familiarity and confidence in the technique, it should become possible to reexamine once again the possibility of working in buffered systems.

As a third possible reason, it should be pointed out that the derivation of eq 6 assumes the absence of enthalpy effects, the appearance of which would distort the sigmoidal shape and introduce an error whose magnitude is difficult to estimate.

It is, however, apparent from the studies that have been made to date that the technique of differential thermal analysis provides a sensitive tool for examining thermally induced order–disorder transitions occurring in solutions of biopolymers. While the present paper has been primarily concerned with the application of this technique to protein solutions, we have also observed and reported upon transitions in solutions of deoxyribonucleic acid.

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Relative Rates of Methylene Radical Reactions with Silicon–Hydrogen, Silicon–Deuterium, and Carbon–Hydrogen Bonds in the Methylsilane System[1a]

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Abstract: A study of the reactions of methylene radicals with methylsilane and methyltrideuteriosilane is reported. The reactions were studied by photolyses at 3660 Å of methylsilane–diazomethane, methylsilane–*n*-butane–diazomethane, methyltrideuteriosilane–diazomethane, and methyltrideuteriosilane–*n*-butane–diazomethane mixtures in the presence and absence of oxygen. Singlet methylene radicals were found to insert into the Si–H bonds 8.9 times faster than the C–H bonds of methylsilane, indicating that Si–H insertion is one of the fastest methylene radical reactions known. The isotope effect for Si–H insertion was determined to be 1.15 which is somewhat smaller than earlier measurements of C–H insertion isotope effects. Evidence for the decomposition of chemically activated dimethylsilane and ethylsilane produced by insertion at quite high pressures is presented.

Recently it has been shown by the gas-phase photolysis of diazomethane at 3660 Å in the presence of excess monosilane that methylene radicals insert into the Si–H bonds of monosilane and also abstract H atoms.[2] Previous work[3] on the liquid-phase photolysis of diazomethane in the presence of compounds containing Si–H bonds gave a higher yield of products resulting from the reaction of methylene radicals with Si–H bonds (presumably insertion although abstraction cannot be ruled out[2]) than with C–H bonds. Kramer and Wright found a minimum ratio of 100 for the ratio of Si–H/C–H "insertion" in ether solvent.[3]

A gas-phase study at high pressures of the reactions of methylene radicals with methylsilane should allow intramolecular comparisons to be made of the Si–H insertion and abstraction rates relative to C–H insertion. It should be possible to study the Si–H and C–H insertion reactions independent of abstraction by the addition of a suitable scavenger for the radicals produced by abstraction. Evidence for the chemical removal of doublet- and triplet-state radicals by oxygen is provided by a number of workers.[4,5] Previous studies of diazomethane and ketene photolysis systems indicate that in the presence of oxygen the C—H insertion and C=C addition reactions of excited singlet-state methylene radicals are not markedly altered, whereas the ground-state triplet methylene radical reaction products are efficiently scavenged.[6–9] Thus, one might expect that the photolysis of diazomethane–methylsilane mixtures in the presence of oxygen would yield volatile products resulting only from the insertion of singlet methylene radicals into the Si–H and C–H bonds of methylsilane. The products resulting from the radicals produced by abstraction and scavenged by oxygen would presumably be of higher molecular weight.[6–9] A comparison of Si—H insertion rates to those for C=C addition and C—H insertion[10,11] is of particular interest.

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[1] (a) This work was supported in part by the NSF under Grant No. GP-6124 and in part by PRF under Grant No. 511-G2. (b) New Mexico State University Physical Science Laboratory Predoctoral Fellow.

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Isotope effects for singlet methylene radical insertion into C–H and C–D bonds have been reported.[12–15] The analogous isotope effects for Si–H and Si–D insertion should result from a study of the photolyses of diazomethane–methyltrideuteriosilane mixtures in the presence of oxygen by comparison to a similar study of the light system.

