11] in other respects. The experimental rate constant for SiH$_3$/C$_3$H$_6$ is a factor of 50 higher than the value for Me$_3$Si/C$_2$H$_4$. The discrepancy becomes even larger when the fact that silyl radicals behave as nucleophiles is taken into account; in such a case the reactivity of Me$_3$Si should be greater than that of SiH$_3$. This discrepancy was not the only motivating factor in beginning this work. We have published a number of papers[12] dealing with the mechanistic pathways followed by silyl radicals, and therefore, of at least equal interest to us were the radical–radical reactions which lead to the final products.

Relatively little is known about the corresponding reactions of alkyl–silyl radicals. Niiranen and Gutman[13] have determined absolute rate constants and, in some instances, also Arrhenius parameters for the reactions of SiH$_3$, Me$_3$Si, and SiCl$_3$ with CH$_3$. To what extent disproportionation reactions play a role is not known but can in principle be determined by end-product analysis. The geometric mean rule applies well to the reaction of SiH$_3$ with CH$_3$.[13]

In this work we describe the H/Me$_3$SiH/C$_2$H$_4$ reaction system, which embraces H atom addition to the olefin, hydrogen atom abstraction from the silane, silyl radical addition to the olefin, and radical–radical reactions leading to the stable end products. We present a mechanism which satisfactorily describes the experimental results at elevated temperatures as well as at room temperature.

Experimental Section

All substances, H$_2$, Me$_3$SiH, C$_2$H$_4$, and n-C$_5$H$_{12}$, were of commercial origin. Under the conditions used for product identification, no impurities were detected.

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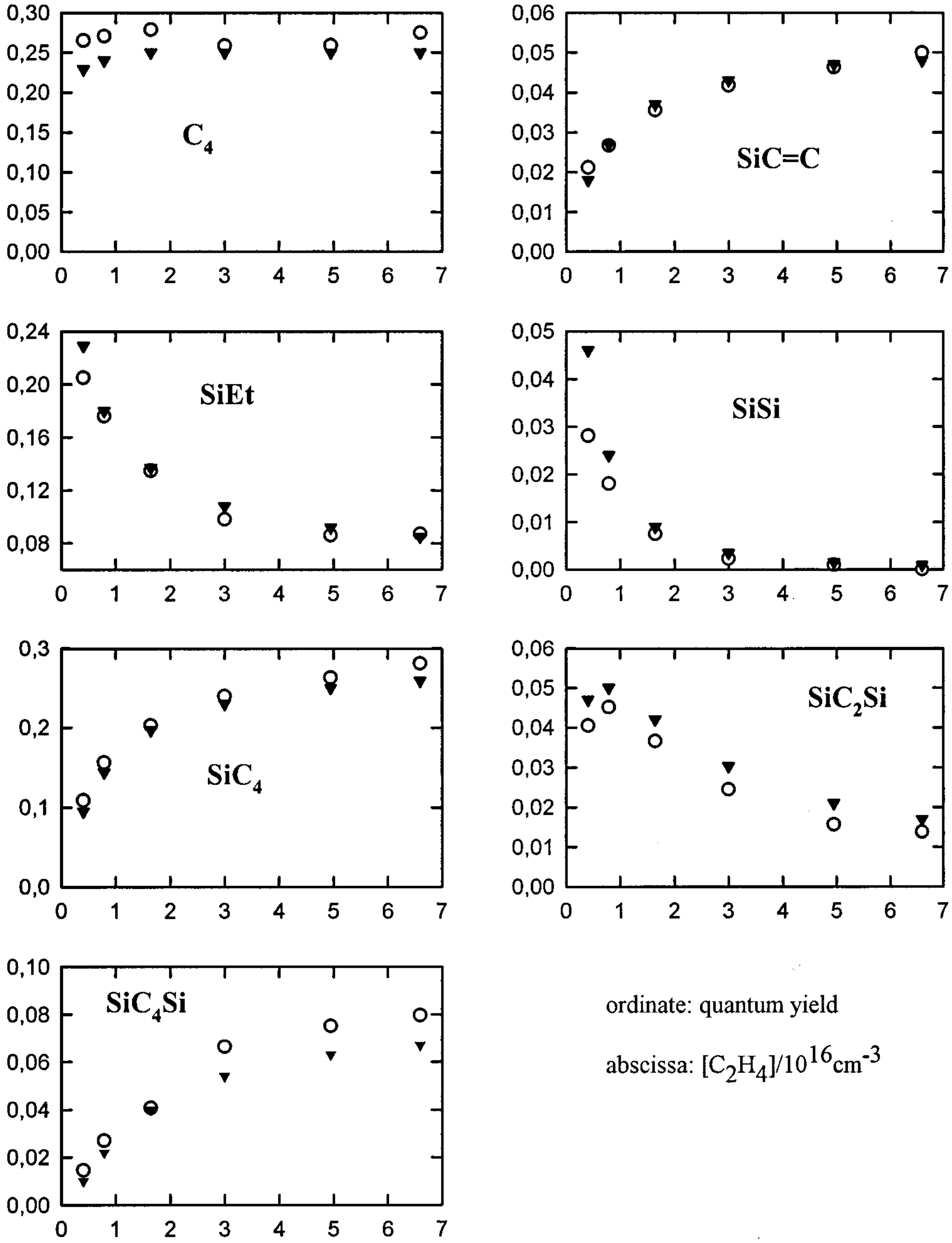

Figure 2. Dependence of the product quantum yields on ethene concentration for a constant reactant ratio $[C_2H_4]/[Me_3SiH] = 0.488$: (○) experimental values; (▼) calculated values.

Gas handling was performed on a convential vacuum line equipped with three capacitance manometers: MKS Baratron-22A (1000 mbar), Baratron-220BA (10 mbar), and Baratron-622A (1 mbar). Five reactant mixtures with different but precisely known Me_3SiH/C_2H_4 concentration ratios were prepared and stored on the vacuum line. Every mixture contained a small, known amount of n-C_5H_{12} as an internal standard for subsequent gas chromatographic analysis.

Static Hg-sensitized photolyses were carried out in a 180 cm^3 cylindrical quartz cell with an optical path length of 10 cm. The photolysis cell was reproducibly positioned in the optical light path and at the same time attached to the vacuum line. It could be removed for analysis of its contents. The photolysis cell is heated by an oven consisting of two removable copper blocks which tightly enclose the cell, and its temperature is controlled to about 1 K. The Hg concentration in the cell was determined by an absorption experiment and adjusted until about 50% attenuation of the Hg resonance radiation resulted. The amount of reactant mixture and H_2 was determined by pressure measurement.

The light source was a low-pressure mercury lamp (Gräntzel Type 5) operating in dc mode, thermostatically controlled and purged by a continuous flow of nitrogen. The lamp current was kept constant by a FuG MCN 140-65 power supply. A Vycor filter removed the 185 nm line. The intensity of the 254 nm light transmitted through the cell was measured by a 254 nm interference filter−photomultiplier arrangement. After the lamp had stabilized, the light intensity passing through the empty cell was set to a standard value by adjusting the lamp current.

The absorbed light intensity has been previously determined in this laboratory by N_2O actinometry[14] ($\Phi(N_2) = 1$). This actinometer has been checked versus the *cis*-butene-2 actinometer[15] (Φ(*trans*-butene-2) = 0.5), and the values of the two actinometers agreed within 1.6%.[16] The light intensity deter-

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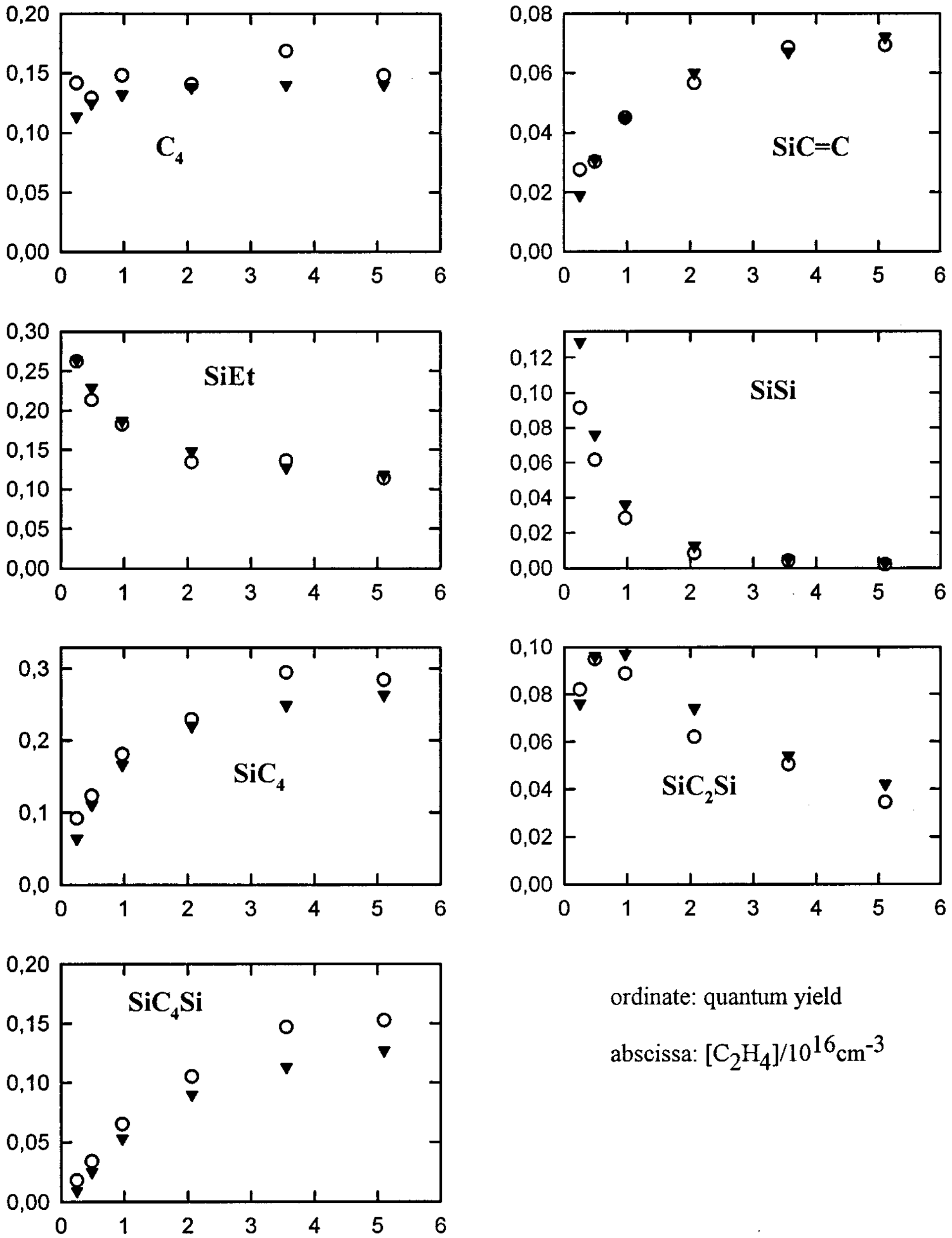

Figure 3. Dependence of the product quantum yields on ethene concentration for a constant reactant ratio [C$_2$H$_4$]/[Me$_3$SiH] = 0.257: (○) experimental values; (▼) calculated values.

mined actinometrically was shown to depend linearly on the measured absorption in the range 0−80%.[17]

