Experimental Section

Preparations.—Both the ligand and the complex were prepared following the procedures of Chiswell, *et al.*[4]

The preparations of the complex were performed under N_2 and all of the solvents were deoxygenated by bubbling N_2 through them. In a typical preparation, a solution of 2.2 g of the ligand in 10 ml of ethanol was added to a solution of 1.8 g of iron(II) perchlorate hexahydrate in 10 ml of water. The dark red solution was concentrated to half-volume by warming and passing N_2 through. The complex precipitated on cooling and scratching. It was recrystallized from 1:1 ethanol–water (20 ml), dark red crystals being obtained. These were washed with ether and dried under vacuum (over P_2O_5) for 24 hr (68% yield). *Anal.* Calcd for $C_{24}H_{23}Cl_2FeN_9O_9$: C, 40.7; H, 3.3; Fe, 7.9; N, 17.8. Found: C, 40.9; H, 3.3; Fe, 7.9; N, 17.4.

Magnetic Measurements.—These were carried out over the range 80–350°K, at field strengths of 5.0, 5.4, and 5.9 kOe, using powdered samples and the Gouy balance previously described[12] (calibrated with $HgCo(NCS)_4$). The following diamagnetic contributions were used: Fe^{2+}, −13; ClO_4^-, −32; H_2O, −13; L, −84 (all 10^{-6} cgsu/mol).

Mössbauer Measurements.—These were made with a conventional constant-acceleration spectrometer using a Laban 400 channel analyzer and a ^{57}Co–Pd source.

Acknowledgments.—A. A. S. C. M thanks the Calouste Gulbenkian Foundation, Lisbon, for a Research Studentship and the Laboratório de Química de Faculdade de Ciências do Porto for leave of absence. We thank the SRC for the use of the Mössbauer spectrometer at Queen Elizabeth College, London.

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Direct Photolysis and Electric Discharge Decomposition of Silane–Silane-d_4 Mixtures

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Received February 3, 1969

Disilane has been prepared from silane by the reaction

$$2SiH_4 \xrightarrow{\text{energy}} Si_2H_6 + H_2 \qquad (1)$$

The energy has been supplied by heat,[1] silent electric discharge,[2] and mercury photosensitization.[3]

In this note, we report our results on the photolysis (1470 Å) and silent electric discharge decomposition of equimolar silane–silane-d_4 mixtures in an attempt to elucidate the primary decomposition modes of silane for these processes.

The decomposition of silane most likely proceeds by one of the following two routes. The first is the silyl mechanism proposed for the mercury photosensitized decomposition[3]

$$SiH_4 \longrightarrow SiH_3 + H \qquad (2)$$

$$H + SiH_4 \longrightarrow SiH_3 + H_2 \qquad (3)$$

$$2SiH_3 \longrightarrow Si_2H_6 \qquad (4)$$

or possibly

$$SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H \qquad (5)$$

Without isotope effects, the products would be Si_2H_6, H_3SiSiD_3, and Si_2D_6 in a 1:2:1 ratio and H_2, HD, and D_2 in a 1:2:1 ratio, also. The second route is the silene mechanism similar to that found for the photolysis of methane[4]

$$SiH_4 \longrightarrow SiH_2 + H_2 \qquad (6)$$

$$SiH_2 + SiH_4 \longrightarrow Si_2H_6 \qquad (7)$$

For this route, the products would be equal quantities of Si_2H_6, 1,1-$D_2Si_2H_4$, 1,1-$H_2Si_2D_4$, and Si_2D_6 and also equal quantities of H_2 and D_2.

The results from the photolysis of equimolar mixtures of SiH_4 and SiD_4 are listed in Table I. The low quantity of HD and lack of $Si_2H_3D_3$ argue against the silyl mechanism. The lack of $Si_2H_3D_3$ also implies that H atoms were not present (from any other process) since they would produce silyl radicals from the hydrogen abstraction of silane.

We propose that the main primary process is molecular hydrogen elimination (eq 6). The energy at 1470 Å is equal to 195 kcal/mol and therefore the silenes produced would be hot. Thus the disilanes formed from silene insertion would be hot by about 155 kcal/mol. Our results on the pyrolysis of disilane[5] are in accord with decomposition into silene and silane. If the hot disilanes (Si_2D_6, 1,1-$H_2Si_2D_4$, 1,1-$D_2Si_2H_4$, and Si_2H_6) decompose into silanes and silenes, the silenes formed would be SiD_2, SiH_2, and HSiD. The insertion of HSiD into SiH_4 and SiD_4 would explain the presence of DSi_2H_5 and HSi_2D_5. The mixed silanes formed from the decomposition of the hot disilanes would also be hot, by about 82 kcal/mol, and would decompose into silenes, H_2, HD, and D_2.