The addition of *n*-butane to the reaction mixtures in which oxygen is also present should provide an internal comparison of the rates of both Si–H and C–H insertion with methylsilane to the rate of C–H insertion with *n*-butane. The use of *n*-butane in the methyltrideuteriosilane system should represent an internal standard from which primary and secondary isotope effects for insertion into the Si–H and C–H bonds, respectively, of the methylsilane molecule can be determined. The use of a *n*-butane internal standard also provides a method of determining the pressure above which all of the "hot" insertion products are collisionally stabilized.[16]

Experimental Section

Materials. The preparation and storage of diazomethane was the same as previously described.[2]

Methylsilane was prepared *in vacuo* by the reaction of methyltrichlorosilane with $LiAlH_4$ in dibutyl ether.[17] Gas chromatographic purification and analysis indicated no impurities. Methyltrideuteriosilane was prepared in a similar manner using $LiAlD_4$. The ether solvent was dried over $LiAlH_4$ prior to its use. The infrared spectrum of methyltrideuteriosilane as well as that of methylsilane compared well with those in the literature.[18] Matheson lecture-bottle *n*-butane was purified by gas chromatography and analysis showed it to be free of impurities.

Apparatus and Procedure. All gas handling was performed in a conventional vacuum system. A Toepler pump was used to measure and transfer the noncondensables to a liquid nitrogen-cooled silica gel tube for further analysis. The photolysis lamp and filter assembly were as previously described.[2]

Mixtures of methylsilane–diazomethane (usually 10:1) were photolyzed for times varying from 1 to 4 hr with and without added oxygen. Methyltrideuteriosilane was also studied in the presence and absence of added oxygen.

Mixtures of methylsilane and *n*-butane with diazomethane (10:1, mix/DM) were photolyzed with and without oxygen. The volume of the reactors varied from 1.6 to 16.5 cc. No surface effects were observed by varying reactor volumes at the same pressure.

The reactor loading procedure involved first trapping the measured amounts of reactants in a U tube at $-196°$ and secondly distilling these reactants from $-78°$ to the reactor cooled to $-196°$. This procedure ensured that the reactors contained no mercury.

Analysis. Gas–liquid partition chromatography (glpc) was used for the quantitative analysis of all product condensables at $-196°$. The analytical column consisted of a 25-ft polyethylene column packed with 30% dibutyl phthalate on Chromosorb (80–100) and operated at 25°. No decomposition of reaction products occurred on this column. A mixture of known composition, and similar in relative magnitudes to a typical reaction mixture, was used to calibrate this analytical column. Later, a 4-ft extension consisting of didecyl phthalate on Chromosorb was added to achieve a more efficient separation between the products, dimethylsilane and ethylsilane. Since ethane and ethylene had the same retention time on the DBP column, a separate column consisting of 10 ft of $AgNO_3$, 40 ft of dinonyl phthalate, and a 1-ft section of Ascarite (to remove CO_2) was used for ethane analyses. A sample of diazomethane passed through this column showed only negligible amounts of ethane impurity.

Noncondensables were analyzed on a 9-ft column containing 5-Å molecular sieves and operated at 25°. Separations on this column were achieved for H_2, O_2, N_2, and CH_4. Helium served as a carrier gas for all columns.

Results

Products. The major products found in all cases were dimethylsilane (DMS) and ethylsilane (ES). Isopentane and *n*-pentane were major products for those systems with added *n*-butane (B). Minor amounts of ethane, methane, propane, hydrogen, methyldisilane, and possibly 1,2-dimethyldisilane and methylethylsilane were identified as products in the absence of oxygen but were not quantitatively determined. All products were identified by ir spectra and glpc retention times compared with those of known samples and ir spectra given in the literature.[19] Upon addition of oxygen to the reaction mixtures all of the above minor products vanished except hydrogen. It was found that a slow dark reaction occurred between methylsilane (MS) and oxygen to produce hydrogen as the only major volatile product. Although increasing pressures of added oxygen and increasing time exposed to oxygen produced increasing amounts of hydrogen, no further changes in the proportions of the other major products occurred above those observed for smaller additions of oxygen. It was concluded that the dark reaction with oxygen neither produced nor destroyed the main products of interest. In all experiments with added oxygen reported here, the oxygen was removed after a 3-hr photolysis time. After several photolyses with added oxygen, a white solid deposit was observed in the reactors. This silicon-containing solid was probably a polymer resulting from oxygen-scavenged radicals.