End-product analyses were carried out on a HP 5980 gas chromatograph equipped with a flame ionization detector. The inlet system consisted of a pneumatically actuated multivalve arrangement which could be evacuated. Gas samples were expanded from the photolysis cell into a thermostated sample loop. The pressure in the sample loop was measured by a capacitance manometer. Product separation was performed on a 50 m × 0.32 mm fused silica capillary column coated with dimethylpolysiloxane (1.5 μm, OV1, Weeke). The temperature program, −15 °C (10 min)−10 °C/min−220 °C (6 min), ensured a good separation of the products with one notable exception: C$_2$H$_6$ could not be separated from the reactant C$_2$H$_4$. Starting with an even lower temperature (−35 °C) did not improve the situation. All samples were analyzed at least twice. For quantitative analysis of the chromatograms the response factors were taken to be proportional to the number of C atoms in the molecule.[18]

Results and Discussion

Mechanism. The mercury-sensitized photolysis of H$_2$/C$_2$H$_4$/Me$_3$SiH mixtures was carried out in the presence of a large excess of H$_2$. The excited mercury atoms therefore interact almost exclusively with H$_2$. This interaction is described by a rather complex mechanism,[19] but reaction conditions were chosen such that to a good approximation the overall reaction can be described by

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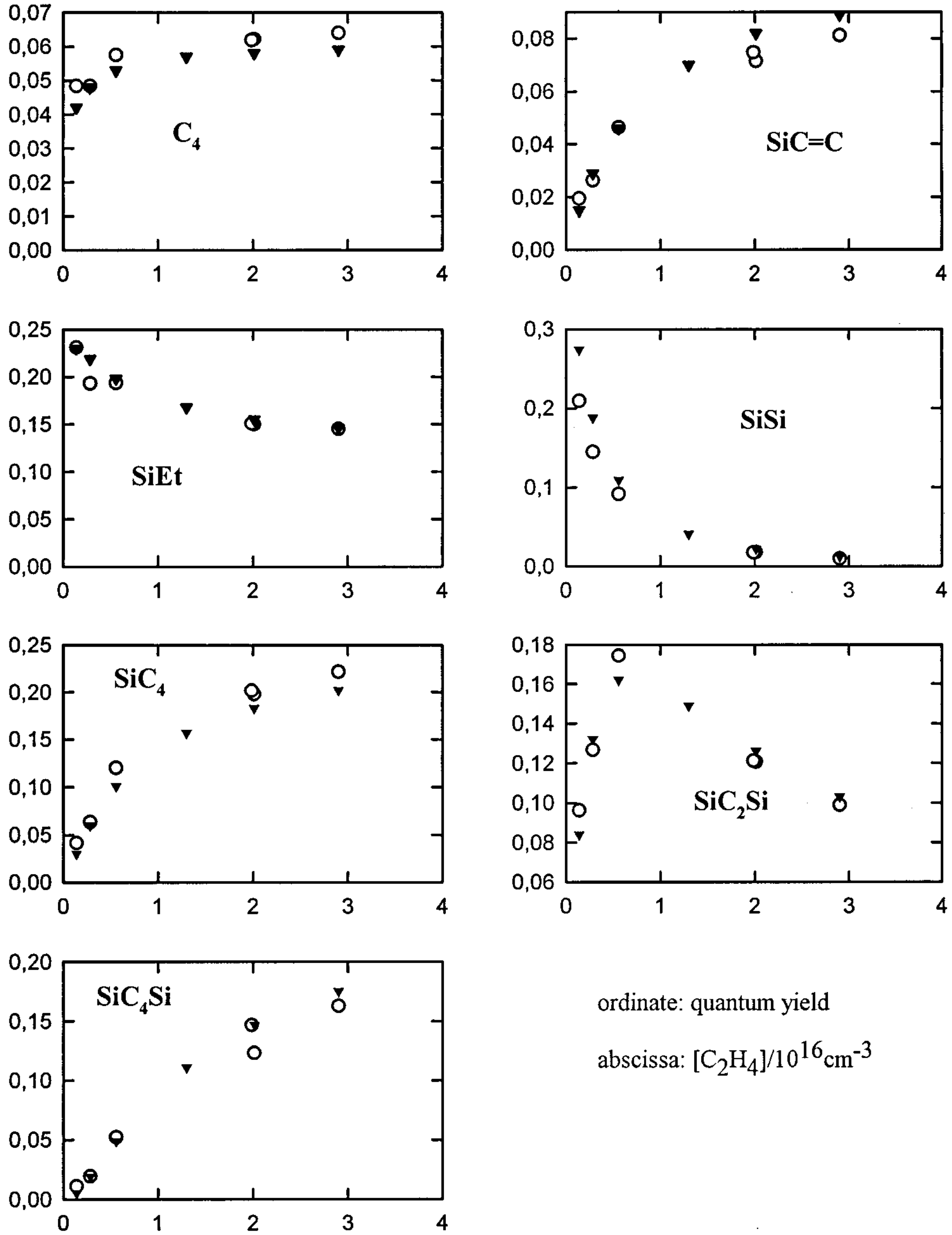

Figure 4. Dependence of the product quantum yields on ethene concentration for a constant reactant ratio $[C_2H_4]/[Me_3SiH] = 0.130$: (○) experimental values; (▼) calculated values.

$$Hg(^3P_1) + H_2 \rightarrow 2H + Hg(^1S_0) \qquad (1)$$

The H atoms then react further with C_2H_4 and Me_3SiH. Five different $[C_2H_4]/[Me_3SiH]$ ratios were employed in the range 0.061−1.02, and for each of the five reactant ratios a series of experiments with different C_2H_4 concentrations were performed.

The mechanisms of the H atom initiated transformation of C_2H_4[20] and of Me_3SiH[21] have been well studied. In the case of C_2H_4 the first step is an addition reaction

$$H + C_2H_4 \rightarrow C_2H_5 \qquad (2)$$

with the high-pressure rate constant $k_2 = 1.09 \times 10^{-12}$ cm^3 s^{-1}.[22] In the case of Me_3SiH, an abstraction reaction, almost exclusively from the Si−H bond, takes place:

$$H + Me_3SiH \rightarrow H_2 + Me_3Si \qquad (3)$$

The most recently determined value of the rate constant is $k_3 = (2.78 \pm 0.19) \times 10^{-13}$.[23]

The two radicals generated in (2) and (3), C_2H_5 and Me_3Si, give rise to the following products: C_4H_{10} (≡ C_4), $Me_3SiCH{=}CH_2$ (≡ SiC=C), $Me_3SiC_2H_5$ (≡ SiEt), $Me_3SiSiMe_3$ (≡ SiSi), $Me_3Si(CH_2)_3CH_3$ (≡ SiC_4), $Me_3Si(CH_2)_2SiMe_3$ (≡ SiC_2Si), and $Me_3Si(CH_2)_4SiMe_3$ (≡ SiC_4Si). A number of products with very small quantum yields ($<1 \times 10^{-3}$) were detected but not identified

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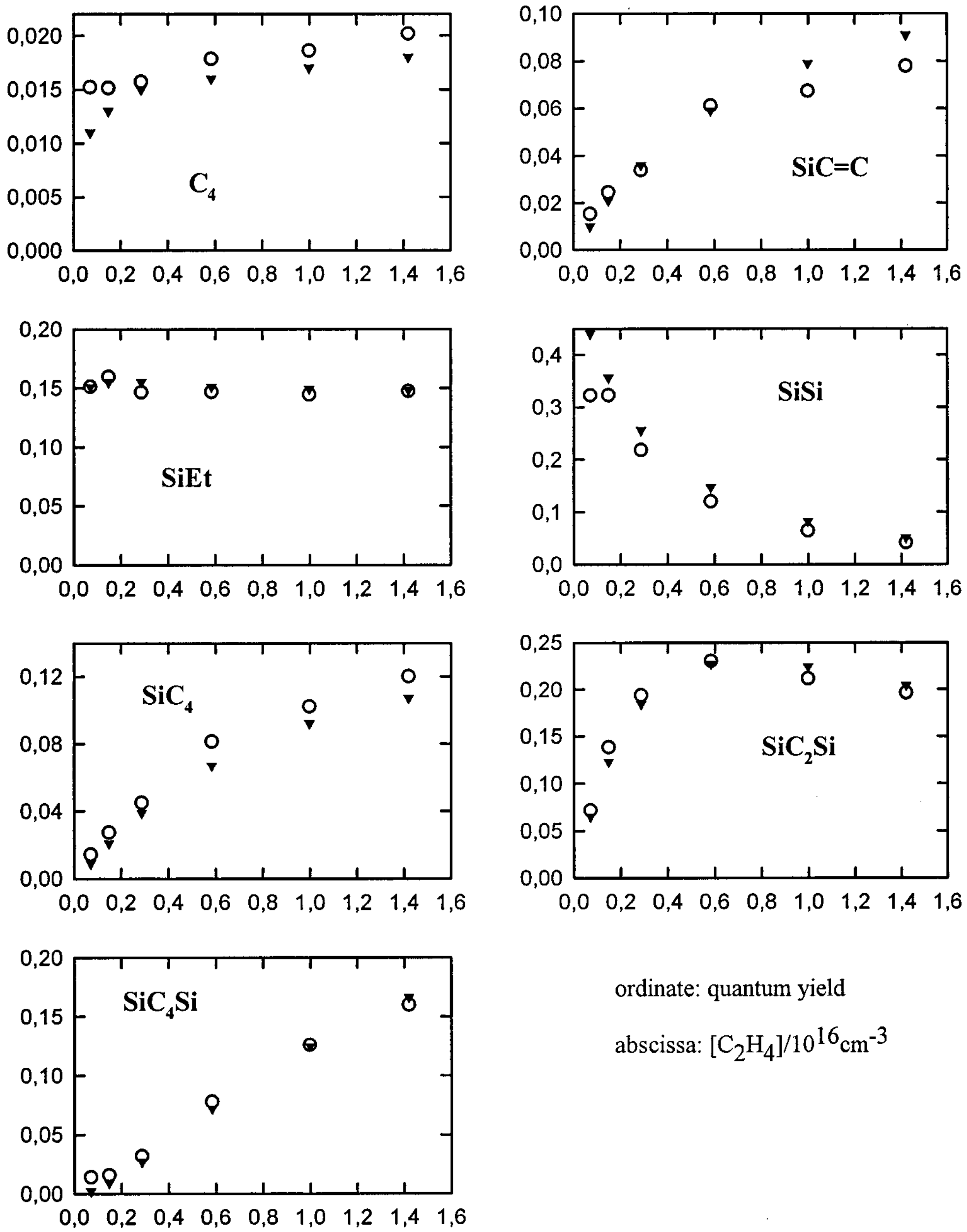

Figure 5. Dependence of the product quantum yields on ethene concentration for a constant reactant ratio [C$_2$H$_4$]/[Me$_3$SiH] = 0.061: (○) experimental values; (▼) calculated values.

or measured. The dependences of the main products on ethylene concentration for the five [C$_2$H$_4$]/[Me$_3$SiH] reactant concentration ratios are given in Figures 1−5. The experimental data have also been evaluated as a function of [C$_2$H$_4$]/[Me$_3$SiH] for a fixed ethene concentration, [C$_2$H$_4$] = 2×10^{16} cm^{-3}. In this case two points are interpolated and one point is extrapolated, giving rise to the error bars shown in Figure 6.

The quantum yield of C$_4$, Φ(C$_4$), is almost independent of [C$_2$H$_4$] (Figures 1−5), but it depends strongly on the [C$_2$H$_4$]/[Me$_3$SiH] reactant ratio, increasing almost linearly from zero. Φ(SiSi) decreases not only as a function of [C$_2$H$_4$]/[Me$_3$SiH] but also as a function of [C$_2$H$_4$], a clear indication that the Me$_3$Si radical is involved in a reaction with ethene. Φ(SiEt) is a major product under all conditions: it decreases with increasing [C$_2$H$_4$] but less strongly than Φ(SiSi), and in contrast to Φ(C$_4$), it shows only a weak dependence on [C$_2$H$_4$]/[Me$_3$SiH]. This behavior identifies SiEt as a cross-combination product of C$_2$H$_5$ and Me$_3$Si.

