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Photolysis of Hydrogen Sulfide in the Presence of Dimethylsilane

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The photolysis of H_2S in the presence of $(CH_3)_2SiD_2$ leads to the formation of large yields of D_2. The apparent exchange reaction is due to a photochain sequence involving $(CH_3)_2SiDSH$ and $(CH_3)_2SiDS\cdot$ as reactive intermediates. The transient presence of the silylthiol was indeed confirmed by flash photolysis experiments using kinetic mass spectrometry and kinetic absorption spectroscopy. Abstraction of hydrogen from the methyl groups by H atoms and the direct exchange reaction, $H + (CH_3)_2SiD_2 \rightarrow (CH_3)_2SiDH + D$, are unimportant at room temperature when the H atom possesses translational energy in the 0 to 35 kcal/mol interval.

Several studies have been reported in recent years on the reactions of alkyl radicals and hydrogen atoms with silicon hydrides.[1-5] For the gas-phase reactions of H and D atoms, absolute rate constants have been measured with SiH_4, Si_2H_6, CH_3SiH_3, $(CH_3)_2SiH_2$, and $(CH_3)_3SiH$ as substrates. In the case of the latter molecule the Arrhenius parameters have also been determined. Owing to the lower activation energy requirements of the reactions, these rate constants are generally higher than those of the reactions of the corresponding hydrocarbon molecules, even in cases where the H atoms contain substantial excess translational energy. Apart from the disilane reaction the only important step occurring in these systems is selective hydrogen atom abstraction from the silicon moiety. With disilane, parallel to abstraction, a displacement type reaction, $H + Si_2H_6 \rightarrow SiH_4 + SiH_3$, also takes place at a rate comparable to abstraction.

The present study was undertaken in order to elucidate two outstanding questions related to the H atoms + silicon hydride systems. Specifically these were (a) the nature and extent of the exchange reaction, $H + D\text{-}SiR_3 \rightarrow D + H\text{-}SiR_3$, as a function of excess translational energy in the H atoms, and (b) the role and nature of long-lived, non-stoichiometric complexes in the overall reactions.

Experimental Section

All studies were carried out under static conditions using standard high-vacuum techniques. The apparatus was free of stopcock grease for all runs except those done with CH_2O. A cylindrical quartz reaction cell, 36 mm in diameter and 150 mm in length with a cold finger, was used. Its volume was 166 cc.

The cadmium lamp used was Gates M 12-S and the medium-pressure mercury lamp was Hanovia Type 30620. Pyrex, Vycor 791, Corex D, as well as 3130-Å interference filters were used at various stages.

$(CH_3)_2SiH_2$ (Peninsular) and $(CH_3)_2SiD_2$ (Merck) were purified prior to each run by low-temperature distillation at −130° (*n*-pentane slush). The extent of deuteration of $(CH_3)_2SiD_2$ on the silicon atom was determined to be at least 98% by 100-MHz nmr using the appearance of ^{13}C satellite peaks as reference. $(CH_3)_3SiD$ (Merck) was found to be at least 98% deuterated on the silicon atom by the same method. H_2S (Matheson) and D_2S (Merck) were distilled prior to each run. Paraformaldehyde (Shawinigan) was heated to form CH_2O vapor by a hand torch.

The reaction product, noncondensable at −196°, was removed by a Toepler pump and analyzed by a thermal conductivity gas chromatograph on a molecular sieve 13X column or by mass spectrometry. The condensable fraction was analyzed on a silicon oil DC 200 column by a flame ionization gas chromatograph.

Isotopic analysis of the hydrogen product was achieved in an MS 10 mass spectrometer and that of the condensable fraction in an MS 12 instrument coupled to a gas chromatograph.

The flash photolysis apparatus using kinetic optical spectroscopy[6] and kinetic mass spectrometry[7] has been described before.

The uv spectra were recorded on a Cary 14 spectrometer.

Results

The source of H (D) atoms used in the present study was the photolysis of H_2S (D_2S) and CH_2O.

Hydrogen sulfide exhibits a continuum in the ultraviolet region[8] extending from 2700 to 1850 Å with maximum absorption at about 2000 Å. The HS-H bond strength is approximately 90 ± 2 kcal/mol[9] and at the 2288-Å cadmium resonance line the excess energy, carried mainly by the H atom, would be about 35 kcal/mol.[10] The extinction coefficient is small, 170 M^{-1} cm^{-1} at 2288 Å, but since simple silicon hydrides do not absorb at this wavelength,[11] this was not considered a handicap.