Light Systems. The DMS/ES ratios as a function of the pressure of added oxygen for the 3660-Å photolysis of MS–DM mixtures (~10:1) and MS–B–DM mixtures (~5:5:1 and ~7.5:2.5:1) are given in Figure 1 at various total pressures of MS + B + DM. It is seen from Figure 1 that at any given total pressure the DMS/ES ratio drops markedly upon addition of the first few per cent of oxygen and remains relatively constant upon further additions of oxygen up to quite large amounts. Variations in the MS/B ratio or the DM concentration had no effect on the DMS/ES results in the *presence* of oxygen. In the *absence* of oxygen an increase in the DM concentration caused a small decrease in the DMS/ES ratio and *vice versa*. The constant results in the presence of oxygen given in Figure 1 were averaged at each pressure and are summarized along with those in the absence of oxygen in Table I. The results in Table I show a decrease in the value of DMS/ES with increasing pressure up to 200 cm with no further change at 400 cm. The small decrease shown in going from 200 to 400 cm for the results in the absence of oxygen is probably within experimental error.

The DMS/total pentane (TP) ratios as a function of the pressure of added oxygen for various total pressures of MS + B + DM are shown in Figure 2. The variation with oxygen pressure is qualitatively similar to that found for the DMS/ES ratio. The constant results

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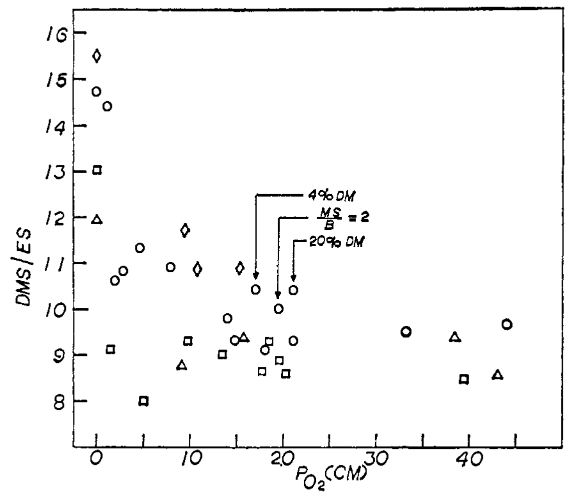

Figure 1. Variation of dimethylsilane/ethylsilane product ratios with pressure of added oxygen at various total pressures for the light system. The zero oxygen pressure values represent averages, in most cases, of several experiments: ◇, 25 cm with MS/B ≃ 1.0; ○, 50 cm with MS/B ≃ 1.0; □, 200 cm with no added *n*-butane; △, 400 cm with MS/B ≃ 3.0. Except for those data marked differently, the reactant/diazomethane ratio was relatively constant at approximately 10:1.

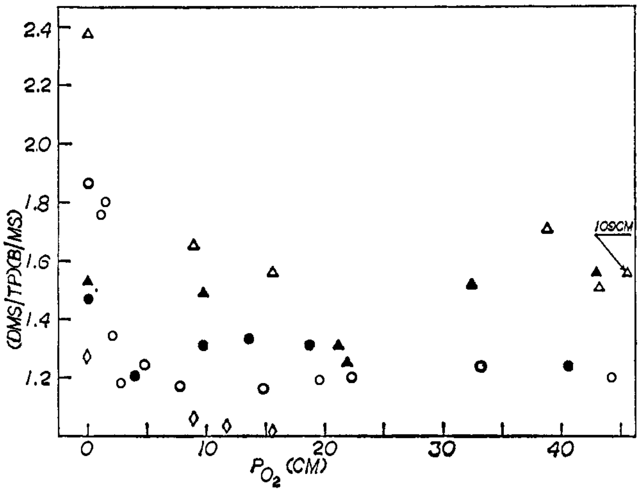

Figure 2. Variation of dimethylsilane/total pentane ratios, corrected to a *n*-butane/methylsilane ratio of 1, with pressure of added oxygen at various total pressures: open symbols for the CH_3SiH_3 system and solid symbols for the CH_3SiD_3 system. Total pressures: △, ▲, 400 cm; ○, ●, 50 cm; ◇, 25 cm.