All the remaining products are characterized by an increase in their quantum yields with increasing [C$_2$H$_4$], their quantum yields either reaching a plateau value or going through a maximum. These products must result from the reaction of Me$_3$Si with C$_2$H$_4$. With the exception of Φ(SiC$_4$), which goes through a maximum, the quantum yields of all "ethene products" decrease steadily with increasing [C$_2$H$_4$]/[Me$_3$SiH].

These results suggest the following simple mechanism: the primary photolysis step, reaction 1, is followed by (2) and (3), and the ethyl[20] and trimethylsilyl[21] radicals formed combine and disproportionate:

$$2C_2H_5 \rightarrow C_4H_{10} \quad (4)$$

$$2C_2H_5 \rightarrow C_2H_4 + C_2H_6 \quad (5)$$

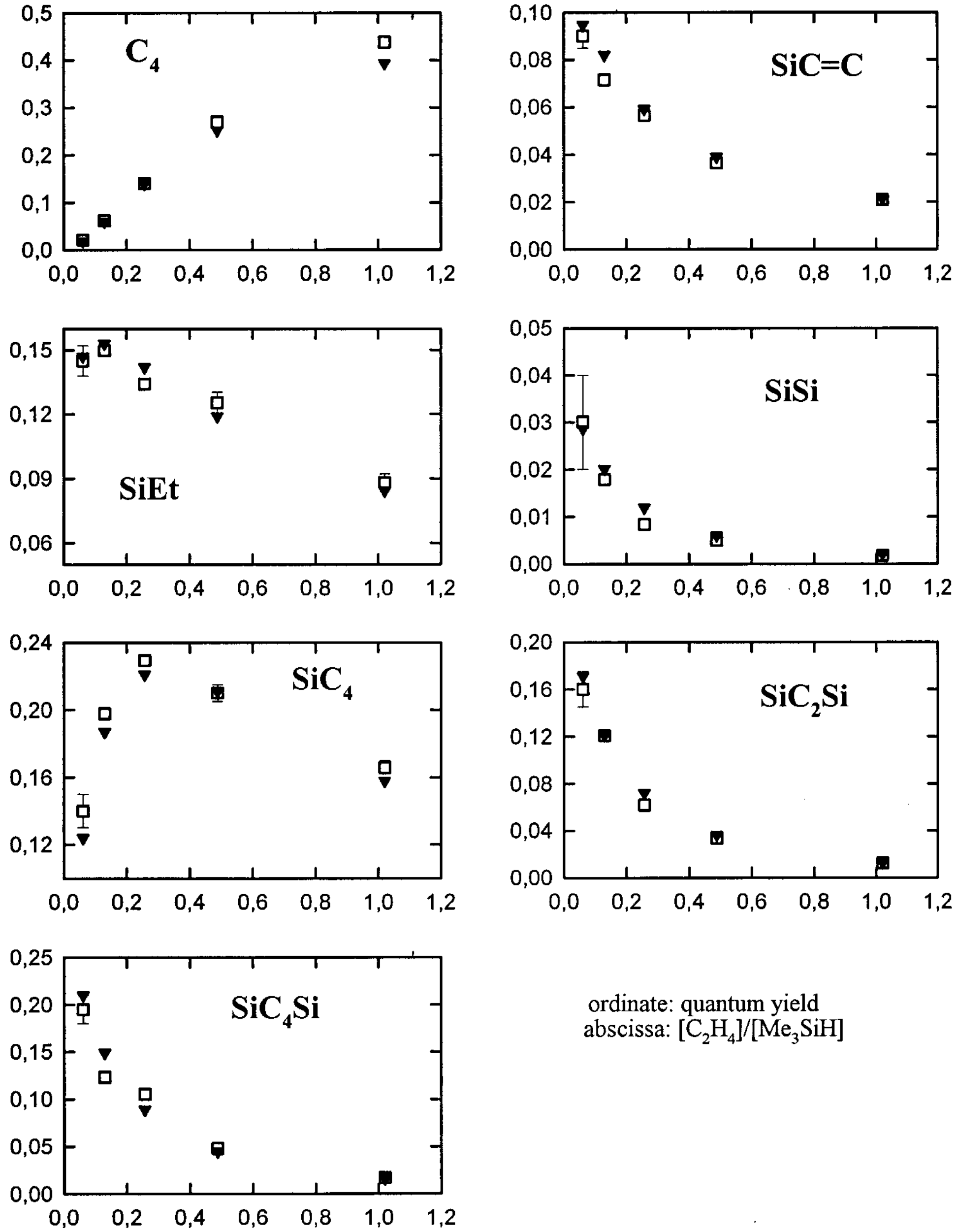

Figure 6. Dependence of the product quantum yields on reactant ratio for a constant ethene concentration $[C_2H_4] = 2 \times 10^{16}$ cm^{-3}.

$$2Me_3Si \rightarrow Me_6Si_2 \qquad (6)$$

$$2Me_3Si \rightarrow Me_3SiH + Me_2Si{=}CH_2 \qquad (7)$$

We attribute the prominent product SiEt to a cross-combination step, and we also add two possible disproportionation steps:

$$C_2H_5 + Me_3Si \rightarrow Me_3SiC_2H_5 \qquad (8)$$

$$C_2H_5 + Me_3Si \rightarrow Me_3SiH + C_2H_4 \qquad (9)$$

$$C_2H_5 + Me_3Si \rightarrow C_2H_6 + Me_2Si{=}CH_2 \qquad (10)$$

A further important step in our mechanism is the addition of the trimethylsilyl radical to ethene

$$Me_3Si + C_2H_4 \rightarrow Me_3SiCH_2CH_2 \qquad (11)$$

giving rise to a new substituted ethyl radical, which will combine and disproportionate with all other radicals present:

$$Me_3SiCH_2CH_2 + C_2H_5 \rightarrow Me_3Si(CH_2)_3CH_3 \qquad (12)$$

$$Me_3SiCH_2CH_2 + C_2H_5 \rightarrow Me_3SiC_2H_5 + C_2H_4 \qquad (13)$$

$$Me_3SiCH_2CH_2 + C_2H_5 \rightarrow C_2H_6 + Me_3SiCH{=}CH_2 \qquad (14)$$

$$Me_3SiCH_2CH_2 + Me_3Si \rightarrow Me_3Si(CH_2)_2SiMe_3 \qquad (15)$$

$$Me_3SiCH_2CH_2 + Me_3Si \rightarrow Me_3SiH + Me_3SiCH{=}CH_2 \qquad (16)$$

$$Me_3SiCH_2CH_2 + Me_3Si \rightarrow Me_3SiC_2H_5 + Me_2Si{=}CH_2 \qquad (17)$$

$$2Me_3SiCH_2CH_2 \rightarrow Me_3Si(CH_2)_4SiMe_3 \qquad (18)$$

$$2Me_3SiCH_2CH_2 \rightarrow Me_3SiC_2H_5 + Me_3SiCH{=}CH_2 \qquad (19)$$

This mechanism has the following consequences. For a given [C_2H_4]/[Me_3SiH] reactant ratio the quantum yields of all the products formed via reaction 11, Φ(SiC═C), Φ(SiC_4), Φ(SiC_2Si), and Φ(SiC_4Si), should go to zero with vanishing ethene concentration. The quantum yields of the products C_4, SiEt, and SiSi should reach a limiting value dependent on the reactant ratio and the factor f in the cross-combination relation ($k_8 = f_8(k_4k_6)^{1/2}$). In the limit of a very large ethene concentration all the Me_3Si radicals formed would disappear via reaction 11. Therefore, the quantum yields of all products which are formed by combination or disproportionation with a Me_3Si radical should go to zero. This should be especially obvious in the case of SiSi, but also SiEt and SiC_2Si should vanish. Φ(SiC_2Si) as a function of [C_2H_4] begins from zero and also tends to zero for very large ethene concentrations; it must therefore go through a maximum.

In the experiments where the product quantum yields were investigated as a function of the reactant ratio at constant ethene concentration, only Me_3Si radicals are formed as the reactant ratio tends to zero. Therefore, the quantum yields of all the products whose formation involves C_2H_5 radicals, Φ(C_4), Φ(SiEt), and Φ(SiC_4), must go to zero. The Me_3Si radicals will combine and disproportionate and also undergo reaction 11, and therefore Φ(SiSi), Φ(SiC═C), Φ(SiC_2Si), and Φ(SiC_4Si) should reach limiting values. At the other extreme, as [C_2H_4]/[Me_3SiH] → ∞, only C_2H_5 radicals are formed, and all products where Me_3Si radicals are involved must tend to zero; thus all products with the exception of C_4, SiEt, and SiC_4 must go through a maximum. All these predictions are in accord with the experimental results.

Rate Constant Ratios. Within the framework of the assumed mechanism, we are able to deduce a number of relations. The cross-combination rate constants, k_{12} and k_{15}, can be derived immediately from our experimental results:

$$k_{12} = f_{12}(k_4k_{18})^{1/2} = \frac{\Phi(\mathrm{SiC_4})}{[\Phi^{1/2}(\mathrm{C_4})][\Phi^{1/2}(\mathrm{SiC_4Si})]}(k_4k_{18})^{1/2} = (1.98 \pm 0.15)(k_4/k_{18})^{1/2}$$

$$k_{15} = f_{15}(k_6k_{18})^{1/2} = \frac{\Phi(\mathrm{SiC_2Si})}{[\Phi^{1/2}(\mathrm{SiSi})][\Phi^{1/2}(\mathrm{SiC_4Si})]}(k_6k_{18})^{1/2} = (2.21 \pm 0.23)(k_6k_{18})^{1/2}$$

The f values are mean values of all the experiments done at room temperature (Figures 1−5), and the errors quoted are 1 standard deviation. The third cross-combination rate constant

$$k_8 = f_8(k_4k_6)^{1/2} = \frac{\Phi(\mathrm{SiEt(8)})}{[\Phi^{1/2}(\mathrm{C_4})][\Phi^{1/2}(\mathrm{SiSi})]}(k_4k_6)^{1/2}$$

cannot be determined as directly as in the two cases above, as the contribution of the disproportionation reactions, (13), (17), and (19), to Φ(SiEt) also needs to be taken into account. However, f_8 can be found by recognizing that the quantum yield of SiEt formed in reaction 8, Φ(SiEt(8)), equals the value of Φ(SiEt) in the limit of vanishing C_2H_4 concentration:

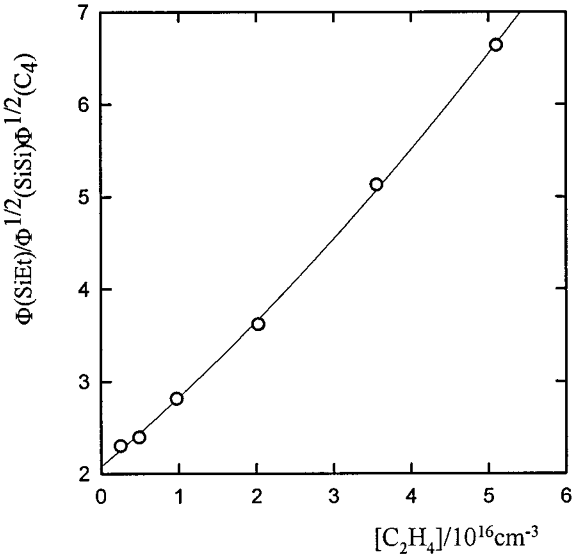

Figure 7. Determination of the factor f_8 in the geometric mean rule relation $k_8 = f_8(k_4k_6)^{1/2}$.

$$f_8 = \lim([\mathrm{C_2H_4}]\to 0)\,\frac{\Phi(\mathrm{SiEt})}{[\Phi^{1/2}(\mathrm{C_4})][\Phi^{1/2}(\mathrm{SiSi})]}$$