The primary step in the photolysis of H_2S is the free-radical mode of decomposition[12]

$$H_2S + h\nu \longrightarrow H^* + HS \qquad (1)$$

where the asterisk signifies translational excitation. This is followed by the sequence

$$H^* + H_2S \longrightarrow H_2 + SH \qquad (2)$$

$$H^* + H_2S \longrightarrow H + H_2S \qquad (3)$$

$$2SH \longrightarrow H_2 + S_2 \qquad (4)$$

$$2SH \longrightarrow H_2S + S(^3P) \qquad (5)$$

$$2SH + M \longrightarrow H_2S_2 + M \qquad (6)$$

with the predominant step removing SH being reaction 5.[13] The S and S_2 species disappear by subsequent polymerization.

Previous studies have shown that hydrogen abstraction from methylsilanes occurs selectively from the silicon moiety.[14] In order to examine the effect of excess translational energy in the H atoms on the competition of Si-H *vs.* C-H abstraction, D_2S was photolyzed in the presence of $(CH_3)_2SiD_2$.

1. The D_2S-$(CH_3)_2SiD_2$ System. In the photolysis of pure hydrogen sulfide the sulfur formed in reactions 4 and 5 was deposited in the form of a white film of elemental sulfur on the walls of the reaction cell. Addition of the silane to the system prevented the deposition of sulfur. Therefore, it would appear that the DS radical is removed by combination with the dimethylsilyl radical

$$(CH_3)_2SiD\cdot + DS \longrightarrow (CH_3)_2SiDSD \qquad (7)$$

It should be noted that the alternative abstraction reaction

$$(CH_3)_2SiD_2 + DS \longrightarrow (CH_3)_2SiD\cdot + D_2S \qquad (8)$$

is endothermic and cannot compete with steps 4-7.

The retrievable products of the reaction were hydrogen, tetramethyldisilane, and tetramethyldisiloxane. Hydrogen was measured quantitatively and analyzed for isotopic distribution. The results obtained using the 2288-Å Cd resonance line are presented in Table I. Evidently the D_2S used contained a substantial amount of isotopic impurity as indicated by the high yield of HD. Upon addition of $(CH_3)_2SiD_2$ the HD showed a small increase. One may be tempted to assign this to the contribution of C-H bond abstraction

$$D + (CH_3)_2SiD_2 \longrightarrow HD + \cdot CH_2SiD_2CH_3 \qquad (9)$$

and the large yields of D_2 to the simultaneous, competing reaction

$$D + (CH_3)_2SiD_2 \longrightarrow D_2 + (CH_3)_2SiD\cdot \qquad (10)$$

This, however, is not the case as it will be shown below.

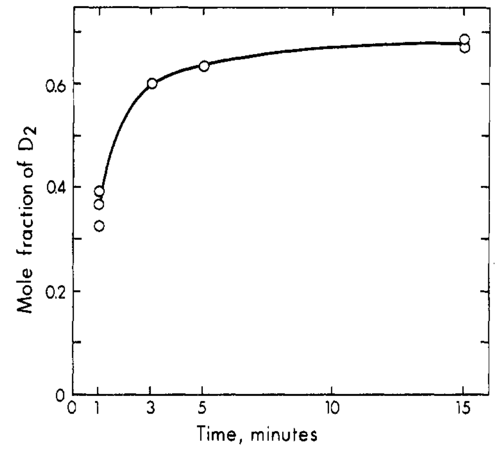

Figure 1. Mole fraction of D_2 as a function of exposure time from the H_2S-$(CH_3)_2SiD_2$ system.

Tetramethyldisilane forms from the combination of dimethylsilyl radicals

$$2(CH_3)_2SiD\cdot \longrightarrow ((CH_3)_2SiD)_2 \qquad (11)$$

and tetramethyldisiloxane presumably *via* the condensation and exchange reactions of dimethylsilylmercaptan

$$2(CH_3)_2SiDSD \longrightarrow (CH_3)_2SiDSSiD(CH_3)_2 + D_2S \qquad (12)$$

$$(CH_3)_2SiDSSiD(CH_3)_2 + H_2O \longrightarrow (CH_3)_2SiDOSiD(CH_3)_2 + H_2S \qquad (13)$$

The latter reaction may occur on the glass surface. Thus, the appearance of dimethyldisiloxane is attributed to the reaction sequence 7, 12, 13.