with increasing oxygen pressure in Figure 2 were averaged at each total pressure giving the results in Table II. The results in Table II indicate that DMS decreases relative to TP as the total pressure decreases both in the presence and absence of oxygen.

Table I. DMS/ES at Various Total Pressures

Pressure, cm	Light system (CH_3SiH_3) Oxygen	No oxygen	Heavy system (CH_3SiD_3) Oxygen	No oxygen
25	11.1 ± 0.4	15.5		
50	10.0 ± 0.6	14.7 ± 0.2	8.6 ± 0.2	8.9 ± 0.2
200	8.8 ± 0.3	13.0 ± 0.4	7.5 ± 0.3	7.9 ± 0.7
400	9.0 ± 0.4	12.0 ± 0.2	7.8 ± 0.2	8.1 ± 0.2
Average of 200–400 cm	8.9 ± 0.3	12.6 ± 0.6	7.7 ± 0.3	8.0 ± 0.4

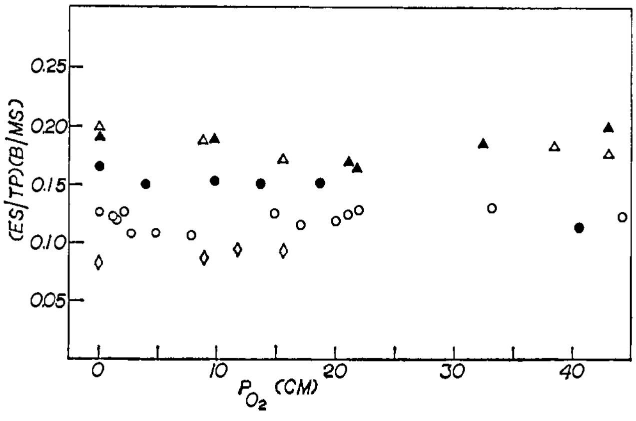

Figure 3. Variation of ethylsilane/total pentane ratios, corrected to a *n*-butane/methylsilane ratio of 1, with pressure of added oxygen at various total pressures: open symbols for the CH_3SiH_3 system, solid symbols for the CH_3SiD_3 system. Total pressures: △, ▲, 400 cm; ○, ●, 50 cm; ◇, 25 cm.

The ES/TP ratios obtained in the same experiments as those in Figure 2 are given in Figure 3. An important observation from Figure 3 is that the ES/TP ratio is virtually unaffected by the addition of oxygen. The results in Figure 3 were averaged at each total pressure with and without added oxygen and are summarized in Table III. The relative decrease observed in the ES/TP ratio with decreasing total pressure is greater than that observed for the DMS/TP ratio in Table II.

Table II. DMS/TP · B/MS Variation with Total Pressure

Pressure, cm	Light system (CH_3SiH_3) Oxygen	No oxygen	Heavy system (CH_3SiD_3) Oxygen	No oxygen
400	1.60 ± 0.06	2.38 ± 0.02	1.43 ± 0.12	1.53 ± 0.03
50	1.20 ± 0.02	1.88 ± 0.04	1.26 ± 0.05	1.43 ± 0.03
25	1.03 ± 0.03	1.23		

Table III. ES/TP · B/MS Variation with Total Pressure

Pressure, cm	Light system (CH_3SiH_3) Oxygen	No oxygen	Heavy system (CH_3SiD_3) Oxygen	No oxygen
400	0.179 ± 0.01	0.20	0.181 ± 0.01	0.19
50	0.120 ± 0.007	0.128 ± 0.003	0.148 ± 0.004	0.160
25	0.092 ± 0.003	0.083		