In Figure 7 the experimental data are shown for one of the five [C_2H_4]/[Me_3SiH] reactant concentration ratios. It can be seen that disproportionation does indeed make a noticeable contribution to Φ(SiEt). A value for f_8 was obtained by fitting the experimental points to a second degree power series and extrapolating to zero ethene concentration. A similar extrapolation was carried out for the remaining four experimental series, and from the combined results a mean value, $f_8 = 2.04 \pm 0.14$, was obtained. In all three cases the value of f is close to the expected value: statistical considerations require a value of 2, while simple collision theory demands a value greater than 2.[24]

Further relative rate constants may be derived from the relations:

$$\Phi(\mathrm{SiC{=}C}) = \frac{k_{14}}{k_{12}}\Phi(\mathrm{SiC_4}) + \frac{k_{16}}{k_{15}}\Phi(\mathrm{SiC_2Si}) + \frac{k_{19}}{k_{18}}\Phi(\mathrm{SiC_4Si}) \quad \text{(I)}$$

$$\Phi(\mathrm{SiEt}) - \Phi(\mathrm{SiEt(8)}) = \frac{k_{13}}{k_{12}}\Phi(\mathrm{SiC_4}) + \frac{k_{17}}{k_{15}}\Phi(\mathrm{SiC_2Si}) + \frac{k_{19}}{k_{18}}\Phi(\mathrm{SiC_4Si}) \quad \text{(II)}$$

$$\Phi(\mathrm{SiEt(8)}) = 2.04[\Phi^{1/2}(\mathrm{C_4})][\Phi^{1/2}(\mathrm{SiSi})] \quad \text{(III)}$$

A least-squares analysis using the Marquardt−Levenberg algorithm (SigmaPlot 5.0) gives the following values for these relative rate constants:

$$k_{14}/k_{12} = 0.097 \pm 0.005,\ k_{16}/k_{15} = 0.125 \pm 0.008,\ k_{19}/k_{18} = 0.268 \pm 0.014 \text{ (from (I))}$$

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$$k_{13}/k_{12} = 0.12 \pm 0.01,\ k_{17}/k_{15} = 0.09 \pm 0.01,\ k_{19}/k_{18} = 0.33 \pm 0.02 \text{ (from (II))}$$

The good agreement between the two k_{19}/k_{18} values is particularly satisfying. The smaller value was obtained more directly and is used in subsequent calculations.

It is interesting to note that the disproportionation–combination ratios are similar for the SiCC/C_2H_5 (reactions 12–14) and SiCC/Me_3Si (reactions 15–17) systems. For the SiCC/SiCC system (reactions 18 and 19) the value seems to be much larger than for either of the SiCC/C_2H_5 or SiCC/Me_3Si systems, but in this case one has to bear in mind that two like radicals are involved, and therefore a statistical factor of 2 is hidden in the value of k_{19}/k_{18}. In fact, the ratio of disproportionation to combination is very similar in all three radical systems. Unfortunately we are not able to make any assertions about the two disproportionation reactions (9) and (10). Reaction 9 results in the formation of the starting materials, and investigation of reaction 10 requires the detection of C_2H_6, which we were unable to accomplish. Further evaluation of our data requires values for the two relative rate constants, k_9/k_8 and k_{10}/k_8, and in this connection we define a lower limit, a probable value, and an upper limit:

$$0 \le k_9/k_8 \approx k_{16}/k_{15}$$

$$0 \le k_{10}/k_8 \approx k_{17}/k_{15}$$

$$(k_9 + k_{10})/k_8 \le ((k_9 + k_{10})/k_8)_{\max}$$

$((k_9 + k_{10})/k_8)_{\max}$ is chosen in such a way that the condition $\Phi(C_2H_5(2)) + \Phi(Me_3Si(3)) = 2.0$ is fulfilled. If the two reactions (9) and (10) play a role, the sum of the quantum yields of Me_3Si and C_2H_5 as calculated from the observed product quantum yields will be smaller than 2. An evaluation of the literature data by Baulch et al.[22] for the self-reaction of two C_2H_5 radicals yielded the disproportionation–combination ratio $k_5/k_4 = 0.126$. Under the present experimental conditions, using the Hg-sensitized photolysis of H_2/C_2H_4 mixtures, we obtained $k_5/k_4 = 0.135 \pm 0.005$. k_7/k_6 has been determined in two recent publications,[21,25] the value obtained being 0.07 ± 0.01.

We are now in a position to calculate the quantum yields of formation of the two primary radicals C_2H_5 and Me_3Si:

$$\Phi(C_2H_5(2)) = 2\Phi(C_4) + 2\Phi(C_2H_6(5)) + \Phi(\mathrm{SiEt}(8)) + \Phi(Me_3SiH(9)) + \Phi(C_2H_6(10)) + \Phi(SiC_4) + \Phi(\mathrm{SiEt}(13)) + \Phi(C_2H_6(14)) \quad (IV)$$

$$\Phi(Me_3Si(3)) = 2\Phi(\mathrm{SiSi}) + 2\Phi(Me_3SiH(7)) + \Phi(\mathrm{SiEt}(8)) + \Phi(Me_3SiH(9)) + \Phi(C_2H_6(10)) + \Phi(SiC_4) + \Phi(\mathrm{SiEt}(13)) + \Phi(C_2H_6(14)) + 2\Phi(SiC_2Si) + 2\Phi(\mathrm{SiC{=}C}(16)) + 2\Phi(\mathrm{SiEt}(17)) + 2\Phi(SiC_4Si) + 2\Phi(\mathrm{SiC{=}C}(19)) \quad (V)$$

Both quantities can be expressed in terms of already evaluated rate constants and measured product quantum yields:

$$\Phi(C_2H_5(2)) = 2\Phi(C_4)\{1 + k_5/k_4\} + \{\Phi(\mathrm{SiEt}) - k_{13}/k_{12}[\Phi(SiC_4)] - k_{17}/k_{15}[\Phi(SiC_2Si)] - k_{19}/k_{18}[\Phi(SiC_4Si)]\}\{1 + k_9/k_8 + k_{10}/k_8\} + [\Phi(SiC_4)]\{1 + k_{13}/k_{12} + k_{14}/k_{12}\} \quad (IVa)$$

$$\Phi(Me_3Si(3)) = 2[\Phi(\mathrm{SiSi})]\{1 + k_7/k_6\} + \{\Phi(\mathrm{SiEt}) - k_{13}/k_{12}[\Phi(SiC_4)] - k_{17}/k_{15}[\Phi(SiC_2Si)] - k_{19}/k_{18}[\Phi(SiC_4Si)]\}\{1 + k_9/k_8 + k_{10}/k_8\} + [\Phi(SiC_4)]\{1 + k_{13}/k_{12} + k_{14}/k_{12}\} + 2[\Phi(SiC_2Si)]\{1 + k_{16}/k_{15} + k_{17}/k_{15}\} + 2[\Phi(SiC_4Si)]\{1 + k_{19}/k_{18}\} \quad (Va)$$

Assuming $(k_9 + k_{10})/k_8 = 0.0$ gives $\Phi(C_2H_5(2)) + \Phi(Me_3Si(3)) = 1.59 \pm 0.13$ for the sum of the two quantum yields. Its value increases to 1.63 ± 0.13 if the more probable value of 0.215 for $(k_9 + k_{10})/k_8$ is chosen. In both cases the sum of the two quantum yields is much smaller than the expected value of 2. If the difference is attributed solely to an incorrect choice of value for k_9 and k_{10}, the ratio of disproportionation to combination of C_2H_5 and Me_3Si radicals, $(k_9 + k_{10})/k_8$, has to be increased to a value of 1.80 ± 0.18 to achieve a quantum yield of 2.0. We consider this value to be unacceptably high and believe that the results of the present experiment are in line with previous reports[17,21] from this laboratory, where similar losses in the quantum yields of the primarily generated atoms in the presence of Me_3SiH were found.

The quantum yield values for C_2H_5 and Me_3Si allow us to derive a value for the relative rate constant for reaction 3 from relation VI:

$$\frac{\Phi(Me_3Si(3))}{\Phi(C_2H_5(2))} = \frac{k_3}{k_2}\frac{[Me_3SiH]}{[C_2H_4]} \quad (VI)$$

As shown in Figure 8, the ratio of the radical quantum yields versus the reactant concentration ratio shows the expected linear dependence with negligible intercept. The slope also depends on $(k_9 + k_{10})/k_8$, and this dependency is documented in Table 1. Also given there are the absolute rate constants for k_3 calculated with the help of the value for k_2 recommended by Baulch et al.[22]

Our maximum range for k_3, $(3.24–3.90) \times 10^{-13}$ cm^3 s^{-1}, overlaps with only one of the published literature values, that of Cowfer et al.[26] Their value was obtained by a flow experiment with mass-spectrometric detection and is loaded with a relatively large error. The much more precise values reported by Arthur et al.[23,27] are considerably lower and were both obtained by a pulse photolysis–Lyman–α-absorption experiment. The value of Austin and Lampe[28] lies beyond our upper limit. These authors used an experimental technique very similar to ours: Hg-sensitized photolysis of H_2 in the presence of C_2H_4 and Me_3SiH with, in addition, NO

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(25) Kerst, C.; Potzinger, P. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1071.

(26) Cowfer, J. A.; Lynch, K. P.; Michael, J. K. *J. Chem. Phys.* **1975**, *79*, 1139.

(27) Arthur, N. L.; Potzinger, P.; Reimann, B.; Steenbergen, H. P. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 1447.

(28) Austin, E. R.; Lampe, F. W. *J. Phys. Chem.* **1977**, *81*, 1134.

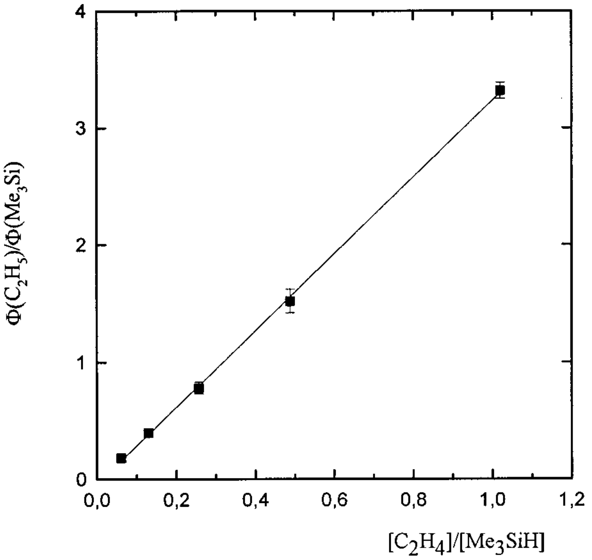

Figure 8. Determination of the relative rate constant k_2/k_3. Radical quantum yields were calculated with $(k_9 + k_{10})/k_8 = 0.215$.

added as a radical scavenger. Their method is less subject to error than the approach used in the present work, as the relative rates of C_2H_4 and Me_3SiH disappearance were measured directly. Their experiments were performed at a H_2 pressure (~40 mbar) where the reaction of H + C_2H_4 lies deep in the falloff range. This was recognized by the authors, but lacking a suitable theory[29] to base calculations upon, they made only coarse corrections to their results.

A correction may also be necessary for our data, which were obtained at a pressure of 400 mbar. To calculate k_2 at a particular pressure with H_2 as a third body, we used the Lennard–Jones parameters given in ref 30 and arrived at the following expression for the ratio of the low-pressure rate coefficients: $k_0(H_2)/k_0(He) = 1.82[\beta_c(H_2)]/\beta_c(He)$. The average energy transferred per collision, β_c, is small and not very different for H_2 and He,[31] and we therefore assumed $k_0(H_2) \approx 2[k_0(He)]$. With the values for k_0(He) and F_c, given in ref 22, and assuming that the latter is also valid for H_2, we obtain $k_2/k_{2\infty} = 0.61$ at 40 mbar and $k_2/k_{2\infty} = 0.86$ at 400 mbar.