The 1470-Å photolysis of methylsilane has been recently examined.[6] The results of this study are in agreement with the formation of silene, methylsilene, and possibly CH_2SiH_2.

The results from the silent electric discharge decomposition of equimolar SiH_4–SiD_4 mixtures are listed in Table II. It is apparent that the reaction is pressure dependent. This could be due to collisional deactivation at higher pressure and/or higher energies at lower pressures. The energy of the exciting electrons is a function of the distance traveled before encountering a molecule. For the high-pressure runs, the decrease in the relative concentration of D_5Si_2H, D_3SiSiH_3, and HD demonstrates that they are products of secondary reactions. Therefore, our results are in accord with the formation of disilanes from the insertion of silene into silane. It should be pointed out that our disilane analyses are most accurate for the more highly deuterated disilanes since at higher m/e values (68, 67, 66, 65) only a few molecules contribute intensities.

Our results also favor the main primary decomposi-

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TABLE I

PRODUCT RATIOS FROM SiH_4–SiD_4 PHOTOLYSES

Pressure, atm	Per cent of disilanes							Per cent of hydrogen		
	Si_2D_6	HSi_2D_5	$H_2Si_2D_4$	$H_3Si_2D_3$	$H_4Si_2D_2$	H_5Si_2D	Si_2H_6	D_2	HD	H_2
0.013	11	21	14	~1	9	14	29	26	21	53
0.014	12	15	21	0	8	5	39	26	20	54
0.014	12	21	16	~1	6	7	36	20	23	57
0.046	10	13	16	0	9	7	44	25	25	50
0.496	8	10	26	0	10	7	39	13	22	65

TABLE II

PRODUCT RATIOS FROM SiH_4–SiD_4 ELECTRIC DISCHARGE DECOMPOSITIONS

Pressure, atm	Per cent of disilanes							Per cent of hydrogen		
	Si_2D_6	D_5Si_2H	$D_4Si_2H_2$	$D_3Si_2H_3$	$D_2Si_2H_4$	DSi_2H_5	Si_2H_6	D_2	HD	H_2
0.014[a]								20	44	36
0.014[b]								19	43	38
0.014[a,c]	9	20	13	14	6	13	25			
0.014[b,c]	8	20	13	14	6	13	26			
0.038[d]	6	11	12	9	7	20	35			
0.288[d]	10	5	21	0	8	12	44	18	29	53
0.314[d]	10	5	21	0	8	12	44	18	29	53

[a] One pass. [b] Two passes. [c] Hydrogen continually removed. [d] Static.

TABLE III

MASS SPECTRA OF DEUTERIODISILANES

Compound	m/e														
	70	69	68	67	66	65	64	63	62	61	60	59	58	57	56
Si_2H_6							5.2	9.5	55.9	44.4	100	40.1	69.9	35.6	24.6
DSi_2H_5						6.8	16.7	64.2	51.2	100	69.5	51.6	70.6	32.2	28.1
1,1-$D_2Si_2H_4$					8.2	17.6	79.5	60.1	100	83.1	58.3	73.4	67.3	33.0	35.9
1,1,2-$D_3Si_2H_3$				6	15	65	54.7	68.7	100	49.0	66.7	74.4	71.0	25.6	40.0
1,1,2,2-$D_4Si_2H_2$			5.0	14.7	62.5	58.6	57.2	100	84.7	41.4	68.8	65.8	53.9	20.4	36.4
D_5Si_2H		4.9	11.7	60.2	51.8	48.8	78.6	100	50.5	29.3	88.0	48.8	51.4	13.8	36.1
Si_2D_6	5.0	7.8	60.6	4.7	33.0	13.8	100	3.2	24.4	11.2	79.6	4.7	36.2	3.4	23.2