Heavy Systems. The results obtained from substitution of methyltrideuteriosilane (CH_3SiD_3) for methylsilane gave the $CH_2DSiD_2CH_3$(DMS)/$CH_3CH_2SiD_3$(ES) ratios as a function of the pressure of added oxygen at various total pressures of MS + DM and MS + B + DM shown in Figure 4. The results in Figure 4 show that the DMS/ES ratio, at various total pressures, decreases only slightly upon the addition of small amounts of oxygen and remains constant upon further addition of oxygen. As in the light system, no effect on the DMS/ES ratio in the presence of oxygen was observed for variations in the MS/B ratio or DM concentrations. The constant results in the presence of oxygen shown in Figure 4 were averaged at each total pressure and are summarized along with the results in the absence of oxygen in Table I. The data in Table I show a slight decrease in the value of DMS/ES with increasing pressure up to 200 cm with no further change at 400 cm. As in the light system, the small change (in this case an increase in the DMS/ES ratio) in going from 200 to 400 cm is within experimental error. Table I clearly shows a dramatic decrease in the DMS/ES ratio at a particular total pressure for the light system upon addition of oxygen compared to a slight decrease in this ratio for the heavy system upon addition of oxygen.

The DMS/TP ratios as a function of the pressure of added oxygen for the two total pressures of MS + B + DM for the heavy system are shown in Figure 2. Again, the variation with oxygen pressure is qualitatively the same as the DMS/ES ratio discussed above. The constant results obtained in the presence of oxygen at each total pressure in Figure 2 were averaged and are shown in Table II. The results in Table II show that DMS for the heavy system decreases relative to TP as the total pressure decreases both in the presence and absence of oxygen. The results in Table II indicate that the DMS is decreased considerably less by the addition of oxygen at a particular total pressure for the heavy system than for the light system.

The ES/TP ratios obtained in the same experiments as those in Figure 2 are shown in Figure 3. This ratio for the heavy system remains virtually unchanged by the addition of oxygen for the two total pressures studied. A summary of these results is given in Table III. The percentage decrease in the ES/TP ratio with decreasing pressure is greater than that observed for the DMS/TP ratio in Table II.

Discussion

The following reaction mechanism offers a reasonable explanation of the results of this study

$$CH_2N_2 \xrightarrow{3660\ \text{Å}} CH_2 + N_2 \tag{1}$$

$$CH_2 + CH_3SiH_3 \xrightarrow{k_2} (CH_3)_2SiH_2^* \tag{2}$$

$$\xrightarrow{k_3} CH_3CH_2SiH_3^* \tag{3}$$

$$\xrightarrow{k_4} CH_3 + CH_3SiH_2 \tag{4}$$

$$(CH_3)_2SiH_2^* \xrightarrow{k_5} \text{decomposition fragments} \tag{5}$$

$$\xrightarrow{\omega} (CH_3)_2SiH_2 \tag{6}$$

$$CH_3CH_2SiH_3^* \xrightarrow{k_7} \text{decomposition fragments} \tag{7}$$

$$\xrightarrow{\omega} CH_3CH_2SiH_3 \tag{8}$$

$$CH_3 + CH_3SiH_2 \longrightarrow (CH_3)_2SiH_2 \tag{9}$$

$$CH_3 + CH_3SiH_3 \longrightarrow CH_4 + CH_3SiH_2 \tag{10}$$

$$2CH_3 \longrightarrow C_2H_6 \tag{11}$$

$$2CH_3SiH_2 \longrightarrow (CH_3SiH_2)_2 \tag{12}$$

$$CH_3 + CH_2N_2 \longrightarrow CH_3CH_2 + N_2 \tag{13}$$

$$CH_3 + CH_3CH_2 \longrightarrow C_3H_8 \tag{14}$$

$$CH_3CH_2 + CH_3SiH_2 \longrightarrow CH_3CH_2SiH_2CH_3 \tag{15}$$

$$CH_2 + n\text{-}C_4H_{10} \xrightarrow{k_{16}} n\text{-pentane}^* \xrightarrow{\omega} n\text{-pentane} \tag{16}$$

$$\xrightarrow{k_{17}} \text{isopentane}^* \xrightarrow{\omega} \text{isopentane} \tag{17}$$