The pressure correction of k_2 brings our value for k_3 into close agreement with the absolute values of Arthur and Miles[23] if a small value for $(k_9 + k_{10})/k_8$ is assumed (Table 1). The value of Austin and Lampe[28] is also reduced, but it still represents the largest of all published values. An argument can be made that this value should be an upper limit. The authors added NO as a radical scavenger to their reaction mixture to avoid secondary reactions between the radicals formed and the reactants C_2H_4 and Me_3SiH. By adding NO, however, they initiated what they tried to avoid: Me_3Si radicals react with NO with the formation of Me_3SiO,[32] which reacts further with Me_3SiH to form Me_3SiOH,[17] in this way starting a chain of small length.

Table 1. Relative and Absolute Rate Constants for Reaction 3

		$k_3/10^{-13}$ cm^3 s^{-1}		
$(k_9 + k_{10})/k_8$	k_3/k_2	exptl[a]	exptl[b]	lit.
0.0	0.297	3.24	2.78	2.6,[27] 2.7[23]
0.215	0.305	3.32	2.86	3.7[26]
1.80	0.358	3.90	3.36	5.8,[28] 4.4[28 c]

[a] $k_2 = 1.09 \times 10^{-12}$ cm^3 s^{-1}. [b] $k_2 = 9.4 \times 10^{-13}$ cm^3 s^{-1}. [c] Recalculated with $k_2 = 6.6 \times 10^{-13}$ cm^3 s^{-1}.

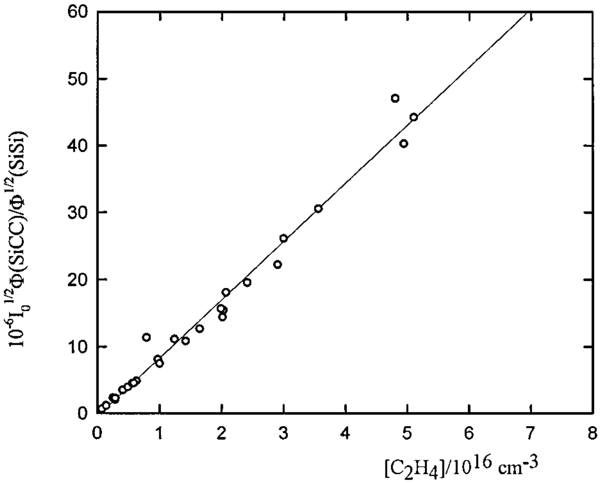

Figure 9. Determination of the relative rate constant $k_{11}/k_6^{1/2}$.

The good agreement for k_3 obtained in this work and by Arthur and Miles[23] attests to the quality of our end-product analysis; no selective losses of silicon compounds occur in our experiments.

In addition to $\Phi(C_2H_5)$ and $\Phi(Me_3Si)$, we are also able to calculate the quantum yield of formation of the $Me_3SiCH_2CH_2$ radical:

$$\Phi(Me_3SiCH_2CH_2) = [\Phi(SiC_4)]\{1 + k_{13}/k_{12} + k_{14}/k_{12}\} + [\Phi(SiC_2Si)]\{1 + k_{16}/k_{15} + k_{17}/k_{15}\} + 2[\Phi(SiC_4Si)]\{1 + k_{19}/k_{18}\} \quad \text{(VII)}$$

This quantity allows us to calculate a relative rate constant for reaction 11 from

$$\frac{\Phi(Me_3SiCH_2CH_2)}{\Phi^{1/2}(SiSi)} I_0^{\,1/2} = \frac{k_{11}}{k_6^{\,1/2}}[C_2H_4] \quad \text{(VIII)}$$

In Figure 9 we have plotted the left-hand side of eq VIII versus the ethylene concentration. From the slope we calculate $k_{11}/k_6^{1/2} = (8.7 \pm 0.2) \times 10^{-10}$ cm$^{3/2}$ s$^{-1/2}$. To compare our relative rate constant with the absolute value reported by Choo and Gaspar,[8] a value for k_6 is needed. This value is not well-known. The reported rate constant values, which always embrace the two reactions 6 and 7, range from $k_6 + k_7 = 3 \times 10^{-10}$ cm^3 s^{-1},[33] obtained by the rotating sector method with end-product analysis, to $k_6 + k_7 = 2 \times 10^{-11}$,[34] obtained by means of the pulsed laser photolysis of hexamethyldisilane. The

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latter experiment has been repeated by Brix et al.,[35] and the mechanism of the direct photolysis of hexamethyldisilane at 206 nm was also investigated. It was found that in addition to the main primary photochemical process, the splitting of the Si−Si bond, a substantial side reaction (27%), the formation of dimethylsilaethene and trimethylsilane, also takes place. At that time it was known that dimethylsilaethene dimerization, radical addition to the Si═C double bond, and radical−radical self-reaction compete successfully with each other, implying that the rate constants for these processes have the same order of magnitude. It was therefore thought necessary to correct the experimentally obtained second-order rate constant for Me_3Si disappearance ($k = (5.5 \pm 1.3) \times 10^{-11}$ cm^3 s^{-1}). A mechanism with estimated rate constants was set up, and a value for $k_6 + k_7 = (3 \pm 1) \times 10^{-11}$ cm^3 s^{-1} was extracted. In the meantime, values have become known for the rate constants, k_{20}[36] and k_{21},[18] of two important reactions involved in the simulation of the hexamethyldisilane system:

$$2Me_2Si{=}CH_2 \rightarrow Me_2SiCH_2Si(Me_2)CH_2 \qquad (20)$$

$$Me_3Si + Me_2Si{=}CH_2 \rightarrow Me_3SiSi(Me_2)CH_2 \qquad (21)$$

However, a number of rate constants are still unknown and have to be estimated. Computer calculations carried out by us now suggest that $k_6 + k_7$ amounts to 4×10^{-11} cm^3 s^{-1}. Without giving too much weight to this number, it is obvious that the measured value is only an upper limit and has to be corrected. The value suggested by Shimo et al.[34] is smaller by a factor of 2, even without correction. However, reevaluation of the data given in Figure 2 of their publication reveals a much higher rate constant for Me_3Si disappearance ($k = 7.5 \times 10^{-11}$ cm^3 s^{-1}), bringing the results of the two pulse experiments into much closer agreement.

The value of k_6 can be estimated by another route. If it is assumed that the geometric mean rule holds for the cross-combination of CH_3 and Me_3Si, the known combination rate constants for $CH_3 + Me_3Si$[13] and $CH_3 + CH_3$[22] give a value of $k_6 = 7.8 \times 10^{-11}$ cm^3 s^{-1}. Taking into account the small value of of $k_7/k_6 = 0.07 \pm 0.01$, the conclusion we reach is that $k_6 = (6 \pm 2) \times 10^{-11}$cm^3 s^{-1}.

With this number we arrive at the value of $k_{11} = (6.7 \pm 2.3) \times 10^{-15}$ cm^3 s^{-1}.

Quantitative Examination of the Mechanism. The mechanism presented so far has been built on the qualitative interpretation of the experimental data, but now we are in a position to examine how well it withstands quantitative verification. The mechanism is too complex for an analytical solution, and we therefore have to be satisfied with a computer simulation of the reaction. The input data required are the experimentally measured reactant concentrations, light intensities, and rate constants. The light intensity is an average of the experimental values and was taken to be the same in all computations. All the rate constants can be expressed in terms of the four rate constants k_2, k_4, k_6, and k_{18}, which can be chosen ad libitum. The numerical factors which relate the remaining rate constants with the chosen rate constants were derived as described above; for k_9 and k_{10} we used what we consider to be the most probable values. To account for the losses in the quantum yields of the primarily generated atoms, we used a stoichiometric factor of 1.5 for H in reaction 1. Calculations were also done where the factor f_9, which relates k_9 to k_4 and k_6, was increased from 0.255 to 3.49, and the stoichiometric factor in (1) was set to 2. All the input parameters are summarized in Table 2. The calculated values are shown as filled triangles in Figures 1−6.

Table 2. Input Parameters for Computer Calculations

I_0/cm^{-3} s^{-1} = 8×10^{12}, [C_2H_4]/cm^{-3} variable, [Me_3SiH]/cm^{-3} variable, k/cm^3 s^{-1}
$k_{11} = (8.7 \times 10^{-10})k_6{}^{1/2}$, $k_3 = 0.305k_2$, $k_5 = 0.135k_4$, $k_7 = 0.07k_6$
$k_8 = 2.04(k_4k_6)^{1/2}$, $k_9 = 0.255(k_4k_6)^{1/2}$, $k_{10} = 0.184(k_4k_6)^{1/2}$, $k_{12} = 1.98(k_4k_{18})^{1/2}$
$k_{13} = 0.238(k_4k_{18})^{1/2}$, $k_{14} = 0.192(k_4k_{18})^{1/2}$, $k_{15} = 2.21(k_6k_{18})^{1/2}$
$k_{16} = 0.276(k_6k_{18})^{1/2}$, $k_{17} = 0.199\ (k_6k_{18})^{1/2}$, $k_{19} = 0.33\ k_{18}$
$k_{11} = (2.6 \times 10^{-7})e^{-1700/T}k_6{}^{1/2}$, $k_3 = 2.28e^{-600/T}k_2$, $k_{22} = (4.5 \times 10^{-2})e^{-4000/T}k_4$
$k_{23} = 0.18e^{-3600/T}k_{18}$

Overall there is good agreement between the calculated and experimental values with respect to the absolute values, as well as with respect to the dependence on ethene concentration (Figures 1−5) and the dependence on the [C_2H_4]/[Me_3SiH] reactant ratio (Figure 6). Whether some of the finer details of the experimental results can be reproduced by the computations provides a crucial test for the correctness of the mechanism and the quality of the input rate constants; for example, the mechanism predicts a small increase in $\Phi(C_4)$ as a function of [C_2H_4] at small ethene concentrations.

These rather subtle features of the results are partially obscured by experimental scatter but can be discerned in Figures 4 and 5. The anticipated maximum of Φ(SiEt) as a function of [C_2H_4]/[Me_3SiH] is only weakly developed, and this is confirmed in the simulation (Figure 6). Much more pronounced is the maximum of SiC_4, and again experimental and calculated values agree reasonably well (Figure 6). $\Phi(SiC_2Si)$ shows a maximum at an ethene concentration of [C_2H_4] = $(7 \pm 2) \times 10^{15}$ cm^{-3}. The smaller the [C_2H_4]/[Me_3SiH] ratio, the clearer this maximum can be seen. Again, this behavior is well reproduced by the calculations (Figures 1−5). Finally, the quantum yield of SiC_4Si shows a sigmoid shape (Figure 5), and such behavior is also shown by the computer simulation. We are therefore confident that the proposed mechanism is largely correct and the values of the relative rate constants derived are trustworthy. If the calculation is repeated with a stoichiometric factor of 2 for H in reaction 1, and the large value for $(k_9 + k_{10})/k_8 = 1.8$ is used instead of 0.215, agreement between experimental and calculated data is appreciably worse, especially for the lowest reactant ratio studied, [C_2H_4]/[Me_3SiH] = 0.061 (Figure 10). If the goodness of the fit is assessed by the relation $\chi^2 = \sum_i\sum_j(\Phi_{ij}(\text{calcd}) - \Phi_{ij}(\text{exptl}))^2/\Phi_{ij}(\text{exptl})$, where the index i runs over the different products and j counts the experiments, substitution of the larger value for $(k_9 + k_{10})/k_8$ leads to an increase in the value of χ^2 by a factor of 10.