2. The H_2S-$(CH_3)_2SiD_2$ System. Because of its high isotopic impurity content the D_2S in further studies was replaced by H_2S. At high ratios of silane to H_2S the product ratio, HD/H_2, is expected to be a representative measure of the relative rates of reactions 9 and 10. The results listed in Table II, however, show abnormally high yields of the apparent exchange product D_2. The reaction yielding D_2 proved to be a typical photoprocess, the rate of which was independent of inert gas pressure (CO_2) up to a 100-fold excess. For a true exchange reaction this was an unusual kinetic feature, since the efficiency of exchange reactions in general is dependent on the translational energy of the exchanging atom.[15] Woolley and Cvetanovic[16] reported that in the presence of a 100-fold excess of carbon dioxide the initially "hot" hydrogen atoms are effectively thermalized, yet the rate of D_2 production was unaffected. Therefore, a time study was made of the reaction to determine whether D_2 is indeed a primary reaction product or whether it arises from some unforeseen complexity of the reaction system.

3. The Effect of Exposure Time on the H_2S-$(CH_3)_2SiD_2$ System. Hydrogen sulfide and dimethylsilane-d_2 mixtures at a constant ratio of 6:100 were photolyzed for various lengths of time and the isotopic composition of the hydrogen product determined. The results are given in Table III and plotted in Figure 1. It is seen that the fractional yield of D_2 is markedly time dependent and tends to fall off with decreasing time of exposure, suggesting that D_2 is a secondary product of the reaction.

In order to assess the possible role of sulfur compounds in the mode of production of D_2, it appeared desirable to examine the H + $(CH_3)_2SiD_2$ reaction in a sulfur free system. To this end, formaldehyde was photolyzed in the presence of $(CH_3)_2SiD_2$.

TABLE I: Isotopic Composition of Hydrogen from the D_2S-$(CH_3)_2SiD_2$ System[a]

$P(D_2S)$, Torr	P(DMS-d_2),[b] Torr	Exposure time, min	Mole fraction of H_2	HD	D_2	Total, μmol
0.0	97.5	15				0.00
6.23	0	15	0.0203	0.118	0.862	5.49
5.83	100.8	15	0.0212	0.138	0.841	5.86
5.70	99.9	15	0.0221	0.138	0.844	4.69
5.40	99.9	15	0.0199	0.135	0.845	4.65

[a] λ = 2288 Å. [b] Dimethylsilane-d_2.

TABLE II: Isotopic Composition of Hydrogen from the H_2S-$(CH_3)_2SiD_2$ System[a]

$P(H_2S)$, Torr	P(DMS-d_2),[b] Torr	Exposure time, min	Mole fraction of H_2	HD	D_2	Total, μmol
2.74	101.5	5	0.0401	0.223	0.736	1.33
4.40	102.5	5	0.0516	0.275	0.674	1.68
8.40	101.9	5	0.0734	0.326	0.601	2.52
12.60	101.9	5	0.106	0.373	0.521	3.39
17.40	101.8	5	0.162	0.433	0.405	3.18
23.40	104.3	5	0.241	0.455	0.305	3.39
20.30	99.4	5	0.217	0.454	0.328	3.70
14.20	104.2	5	0.125	0.393	0.483	3.06
20.0	20.9	5	0.626	0.340	0.0344	2.34
20.0	61.5	5	0.327	0.495	0.178	2.26
20.0	12.1	5	0.771	0.216	0.0128	1.76
20.0	15.3	5	0.749	0.234	0.0172	2.76
7.13	99.9	15	0.0444	0.262	0.694	4.86[c]
0.41	11.2	15	0.0509	0.260	0.689	1.17[c]

[a] λ = 2288 Å. [b] Dimethylsilane-d_2. [c] 1000 Torr of CO_2 added.

TABLE III: Isotopic Composition of Hydrogen as a Function of Exposure Time from the H_2S-$(CH_3)_2SiD_2$ System[a]

$P(H_2S)$, Torr	P(DMS-d_2),[b] Torr	Exposure time, min	Mole fraction of H_2	HD	D_2	Total, μmol
6.03	99.4	15	0.0462	0.268	0.686	5.78
6.74	100.3	15	0.0481	0.280	0.672	6.04
6.40	102.0	5	0.0625	0.301	0.638	2.10
6.40	103.1	3	0.0725	0.326	0.602	1.43
6.30	105.0	1	0.200	0.477	0.324	0.278
6.60	101.5	1	0.164	0.443	0.393	0.439
6.70	103.2	1	0.167	0.468	0.366	0.354

[a] λ = 2288 Å. [b] Dimethylsilane-d_2.