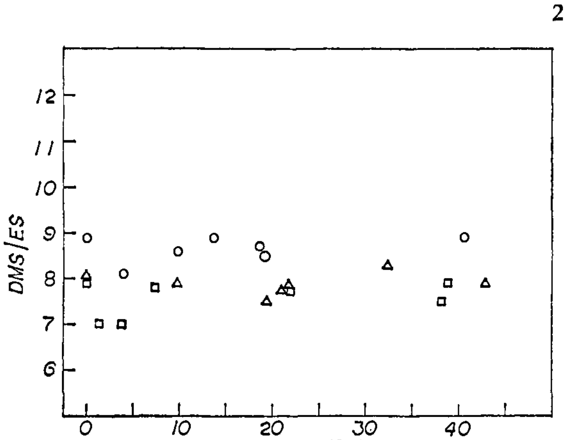

Figure 4. Variation of dimethylsilane/ethylsilane product ratios with pressure of added oxygen at various total pressures for the heavy system: ○, 50 cm; □, 200 cm; △, 400 cm.

where an asterisk represents a species with internal energy in excess of that required for a decomposition reaction, and ω is the collisional stabilization rate constant.

Although some C–H abstraction[10,11] probably occurs in this system, the results of this study indicate that its amount is small compared to the other primary reactions, and, consequently for the sake of brevity, C–H abstraction by methylene radicals has not been included in the mechanism. In the absence of oxygen, the ES/TP ratios at 400 cm differ for the heavy and light systems (Table III) by only a small amount which lends further support to the deduction that C–H abstraction from methylsilane is small.

Reaction 13 which has been proposed previously[11b,20] was included to explain the formation of propane and the variation of the DMS/ES ratio with DM concentration in the absence of oxygen.

In the presence of oxygen, the ES formed in reaction 3 could result from either C–H or C–Si insertion. Earlier results for the unscavenged SiH_4–C_2H_6 system[21] gave a Si–H/C–H insertion product ratio of ~15 which is in fair agreement wiht the Si–H/C–H insertion product ratio (DMS/ES) found in the present unscavenged MS system (range 12–15). Products resulting from C–C insertion in a cyclic hydrocarbon system[22] were very minor compared to the C–H insertion products. From the above evidence, and the fact that the amount of ES is *ca.* one-ninth that of DMS in the presence of oxygen, it can be concluded that C–Si insertion must be quite small and that the ratio of DMS/ES very nearly represents the Si–H/C–H insertion ratio.

Si–H Insertion Rate. In the presence of sufficient oxygen to scavenge radicals the only sources of DMS and ES are the Si–H (reaction 2) and C–H (reaction 3) insertion reactions, respectively, of singlet methylene radicals followed by collisional stabilization (reactions 6 and 8) of the "hot" molecules initially formed. The pressure dependence of the DMS/TP, ES/TP, and DMS/ES ratios found in this study indicate that "hot" DMS and ES are initially formed and that these molecules decompose (reactions 5 and 7) appreciably at pressures

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lower than ~200 cm. The "hot" isopentane and *n*-pentane molecules formed by singlet methylene radical insertion into the C–H bonds of *n*-butane (reactions 16 and 17) do not decompose at the pressures of this study.[16] The DMS/ES ratios found at pressures of 200 cm and above and in the presence of oxygen thus represent the ratio of k_2/k_3 which from Table I has a value of 8.9 ± 0.3. This intramolecular comparison of insertion rates shows that methylene radicals insert into Si–H bonds as fast or faster than methylene radicals add to C=C in hydrocarbon systems.[10]