TABLE IV

INFRARED SPECTRA OF NEW DISILANES

Compound	Absorptions, cm^{-1}							
Si_2H_5D	2160 vs	1570 m	940 m	890 m	800 vs	690 w	565 w	
1,2-$D_2Si_2H_4$	2160 vs	1565 s	930 m	835 m	784 vs	660 m	530 m	
1,1-$D_2Si_2H_4$	2155 vs	1560 s	950 m	890 s	792 vs	670 vs	570 m	
1,1,2-$D_3Si_2H_3$	2160 s	1565 s	930 m	835 m	780 vs	660 s	530 w	510 w
1,2-$H_2Si_2D_4$	2160 s	1565 s	930 m	835 m	778 vs	660 s	575 w	530 w
1,1-$H_2Si_2D_4$	2165 s	1565 s	933 m	820 m	775 s	650 vs	623 vs	525 w
Si_2D_5H	2155 s	1560 vs	930 m	802 s	650 vs	518 m		
Si_2D_5Cl		1585 s	668 s	605 vs	522 m			
1,2-$Cl_2Si_2D_4$		1595 s	670 s	580 vs	528 m			
1,1-$Cl_2Si_2D_4$		1598 s	670 s	600 vs	580 vs	528 m		

tion of silane as that represented by eq 6. It is of interest to note that silene (SiH_2) has been observed spectroscopically in the flash photolysis of phenylsilane and in the flash discharge of silane.[7] In the low-pressure electric discharge decomposition of SiH_4–SiD_4 mixtures, the presence of all the disilanes suggests much scrambling or a variety of primary processes due to higher energies and/or no collisional deactivation.

Experimenal Section

(1) **Preparation of $ClSi_2D_5$, 1,1-$Cl_2Si_2D_4$, and 1,2-$Cl_2Si_2D_4$.**—The compounds $ClSi_2D_5$ and 1,2-$Cl_2Si_2D_4$ were prepared from the reaction between Si_2D_6 and AgCl while 1,1-$Cl_2Si_2D_4$ was prepared from the reaction between Si_2D_6 with DCl. The procedures used were those described by Hollandsworth and Ring[8] for the preparation of the hydrogen derivatives from disilane.

The new chlorodisilanes were identified by mass spectra and vapor pressure measurements which agreed with those for the hydrogen derivatives. The reduction with lithium aluminum hydride or deuteride yielded only trace quantities of monosilanes which demonstrated that chloromonosilanes had not been present.

(2) **Preparation of Deuteriodisilanes.**—The deuteriodisilanes were prepared by the reduction of Si_2H_5Cl, both $Si_2H_4Cl_2$ derivatives, and 1,1,2-$Cl_3Si_2H_3$ with $LiAlD_4$ and from the $LiAlH_4$ reduction of Si_2D_5Cl and both $Si_2D_4Cl_2$ derivatives. The chlorodisilane samples used were those previously identified.[8] The deuteriochlorodisilane samples used were those prepared in the preceding section. The disilanes prepared were identified by their mass spectra. The compounds were not obtained pure owing to several reasons. First, the $LiAlD_4$ used contained hydrogen. Second, some disproportionation reactions of the chlorodisilanes may be expected in ethers. However, the purity of the disilanes was sufficient for this study.

(3) **Mass Spectra of the Deuteriodisilanes.**—The mass spectra used to analyze our deuteriodisilane mixtures are listed in Table III. The mass spectrum of disilane-d_6 is a modified version of the experimental spectrum. The intensity at odd m/e values can only be due to the presence of ^{29}Si and ^{30}Si atoms. However, in our sample some hydrogen was present. The values listed in

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Table III are slightly modified from the experimental values based on the isotope ratios obtained from our disilane spectrum.

We used the values for 1,2-$H_2Si_2D_4$ instead of those for 1,1-$H_2Si_2D_4$, since this sample was of a higher purity. The 1,1-$H_2Si_2D_4$ contained about 15% Si_2D_5H. When the intensities of Si_2D_5H were removed from those of 1,1-$H_2Si_2D_4$, the mass spectra of both $H_2Si_2D_4$ isomers were similar.

The mass spectra of disilane and disilane-d_6 were obtained with butane as an internal standard. These experiments demonstrated that the relative intensity of the parent peak for disilane compared to disilane-d_6 was 1.05 at equal pressures. We have calculated relative quantities with the assumption that the most intense *m/e* values have the same intensities at equal pressure.

(4) **Decomposition Reactions of SiH_4–SiD_4 Mixtures.**—The silent electrical discharge and direct photolysis of equimolar mixtures of silane and silane-d_4 were examined in a mercury-free vacuum system.