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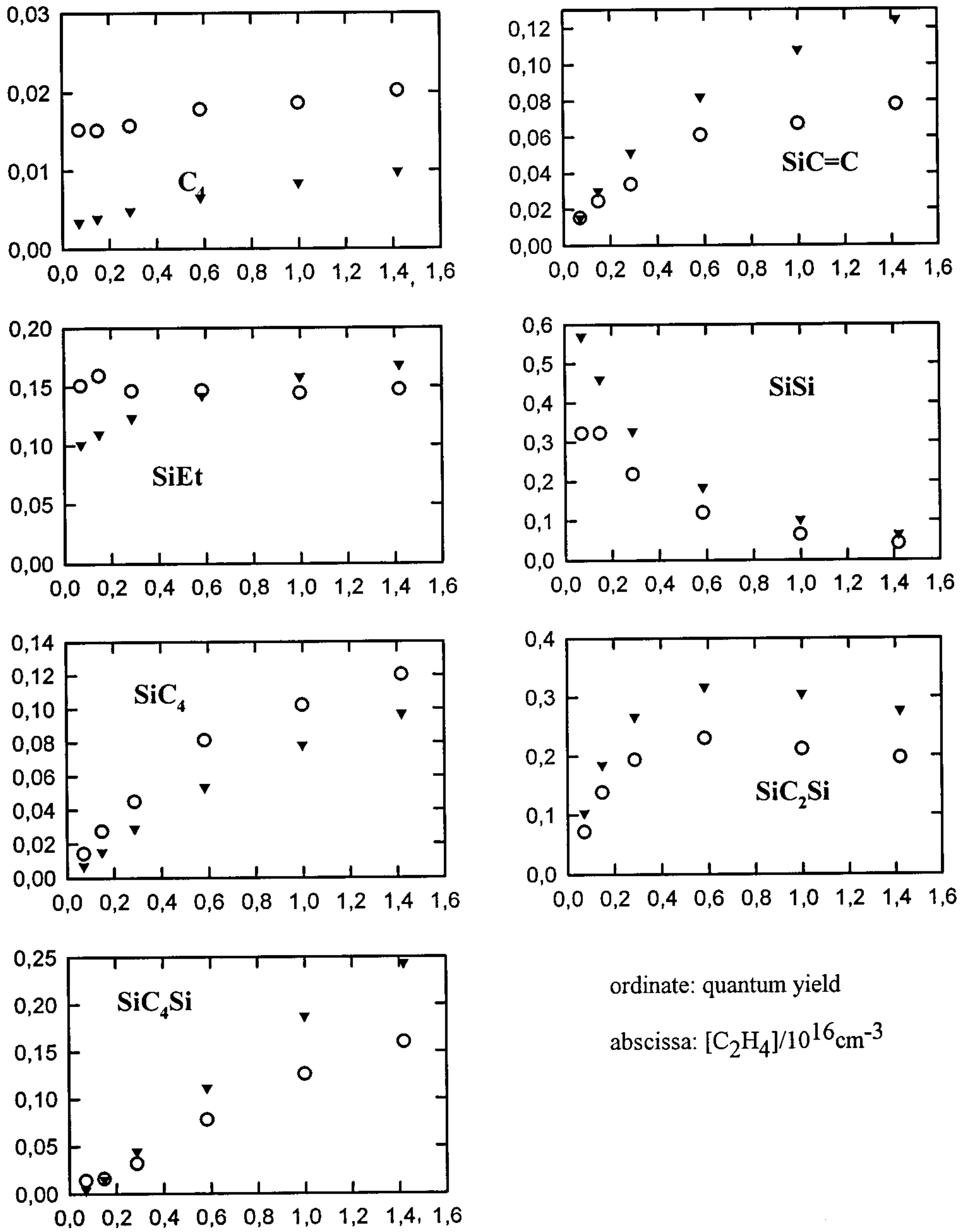

Figure 10. Calculated product quantum yields (▼) as a function of ethene concentration with the assumption $(k_9 + k_{10})/k_8 = 1.8$ ([C$_2$H$_4$]/[Me$_3$SiH] = 0.061).

Temperature Dependence. The temperature dependence of the products has been studied for three reactant ratios, [C$_2$H$_4$]/[Me$_3$SiH] = 1.02, 0.257, and 0.061. The results are shown in Figures 11−13. The reactant ratio has only a weak influence on the temperature behavior of the products. Φ(C$_4$) decreases steadily with increasing temperature, and in the beginning so does Φ(SiSi), but then it goes through a minimum and at about 400 K increases again. At about the same temperature Φ(SiEt) starts to grow exponentially, while Φ(SiC=C), Φ(SiC$_4$), and Φ(SiC$_4$Si) go through a maximum. Φ(SiC$_2$Si) shows more complex behavior: it increases somewhat in the beginning, then goes through a slight maximum or a plateau, and then, also at about 400 K, increases again. The maximum or plateau moves to higher temperature with decreasing [C$_2$H$_4$]/[Me$_3$SiH] ratio.

To a good approximation our mechanism contains only three temperature-dependent steps, namely (2), (3), and (11). The high-pressure activation energy for reaction 2 is given by $E_a(2) = 5.4$ kJ mol^{-1}; at the pressure at which our experiments were performed, no significant decrease in this value would be expected. The most recently determined activation energy for reaction 3 is $E_a(3) = 11.7$ kJ mol^{-1}.[23] Combining this with $k_3/k_2 = 0.305$ at 298 K yields $k_3/k_2 = 3.87 \exp(-757/T)$. Judging from the results of Choo and Gaspar,[8] k_{11}/k_6 will be loaded with a somewhat higher activation energy. As a consequence, a temperature increase will result not only in an increase in the formation of Me$_3$Si at the expense of C$_2$H$_5$ but also in an increase in the rate of disappearance of silyl radicals forming Me$_3$SiCH$_2$CH$_2$. One therefore expects a decrease of Φ(C$_4$), Φ(SiEt), and Φ(SiSi) and a growth of Φ(SiC$_4$Si) with increasing temperature. The observed increase in Φ(SiEt) and Φ(SiSi) at high temperature cannot be explained by the given mechanism. The increase in Φ(SiSi) at high temperature indicates that one or more new channels for generating

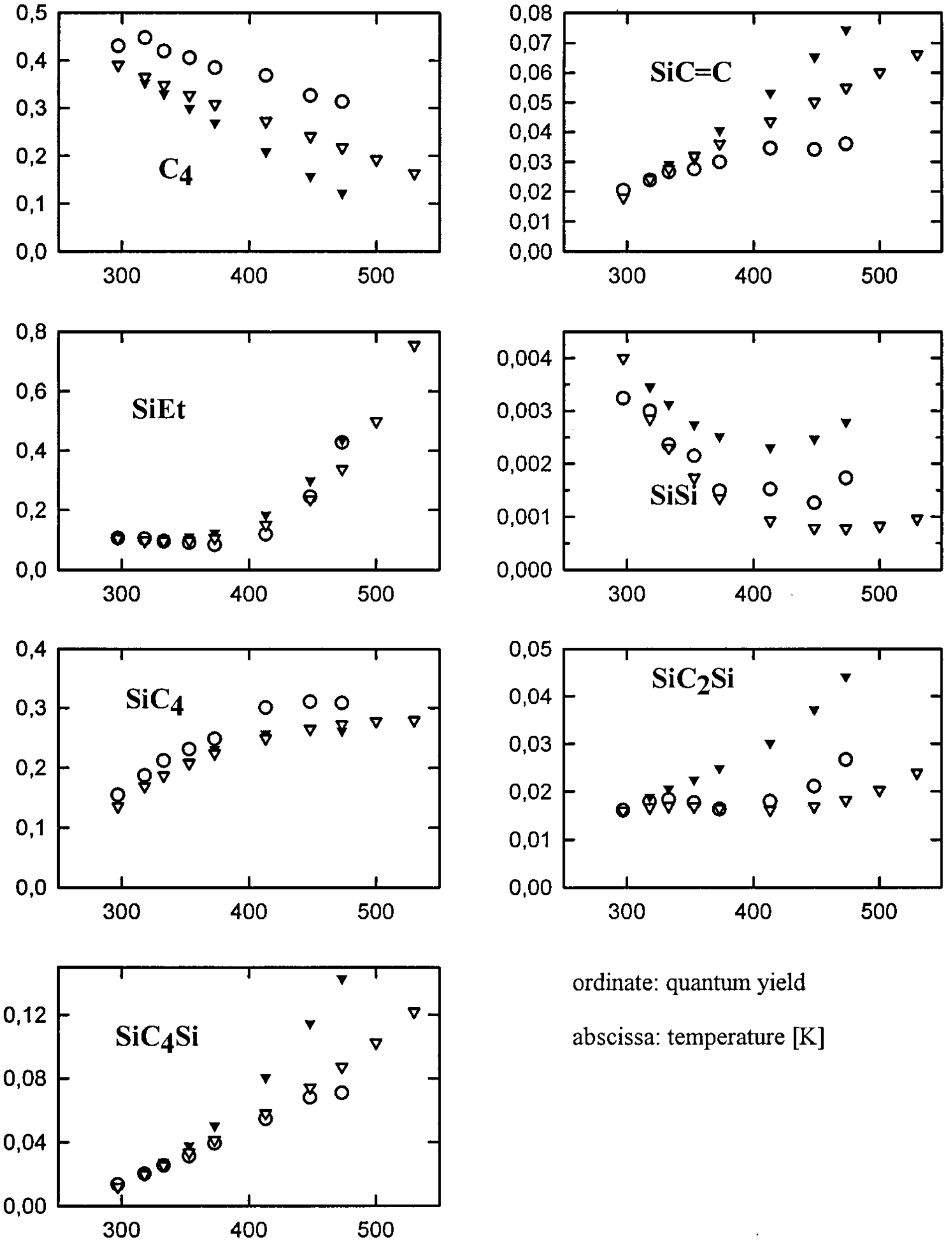

Figure 11. Dependence of the product quantum yields on temperature ($[C_2H_4]/[Me_3SiH] = 1.02$, $[C_2H_4] = 1.2 \times 10^{16}$ cm^{-3}): (○) experimental values; (▼, ▽) calculated values.

Me_3Si radicals are opened. The only way to achieve this goal is to postulate that the two carbon-centered radicals present abstract hydrogen from trimethylsilane:

$$C_2H_5 + Me_3SiH \rightarrow C_2H_6 + Me_3Si \qquad (22)$$

$$Me_3SiCH_2CH_2 + Me_3SiH \rightarrow Me_3SiC_2H_5 + Me_3Si \qquad (23)$$

The reactions of alkyl radicals with silanes have been studied by a number of groups and are reviewed in ref 37. Berkley et al.[38] reported Arrhenius parameters for the reaction of ethyl radicals with SiH_4, the values obtained being $E_a = 30.3$ kJ mol^{-1} and $A = 8.9 \times 10^{-13}$ cm^3 s^{-1}. (For reaction 22, because the Si−H bond energy increases somewhat with methylation,[39] a slightly larger activation energy than for attack on SiH_4 would be expected and, because the number of Si−H bonds is fewer, a slightly smaller *A* factor). The rather large activation energy for reaction 22, and quite probably for reaction 23, led us to the conclusion that these two reactions can be neglected at low temperature. On this basis we calculated $k_{11}/k_6^{1/2}$ from relations VII and VIII at different temperatures. At low temperatures Arrhenius behavior is indeed observed, while at higher temperatures (>400 K) the model fails, as expected. For the three reactant mixtures the results are shown in Figure 14. In view of the assumptions made, the derived mean activation energy, $E_a(11) = 11.5$ kJ mol^{-1}, should be considered only as a lower bound. This value can be compared with the value obtained by Choo and Gaspar, $E_a(11) = 10.4$ kJ mol^{-1}.