Isotope Effect for Si–H Insertion. The proposed reaction mechanism for the heavy system is the same as that for the light system (reactions 2–15). The DMS/ES ratio for the heavy system in the presence of oxygen and at pressures above 200 cm was found to be 7.7 ± 0.3 which represents k_2/k_3 for CH_3SiD_3 as reactant. A ratio of the DMS/ES ratio for the light system to the DMS/ES ratio for the heavy system gives the isotope effect for the Si–H insertion, $k_2(H)/k_2(D)$, of 1.15. That this value represents a Si–H/Si–D insertion isotope effect is supported by the fact that the ES/TP ratios in the presence of oxygen at 400 cm in Table III for both the light and heavy systems are virtually the same; *i.e.*, no secondary isotope effect was observed for C–H insertion in methylsilane. At a lower pressure (50 cm), a larger difference exists between these values which may be explained by differences in "hot" molecule decomposition rates.

The isotope effect (1.15) for Si–H insertion found here is smaller than that previously reported for C–H insertion,[12–15] which is consistent with a similar activated complex to that for C–H insertion considering the lower Si–H bond energy, lower Si–H stretching vibrational frequency, and larger Si–H bond length than the corresponding quantities for C–H bonds.

H-Atom Abstraction from Silicon. The considerably larger amount of DMS observed in the nonscavenged light system compared to the scavenged system (Tables I and II) is explained by methylene radical abstraction of an H atom from silicon (reaction 4) followed by recombination to give DMS (reaction 9). Only minor amounts of ES or pentane arise from an abstraction mechanism. Since other minor products were not quantitatively determined, it is not possible to determine the exact proportion of abstraction. Based only on the DMS resulting from abstraction, a minimum value for $k_4/(k_2 + k_3)$ is $(12.6 - 8.9)/(1 + 8.9) = 0.37$; *i.e.*, at least 27% of the primary reaction of methylene radicals with methylsilane under these conditions is abstraction of an H atom from silicon. Whether abstraction is due to ground-state triplet or excited-state singlet methylene radicals cannot be determined from the present results.

The difference between the amounts of DMS for the scavenged and nonscavenged heavy system is considerably less than that for the light system, suggesting a much larger isotope effect for abstraction than insertion as might be expected. A semiquantitative value for the magnitude of the abstraction isotope effect from Table I is $(12.6 - 8.9)/(8.0 - 7.7) = 12$, or, from Table II, $(2.38 - 1.60)/(1.53 - 1.43) = 8$ with very large probable errors. These calculations are based on the reasonable assumption that the same fraction of the radicals produced by abstraction recombine (reaction 9) to give DMS in both the light and heavy systems. A value of 8 or 12 for the abstraction isotope effect is consistent with a 1–2-kcal/mole activation energy difference.

Although a large isotope effect for abstraction, as discussed above, is our preferred explanation for the large effect of oxygen in the light compared to the heavy systems, it should be pointed out that recent evidence suggests that some vibrationally excited radicals (the methylene radicals in the present work are probably not vibrationally thermalized) abstract H atoms from hydrocarbons faster than thermalized radicals and exhibit no isotope effect.[23]

Decomposition of DMS* and ES*. The "hot" DMS and ES molecules formed by insertion contain enough energy to decompose (reactions 5 and 7) at the lower pressures of this study by a number of paths which have not been specified in the mechanism. It is interesting to note that even though the present results were obtained at relatively high pressures there is noticeable decomposition of DMS and ES which is evident from the decrease in the DMS/TP and ES/TP ratios upon decreasing the total pressure below ~200 cm. The amount of ES decomposition with decreasing pressure (Table III) is larger than the amount of DMS decomposition (Table II) and together these decreases are observed in Table I as an increasing DMS/ES ratio with decreasing pressure. Apparently there are low activation energy decomposition paths for the chemically activated DMS and ES resulting in decomposition at relatively high pressures. Less decomposition of heavy DMS and ES was found to take place (Tables I–III) in the same pressure region which is expected from consideration of the primary and secondary isotope effects for decomposition of chemically activated species.[13] A further study of these decomposition reactions at lower pressures is presently being conducted. From this study, rate constants for the unimolecular decomposition of DMS and ES by various paths hopefully can be determined.

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