4. The CH_2O-$(CH_3)_2SiD_2$ System. The major primary step in the photolysis of formaldehyde at 3261 and 2288 Å is carbon-hydrogen bond cleavage[17]

$$CH_2O + h\nu \longrightarrow CHO + H \qquad (14)$$

At the longer wavelength the reaction is thermoneutral and at the shorter wavelength the excess energy, expected to be carried largely by the H atoms, is about the same as that from the photolysis of H_2S, ~35 kcal/mol.

The photolysis results are summarized in Table IV. It is seen that D_2 is not formed in the 3261-Å photolysis and only small amounts were found in the unfiltered light photolysis. Hence the direct exchange

$$H + (CH_3)_2SiD_2 \longrightarrow (CH_3)_2SiDH + D \qquad (15)$$

can be definitely ruled out and silylthiol or silyl thioether must be responsible for the large yields of D_2 in the H_2S photolysis.

The role of sulfur compounds in the system was further investigated by producing $(CH_3)_2SiDSD$ *via* the insertion reaction of $S(^1D_2)$ atoms, from the *in situ* photolysis of COS, into the Si-D bonds of $(CH_3)_2SiD_2$.

5. The Photolysis of COS in the Presence of $(CH_3)_2SiD_2$. The photolysis of COS and the reaction of $S(^1D_2)$ atoms with silicon hydrides have been described in the literature. The relevant reactions involved in this system are[18,19]

$$COS + h\nu \longrightarrow CO + S(^1D_2) \qquad (16)$$

$$S(^1D_2) + (CH_3)_2SiD_2 \longrightarrow (CH_3)_2SiDSD^* \qquad (17)$$

$$(CH_3)_2SiDSD^* \longrightarrow D_2,\ H_2,\ HD,\ H,\ D \qquad (18)$$

$$(CH_3)_2SiDSD^* + M \longrightarrow (CH_3)_2SiDSD + M \qquad (19)$$

$$(CH_3)_2SiDSD + h\nu \longrightarrow (CH_3)_2SiDS\cdot + D \qquad (20)$$

$$D + (CH_3)_2SiD_2 \longrightarrow D_2 + (CH_3)_2SiD\cdot \qquad (21)$$

$$H + (CH_3)_2SiD_2 \longrightarrow HD + (CH_3)_2SiD\cdot \qquad (22)$$

The major retrievable condensable product was tetramethyldisiloxane and the noncondensable fraction contained a substantial yield of hydrogen. The isotopic composition of the hydrogen was determined in two separate experiments and the results are reported in Table V. Apparently, photolysis of the mercaptan is facile and the extinction coefficient must be much higher than that of carbonyl sulfide or hydrogen sulfide.

Next, it remained to be shown that the primary step in the photolysis of silylthiol is indeed reaction 20 rather than

TABLE IV: Isotopic Composition of Hydrogen from the CH_2O-$(CH_3)_2SiD_2$ System

$P(CH_2O)$, Torr	P(DMS-d_2),[a] Torr	Exposure time, min	Mole fraction of H_2	HD	D_2	Total, μmol	λ, Å
9.4	100.0	5	0.646	0.329	0.0252	1.17	2288, 3261
15.6	104.0	10	0.315	0.685	0.0000	0.216	3261
26.5	107.8	30	0.495	0.505	0.0000	0.400	3261

[a] Dimethylsilane-d_2.

TABLE V: Isotopic Composition of Hydrogen from the COS-$(CH_3)_2SiD_2$ System[a]

P(COS), Torr	P(DMS-d_2),[b] Torr	Mole fraction of H_2	HD	D_2	Exposure time, min	Total, μmol
10.3	102.0	0.0534	0.144	0.803	5	1.68
1.34	100.5	0.0802	0.160	0.760	30	1.59

[a] λ = 2288 Å. [b] Dimethylsilane-d_2.

$$(CH_3)_2SiDSD + h\nu \longrightarrow (CH_3)_2SiSD + D \tag{23}$$

To this end the photolysis of H_2S was studied in the presence of $(CH_3)_3SiD$.