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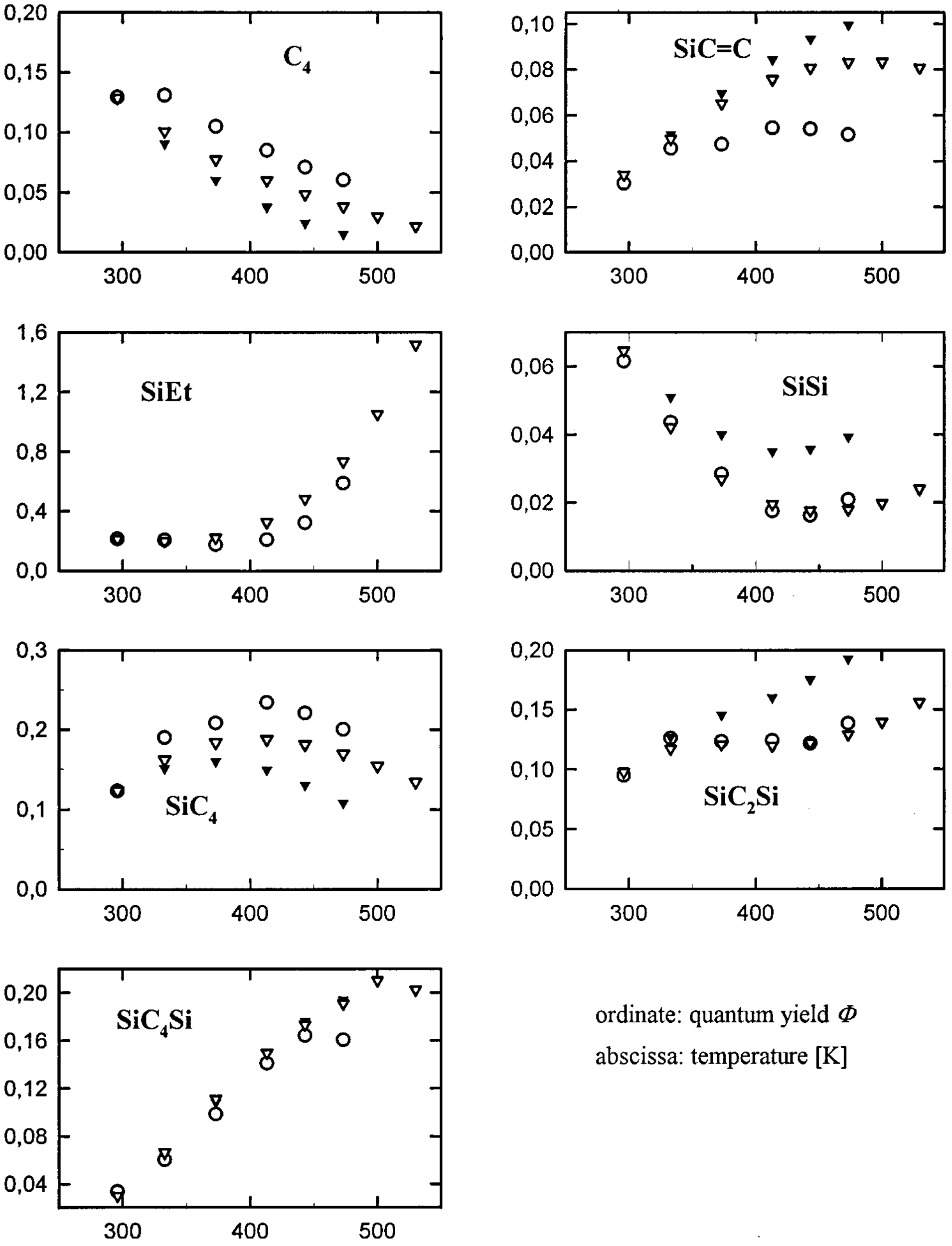

Figure 12. Dependence of the product quantum yields on temperature ([C$_2$H$_4$]/[Me$_3$SiH] = 0.257, [C$_2$H$_4$] = 4.9 × 10^{15} cm^{-3}) (○) experimental values; (▼, ▽) calculated values.

Computer simulations of the temperature dependence of the product quantum yields were also performed with the enlarged mechanism, including reactions 22 and 23. The same values for the temperature-independent rate constants were used as in Table 2. The rate constants k_2, k_3, k_{11}, k_{22}, and k_{23} were considered to be temperature-dependent, and calculations were performed with the following values. The Arrhenius expression for k_3/k_2 has been derived above. The approach used ignored the small effect of the variation of the pressure dependence of k_2 with temperature. The room-temperature value for $k_{11}/k_6^{1/2}$, combined with the mean activation energy for reaction 11, yields $k_{11}/k_6^{1/2} = (9.17 \times 10^{-8})\exp(-1388/T)$ cm$^{3/2}$ s$^{-1/2}$. For k_{22}/k_4 and k_{23}/k_{18} the Arrhenius relations $k_{22}/k_4 = 0.09 \exp(-3600/T)$ and $k_{23}/k_{18} = 0.18 \exp(-3600/T)$ were assumed.

With these rate constants we obtained the results shown in Figures 11–13 (filled triangles). By and large the essential features of the temperature dependence of the product quantum yields are reproduced, but several quantitative differences should be noted. Φ(C$_4$) vs *T* shows approximately the correct slope, but there is a large difference between the calculated and experimental Φ values, probably caused by a shift in all the experimental values observed in photolyses at elevated temperatures (Figures 11 and 12). As we tried to reproduce the slope of Φ(C$_4$) vs *T* and not the quantum yield values themselves, the reason for this shift is unknown. Further systematic differences between calculated and experimental values should be noted for Φ(SiC=C), Φ(SiSi), and Φ(SiC$_4$). For Φ(SiC=C) and Φ(SiSi) the calculated values always come out too large, and for Φ(SiC$_4$) they are too small. As a guide to the directions the six Arrhenius parameters of the four temperature-dependent relative rate constants have to be changed, in Table 3 we give the sensitivity matrix for the reactant ratio [C$_2$H$_4$]/[Me$_3$SiH] = 0.257 and *T* = 443 K. (The *A* factors of $k_{11}/k_6^{1/2}$ and k_3/k_2 cannot be

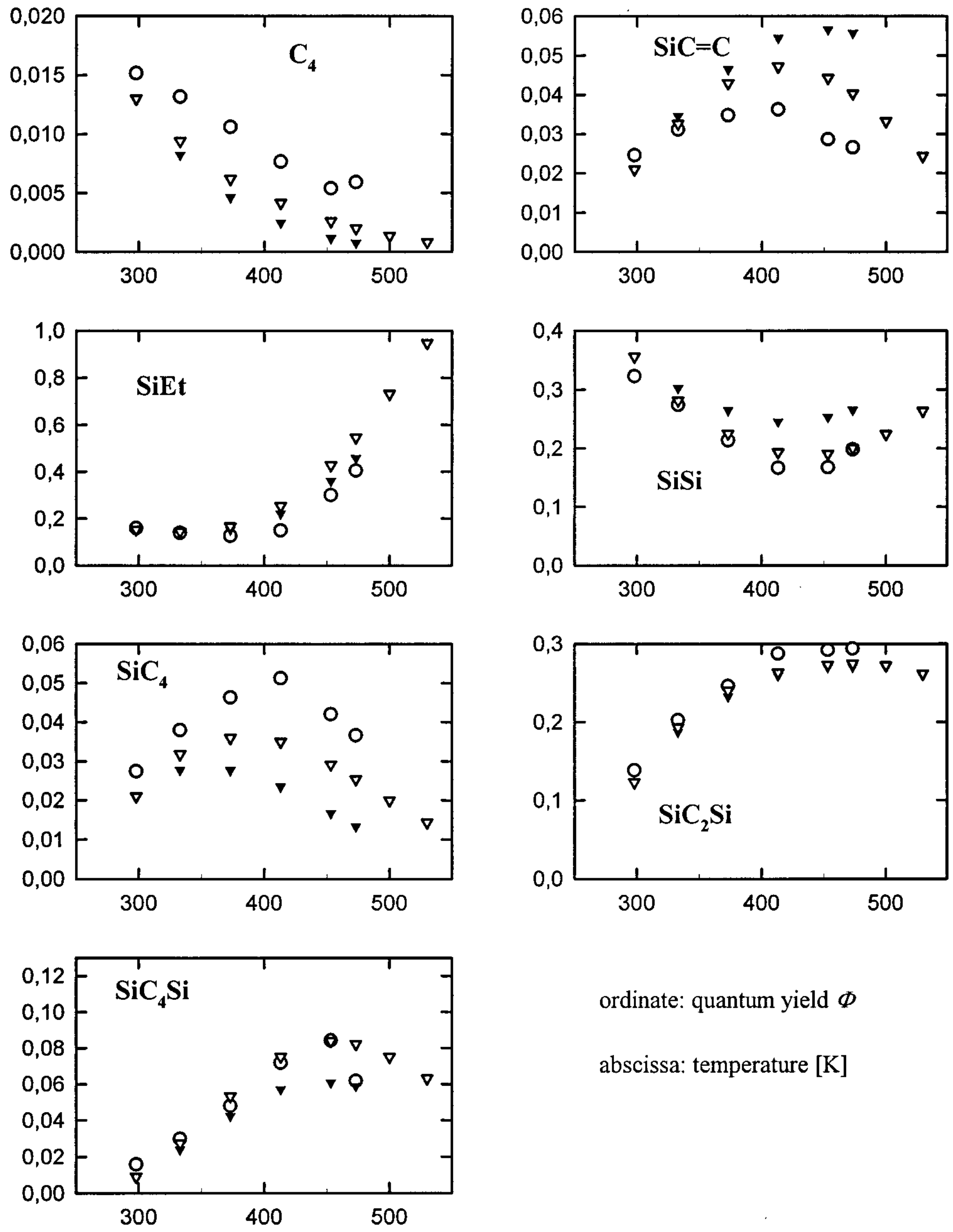

Figure 13. Dependence of the product quantum yields on temperature ($[C_2H_4]/[Me_3SiH] = 0.061$, $[C_2H_4] = 1.37 \times 10^{15}$ cm^{-3}): (○) experimental values; (▼, ▽) calculated values.

chosen independently, because the conditions $k_{11}/k_6^{1/2} = 8.7 \times 10^{-10}$ $cm^{3/2}$ $s^{-1/2}$ and $k_3/k_2 = 0.305$ at room temperature have to be fulfilled.)

A look at Table 3 reveals that $\Phi(C_4)$ is strongly dependent on k_3 but much less so on k_{22}. k_{22} has an even weaker influence on all the other products, and therefore, no statement about the Arrhenius parameters of this rate constant is possible. In the two cases in Figures 11 and 13, the slope of $\Phi(C_4)$ vs T seems somewhat too large, but the experimental results are not precise enough to warrant any changes in k_3 and/or k_{22}. The product SiEt depends predominantly on k_{23}, and the reasonably good agreement between experiment and simulation furnishes no incentive to change the value of this rate constant. To reduce the calculated quantum yields of SiSi, the value of k_{11} has to be increased: large negative changes in k_3 and/or k_{23} are obviously inappropriate because of their devastating influence on $\Phi(C_4)$ and Φ(SiEt). An increase in k_{11}, which implies an increase in the *A* factor as well as in the activation energy, would also improve agreement for SiC_2Si, but the tiny maximum (or plateau) observed could only be reproduced by reducing k_3. A smaller value for k_3 would also help to bring calculated and experimental values for SiC_4 into better agreement. The strong leveling off, and even decrease, of SiC=C with increasing temperature could not be reproduced by the mechanism. A substantial improvement was achieved by introducing the secondary reaction

$$(CH_3)_3Si + (CH_3)_3SiCH{=}CH_2 \longrightarrow \text{products} \qquad (24)$$

and k_{24} was taken to be equal to k_{11}.