Silane and silane-d_4 were prepared by the reduction of silicon tetrachloride with lithium aluminum hydride and lithium aluminum deuteride. The infrared spectrum of the silane-d_4 demonstrated that only a very small amount of silane-d_3[9] was present. Mass spectra of the silanes demonstrated that no disilanes were present.

The electric discharge apparatus was similar to that described by Spanier and MacDiarmid[2] with a transformer potential of 5000 V. A polymer was deposited by the discharge decomposition of silane and the polymer was converted to a mirror by the electric discharge in the presence of hydrogen. All of the discharge reactions were carried out in the tube coated with this silicon mirror.

The xenon lamp (1470 Å) used in the direct photolysis experiments was similar in design to that described by Okabe[10] except that the lithium fluoride window was sealed as described by Bass[11] in order to prevent decomposition of the sealant. The lamp intensity was of the order of 2×10^{15} quanta/sec. However, a mirror was deposited on the LiF window which greatly reduced the effective lamp intensity. The rapid decomposition on the mirror made it impossible to obtain quantum yields.

In the electric discharge reactions, the ratio of mixed silanes (SiH_3D, SiH_2D_2, $SiHD_3$) produced to disilanes formed was less than 1:8. In the photolysis experiments, the mixed silanes were not observed. The total silane decomposition in each experiment was of the order of 2–4%.

Acknowledgments.—The authors are indebted to Dr. H. E. O'Neal for discussions on kinetics and to the Army Research Office (Durham) for financial support.

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Nuclear Magnetic Resonance Studies on Exchange Reactions of Group III Alkyl Derivatives. IV. Trimethylgallium–Trimethylphosphine

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Received April 7, 1969

Earlier papers in this series have investigated group exchange reactions of the type[3–5] shown in eq 1

$$M^*(CH_3)_3 + M(CH_3)_3 \cdot B \rightleftharpoons M(CH_3)_3 + M^*(CH_3)_3 \cdot B \quad (1)$$

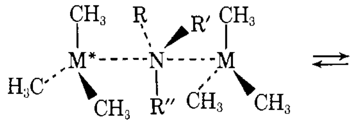
where M = M* = Ga or In and B = trimethylamine (I), dimethylamine (II), monomethylamine (III), or ammonia (IV). For both the gallium and indium systems a dissociative process (shown in eq 2 and 3) is followed when the base is I or II. When the base is

$$M(CH_3)_3 \cdot B \rightleftharpoons M(CH_3)_3 + B \quad (2)$$

$$B + M^*(CH_3)_3 \longrightarrow M^*(CH_3)_3 \cdot B \quad (3)$$

III or IV, the bimolecular process shown in eq 4 becomes lower in energy and is preferred. Because of the nature of the transition state in eq 4, it is reasonably easy to see why, when R, R′, and R″ are all methyl groups, the exchange proceeds by the dissociation mechanism. The transition state in eq 4 is simply too sterically hindered. Only as two methyl groups are replaced by hydrogen atoms does the bimolecular process become energetically favored.

$M^*(CH_3)_3 + M(CH_3)_3 \cdot B \rightleftharpoons$



$M(CH_3)_3 + M^*(CH_3)_3 \cdot B$ (4)

Contrary to this, when the amine adducts of trimethylgallium and trimethylindium are present with excess base, base exchange is postulated to proceed through a bimolecular process in all cases. For these systems the central atom in the transition state is the larger group III atom, and the transition state is able to form even with the fully methylated derivatives. Cowley and Mills have observed that base exchange with the trimethylboron–trimethylamine adduct does proceed through unimolecular dissociation of the adduct,[6] implying steric crowding for the hypothetical bimolecular transition state.

Considering the manner in which steric interactions influence the mechanism of reaction, it was of interest to study $Ga(CH_3)_3$ exchange with the $Ga(CH_3)_3 \cdot P(CH_3)_3$ adduct to see whether the phosphorus atom was large enough to accommodate bimolecular exchange for the fully methylated derivative.

A preliminary report postulated that this exchange might proceed *via* a bimolecular pathway or through the bimolecular and unimolecular processes simultaneously.[3] The more detailed kinetic and activation energy studies undertaken here, however, clearly point toward a dissociation pathway equivalent to that for trimethylamine.

Experimental Section

All materials were prepared by methods reported earlier.[3] Methylene chloride was used as solvent after refluxing over

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