6. The H_2S-$(CH_3)_3SiD$ System. If step 23 is the primary process in the photolysis of dimethylsilylthiol then D_2 formation should not be observed in the photolysis of trimethylsilylthiol since the analogous primary step is not possible. As seen from the data in Table VI the yield of D_2 from the reaction is quite substantial, in fact the D_2/HD ratio in this system is nearly identical with that obtained from the H_2S-$(CH_3)_2SiD_2$ system at equal D_2/H_2 levels. Hence the possibility of reaction 23 being the major mode of D atom formation is ruled out. Instead, a photochain process comprised of the following steps is considered

$$(CH_3)_2SiDSH + h\nu \longrightarrow (CH_3)_2SiDS\cdot + H \tag{24}$$

$$(CH_3)_2SiDS\cdot + (CH_3)_2SiD_2 \longrightarrow (CH_3)_2SiDSD + (CH_3)_2SiD\cdot \tag{25}$$

and/or

$$(CH_3)_2SiDS\cdot + (CH_3)_2SiD\cdot \longrightarrow (CH_3)_2SiDSD + (CH_3)_2Si: \tag{26}$$

followed by 20, 21, and 22. For this to be competitive with H_2S photolysis, a large extinction coefficient is required for the silylthiol, and this offers the possibility of detection by flash spectroscopic techniques.

7. Flash Photolysis with Kinetic Absorption Spectroscopy. The absorption was monitored between 2100 and 2500 Å. Upon flashing mixtures of 0.05 Torr of H_2S and 1 Torr of $(CH_3)_2SiD_2$, the plate showed a small increase in absorption up to 300 μsec. After 300 μsec, the absorption became more intense and reached its maximum at about 1.5 msec after which it began to fall off. The transient absorber is most likely dimethylsilylthiol which, after 1.5 msec, starts to condense to the thioether.

Finally, the transient existence of the silylthiol was also examined by kinetic mass spectrometry.

8. Flash Photolysis with Kinetic Mass Spectrometry. A 10% mixture of H_2S in $(CH_3)_2SiH_2$ was flashed in a Vycor cell and the reaction mixture bled into the mass spectrometer. The only significant m/e values recorded after ~500-μsec delay time of the instrument were 92, 91, 77, and 76. These correspond to the $(CH_3)_2SiHSH^+$, $(CH_3)_2SiHS^+$, CH_3SiHSH^+, and CH_3SiHS^+ ions, respectively. Further experiments showed that silylthiol had a half-life of the order of a few milliseconds.

Weak signals were also observed at m/e values of 150, 149, 135, and 134, probably arising from the condensation product of silylthiol.

TABLE VI: Isotopic Composition of Hydrogen from the H_2S-$(CH_3)_3SiD$ System[a]

$P(H_2S)$, Torr	P(TMS-d_1),[b] Torr	Mole fraction of H_2	HD	D_2	Total, μmol
0.0	104.7				0.00
8.1	104.7	0.211	0.451	0.338	2.18

[a] λ = 2288 Å, exposure time 5 min. [b] $(CH_3)_3SiD$.

Similar studies on the H_2S-$(CH_3)_3SiH$, H_2S-CH_3SiH_3, COS-$(CH_3)_3SiH$, COS-$(CH_3)_2SiH_2$, and COS-CH_3SiH_3 systems all gave the parent and some fragment ions of the corresponding silylthiol with half-lives in the order of a few milliseconds. The most intense signals were recorded with $(CH_3)_3SiH$ and the signal intensities decreased as methylation decreased.

Discussion

The deuterium product of the photolysis of H_2S in the presence of $(CH_3)_2SiD_2$ has been conclusively shown not to arise from the simple exchange reaction 15. In particular the following observations militate against reaction 15, and point to the intervention of silylthiol: (a) the marked exposure time dependence of the fractional yield of D_2, (b) the lack of effect of added CO_2, (c) the absence of D_2 in the hydrogen produced from the photolysis of CH_2O with admixed $(CH_3)_2SiD_2$, (d) the formation of deuterium from the silylthiol produced by the insertion of $S(^1D_2)$ atoms into the Si-D bonds of $(CH_3)_2SiD_2$, (e) the mass spectrometric detection of the transient presence of silylthiols in the H_2S-silane and COS-silane systems.