Guided by these considerations, we arrived at an improved set of temperature-dependent rate constants, whose Arrhenius parameters are listed in Table 2. With these rate constants we obtained the results shown by open triangles in Figures 11–13. No systematic search

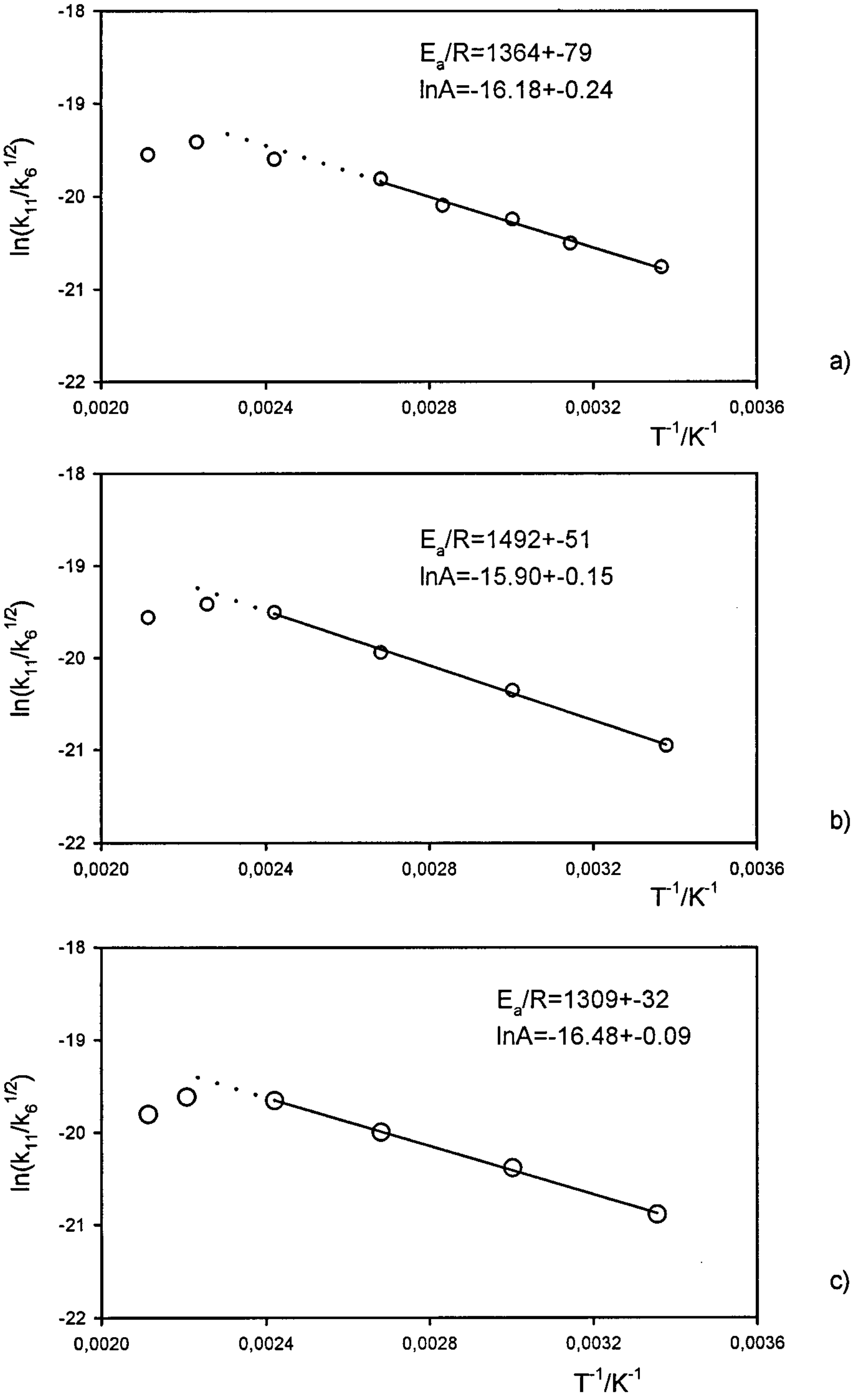

Figure 14. Arrhenius plot for the relative rate constant for Me$_3$Si radical addition to ethene: (a) [C$_2$H$_4$]/[Me$_3$SiH] = 1.02; (b) [C$_2$H$_4$]/[Me$_3$SiH] = 0.257; (c) [C$_2$H$_4$]/[Me$_3$SiH] = 0.061.

Table 3. Sensitivity Matrix $S = d(\ln[X])/d(\ln k)$ for [C$_2$H$_4$]/[Me$_3$SiH] = 0.257 (T = 443 K)

X	k_3	k_{11}	k_{22}	k_{23}
C$_4$	−1.4090	−0.0171	−0.1206	−0.0246
SiC=C	0.3117	0.3636	0.0257	−0.1089
SiEt	0.1543	0.1390	0.0129	0.6287
SiSi	0.5186	−1.3973	0.0479	0.4547
SiC$_4$	−0.4448	0.2660	−0.0387	−0.0938
SiC$_2$Si	0.5190	−0.4244	0.0454	0.1454
SiC$_4$Si	0.5191	0.5506	0.0431	−0.1627

for a minimum of χ^2 was undertaken, and therefore, the calculations do little more than support the conclusions drawn above. The calculations confirm that the activation energy for reaction 11 extracted from the Arrhenius plots (Figure 14) is a lower limit, the value lying between the limits $11.6 \leq E_a(11)/\text{kJ mol}^{-1} \leq 14.1$ and the A factor between the limits $7.1 \times 10^{-13} \leq A/\text{cm}^3\ \text{s}^{-1} \leq 1.9 \times 10^{-12}$. The literature value[23] for the activation energy of reaction 3 seems to be an upper limit, and our results favor a somewhat smaller value.

Silyl Radical Addition to Ethene. The addition of CH$_3$ radicals to C$_2$H$_4$ and substituted ethenes has been widely studied both experimentally[40,41] and theoretically[4,42] and now represents a reference reaction for the whole class of radical addition reactions to alkenes. The essence of the results of investigations can be summarized under the following headings:

(1) There exists an early transition state.

(2) The barrier height is mainly governed by enthalpic effects: the higher the exothermicity of the reaction, the smaller the activation energy.

(3) Polar effects play only a minor role: toward very electron deficient alkenes the CH_3 radical behaves like a nucleophile.

The first statement seems to be valid for all radical addition reactions. The *A* factor for

$$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2 \tag{25}$$

is $A(25) = 3.5 \times 10^{-13}$ cm^3 s^{-1}, while the activation energy is $E_a = 30.8$ kJ mol^{-1}.[40] In the liquid phase, an average *A* factor for methyl radical addition to substituted ethenes of similar magnitude, $A = 5 \times 10^{-13}$ cm^3 s^{-1}, has been found.[41] Our measured *A* factor for reaction 11 is somewhat larger but agrees reasonably well with the liquid-phase values reported by Chatgilialoglu et al.[7] and supports the assumption that the transition state for silyl radical addition to alkenes is also early. This value is, however, at variance with the measured *A* factor of Choo et al.[8] and the estimate by Loh et al.[9]

Thermodynamic control cannot be responsible for the much larger rate of reaction 11 compared to reaction 25. The enthalpy of reaction of (25) amounts to $\Delta_rH°(25) = -98$ kJ mol^{-1}, while for the calculation of $\Delta_rH°(11)$ an estimate of the unknown value of $\Delta_fH°(Me_3SiCH_2CH_2)$ is needed. To take advantage of error cancellation, we decided to estimate the heats of formation of both radicals by a bond energy−bond interaction scheme.[43] Using this approach we get $\Delta_rH°(11) = \Delta_fH°(Me_3SiCH_2CH_2) - \Delta_fH°(Me_3Si) - \Delta_fH°(C_2H_4) = -39 - 14 - 52 = -105$ kJ mol^{-1}.[44] The reaction enthalpies of (11) and (25) appear to be close, but the activation energies are very different.

The reason for the large difference in the activation energies must therefore be sought within the framework of polar effects. According to a theoretical model by Shaik and Pross[6] there are three valence-bond configurations which contribute to the ground-state wave function for the reactive system D (≡ radical) + A (≡ alkene), namely DA, D^3A^*, and D^+A^- or D^-A^+. DA denotes the configuration where the radical is in its doublet state and the alkene is in its singlet ground state. DA is the principal configuration at the reaction coordinate value $-\infty$ (rc $= -\infty$) but becomes a $\sigma\sigma^*$ excited triplet state at rc $= +\infty$. In the D^3A^* configuration the alkene is in its lowest π triplet state; its energy decreases with increasing reaction coordinate value, and it becomes the main configuration at rc $= \infty$. At the intersection of these two configurations the transition state is located, and here, due to Coulombic interaction, the charge-transfer configuration D^+A^- or D^-A^+ also mixes in. For the CH_3/C_2H_4 system both D^+A^- and D^-A^+ lie at very high energy ($E(D^+A^-)$/eV $= 9.84 - (-1.78) = 11.62$ and $E(D^-A^+)$/eV $= 10.51 - 0.08 = 10.43$[47]) and therefore make little contribution to the transition state.

Table 4. Kinetic and Thermochemical Data for Selected Reactions $R^\bullet + C_2H_4 \rightarrow RCH_2CH_2^\bullet$ [a]

$R^\bullet$	A/cm^3 s^{-1}	E_a/kJ mol^{-1}	IP/eV	EA/eV	$\Delta_rH°$/kJ mol^{-1}
$(CH_3)_3Si$	1.2×10^{-12}	13	6.5	1.41	−105
$(CH_3)_3C$	2.6×10^{-13}	29.7	6.7	0.7	−75
CH_3	3.5×10^{-13}	30.8	9.84	0.08	−98
NH_2	3.3×10^{-14}	11.0	11.14	0.78	−87
OH	1×10^{-11}	0	13.0	1.8	−122

[a] The Arrhenius parameters were taken from the NIST Chemical Kinetics Database, ionization potentials and electron affinities were taken from ref 51, and the reaction enthalpies were estimated.[43]

For the Me_3Si/C_2H_4 system the situation is different. The ionization potential of Me_3Si is very much smaller (IP/eV = 6.5, calculated from $AP(Me_3Si^+ \leftarrow Me_3SiH)$/eV $= 10.5 \pm 0.1$,[48] $\Delta_fH°(Me_3Si) = 14$ kJ mol^{-1},[43] and $\Delta_fH°(Me_3SiH) = -163$ kJ mol^{-1} [43]), and the electron affinity is larger than the corresponding value of the CH_3 radical. (Actually, the electron affinity of Me_3Si is not known but it is expected to be only slightly larger than the electron affinity of SiH_3, whose value is known to be EA/eV = 1.41[49]). One then obtains the values $E(D^+A^-) = 8.28$ eV and $E(D^-A^+) \approx 9.1$ eV. The inequality $E(D^+A^-) < E(D^-A^+)$ qualifies the Me_3Si radical as a nucleophile. The energy of D^+A^- is low enough[50] to make a contribution to the ground-state wave function at the transition state, thereby lowering the barrier height. The dependence of the activation energy for radical addition to ethene on polar and enthalpic effects is illustrated in Table 4. The selected radicals range from nucleophilic and nonpolar to electrophilic.

On the basis of these considerations it is evident that the thermodynamic control cannot be responsible for the much larger rate constant of reaction 11 compared with that of reaction 25 and that the observed difference in behavior is due to polar effects. More quantitative statements will have to await the outcome of more experimental and, importantly, theoretical investigations.

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