In addition, the kinetic behavior of the system is also inconsistent with step 15 being the mode of production of D_2. Thus, the kinetic equation

$$\frac{[HD]}{[D_2]} = \frac{k_{22}}{k_{15}} + \left[\frac{k_{22}}{k_{15}}\left(\frac{k_{27} + k_{28}}{k_{21}}\right) + \frac{k_{27}}{k_{21}}\right]\frac{[H_2S]}{[(CH_3)_2SiD_2]}$$

where k_{26} and k_{27} are the rate constants of the reactions

$$D + H_2S \longrightarrow HD + SH \tag{27}$$

$$D + H_2S \longrightarrow H + HDS \tag{28}$$

predicts a straight line relationship between product and reactant ratios which, however, does not appear to hold.

Hence it is concluded that thermalized H atoms do not engage in deuterium exchange with dimethylsilane-d_2 and

TABLE VII: Estimated Upper Limits for the D/H Exchange Reaction[a]

Reaction	% upper limits for exchange		Statistical weight H_2/HD
	Short-lived complex	Long-lived complex	
D + SiH_4	20	8	1.5
D + Si_2H_6	0	0	1.0
D + CH_3SiH_3	20	13	1.0
D + $(CH_3)_2SiH_2$	10	10	0.5
D + $(CH_3)_3SiH$	6	6	

[a] Data taken from ref 4 and 5.

the upper limit of the k_{15}/k_{22} exchange to abstraction ratio, k_{15}/k_{22}, is ~0.08 when the H atoms possess excess translational energy up to 35 kcal/mol.

The products of the reaction, along with all the kinetic observations made on the H_2S-$(CH_3)_2SiD_2$ system, can be satisfactorily interpreted in terms of the following sequence of elementary reactions

$$H_2S + h\nu \longrightarrow H^* + HS \qquad (1)$$

$$H^* + (CH_3)_2SiD_2 \longrightarrow HD + (CH_3)_2SiD\cdot \qquad (29)$$

$$HS + (CH_3)_2SiD\cdot \longrightarrow (CH_3)_2SiDSH \qquad (30)$$

$$(CH_3)_2SiDSH + h\nu \longrightarrow (CH_3)_2SiDS\cdot + H \qquad (24)$$

$$H + (CH_3)_2SiD_2 \longrightarrow HD + (CH_3)_2SiD\cdot \qquad (22)$$

$$(CH_3)_2SiDS\cdot + (CH_3)_2SiD_2 \longrightarrow (CH_3)_2SiDSD + (CH_3)_2SiD\cdot \qquad (25)$$

$$(CH_3)_2SiDSD + h\nu \longrightarrow (CH_3)_2SiDS\cdot + D \qquad (20)$$

$$D + (CH_3)_2SiD_2 \longrightarrow D_2 + (CH_3)_2SiD\cdot \qquad (10)$$

$$2(CH_3)_2SiD\cdot \longrightarrow ((CH_3)_2SiD)_2 \qquad (11)$$

This mechanism is an example of an unusual type of photochemical chain in which secondary photolysis of a self-regenerating primary product is so efficient that it becomes the major photoreaction even at very low conversions. The length of the chain can be established by considering the yields of HD and D_2 at $[(CH_3)_2SiD_2] >> [H_2S]$. Under this condition the ratio $[D_2]/([HD]/2)$ gives the length of the photochemical chain at any given conversion. In the 15-min photolysis, listed in Table III, the chain length is ~5 and decreases to ~1.5 for a photolysis time of 1 min.

The half-life of the silylthiol is a few milliseconds and condensation must compete with photolysis of the thiol. No evidence could, however, be found in the present study for the intermediacy of other nonstoichiometric complexes such as the SiH_5 species postulated by Glasgow, *et al.*[20]

On the contrary, the data of earlier reported studies[4,5] of the H + silane reactions from this laboratory provide unambiguous evidence against the importance of long-lived SiR_4H complexes. Thus, in the reactions of D atoms with SiH_4, Si_2H_6, CH_3SiH_3, $(CH_3)_2SiH_2$, and $(CH_3)_3SiH$ the experimental H_2/HD yields can be taken as upper limits for the values of k(exchange)/k(abstraction). If the transition complex $SiH_4{\cdot}D$ is indeed long lived then the statistical weight of H_2 loss over HD loss is 1.5. Assuming a direct isotope effect for H_2 loss over HD loss of two, this leads to a value of three for the H_2/HD ratio. Table VII summarizes the upper limits estimated in this manner for the five silicon hydride molecules discussed above.

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