The ether extract was dried over sodium sulfate, and removal of the solvent under reduced pressure gave a viscous solid. It was treated with a mixture of 50 ml. of petroleum ether (b.p. 60–70°) and 10 ml. of benzene. The soluble portion gave 5.1 g. of a polymeric substance from which no crystalline product could be isolated. The insoluble portion gave 1.5 g. of octaphenyltrisilane which melted at 260–262°, after crystallization from benzene. The combined yield of octaphenyltrisilane was 3.6 g., 25.7%.

Reaction of Triphenylsilyllithium with Trichlorosilane.—A solution of 0.060 mole of triphenylsilyllithium was added slowly to 2.71 g. (0.020 mole) of trichlorosilane. During the addition, the flask was cooled in a Dry Ice–acetone-bath. The reaction mixture was allowed to warm to room temperature. Color Test I was then negative. Subsequent to hydrolysis and addition of some ether, 3.2 g. (20.6%) of hexaphenyldisilane, m.p. 354–357°, was removed by filtration. The organic layer of the filtrate was dried and the solvent removed. The residue was chromatographed on alumina. Petroleum ether (b.p. 60–70°) eluted 4.6 g. (29.5%) of triphenylsilane, m.p. 45–47°. The product eluted with cyclohexane melted over the range 182–198°. Fractional crystallization from the same solvent yielded a trace of a compound, m.p. 185–187°, the structure of which has not yet been determined. The product eluted with carbon tetrachloride was recrystallized three times from a mixture of ethyl acetate and methanol to give 0.7 g. (4.4%) of tris-(triphenylsilyl)-silane,[17b] m.p. 206–209°. The infrared spectrum of the compound had characteristic absorption bands at 3.3, 4.8 and 9.08 μ, indicative of aromatic C–H, of the Si–H and of the silicon–phenyl linkages, respectively.

Anal. Calcd. for $C_{54}H_{46}Si_4$: Si, 13.92. Found: Si, 13.67, 13.80.

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AMES, IOWA

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Catalysis by Metal Halides. I. Mechanism of the Disproportionation of Ethyltrimethylsilane

BY GLEN A. RUSSELL[1]

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The catalyzed disproportionation of ethyltrimethylsilane has been investigated in regard to the catalytic effects of various metal halides, the effects of co-catalysts on the rate of the aluminum bromide-catalyzed reaction, the effects of solvent and temperature upon the rate and equilibrium, the kinetics of the reaction, and the possible occurrence of reaction intermediates. It is concluded that catalysis involves the ability of the metal halide to function as a Lewis acid. Evidence is presented against the formation of ions or of organometallic intermediates in the reaction. It is concluded that the reaction occurs *via* the interaction of two silane molecules, one containing a polarized silicon–carbon bond formed by the interaction of the metal halide with the tetraalkylsilane.

Introduction

The catalyzed disproportionation of substituted silanes was first recognized by Friedel and Ladenburg who found that triethoxysilane could be disproportionated in the presence of sodium (a reaction undoubtedly catalyzed by ethoxide ion).[2a]

$$4SiH(OC_2H_5)_3 \xrightleftharpoons{C_2H_5O^-} SiH_4 + 3Si(OC_2H_5)_4$$

Numerous other examples of base-catalyzed disproportionations of alkoxysilanes are now known.[3] Ladenburg later discovered that certain tetraalkylsilanes would disproportionate spontaneously at elevated temperatures in the range of 300°,[2b] a reaction investigated in more detail by Ipatieff and Dolgov.[4] Numerous other thermal disproportionations have been realized, particularly when disproportionation involves the exchange of two negative groups,[5] or the migration of a hydrogen atom.[6] These reactions often have been observed as unexpected side reactions.[6b]

The first disproportionation with unquestioned catalysis by a metal halide was reported by Stock and Somieski who found that aluminum chloride would catalyze the reaction between silane and dichlorosilane to yield monochlorosilane.[7] The metal halide-catalyzed disproportionation has subsequently been investigated from a synthetic,[8] equilibrium[9] and mechanistic[10] point of view.

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(3) D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 77 (1946); C. R. Hance and G. H. Wagner, U. S. Patent 2,530,367 (1950); D. L. Bailey, U. S. Patents, 2,723,983, 2,723,985 (1955), 2,745,860 (1956); E. W. Beck, W. H. Daudt, H. J. Fletcher, M. J. Hunter and A. J. Barry, THIS JOURNAL, **81**, 1256 (1959).

(4) V. I. Ipatieff and B. N. Dolgov, *Ber.*, **62B**, 1220 (1929); B. N. Dolgov and Y. N. Volnov, *J. Gen. Chem.* (*USSR*), **1**, 91 (1931).

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(6) (a) H. S. Booth and W. D. Stillwell, *ibid.*, **56**, 1531 (1934); H. J. Emeleus, A. G. Maddock and C. Reid, *J. Chem. Soc.*, 353 (1941); H. J. Emeleus and A. G. Maddock, *ibid.*, 293 (1944); (b) H. Gilman and D. H. Miles, *J. Org. Chem.*, **23**, 326 (1958); N. C. Goodspeed and R. T. Sanderson, *J. Inorg. Chem.*, **2**, 266 (1956); A. F. Reilly and H. W. Post, *J. Org. Chem.*, **16**, 387 (1951); (c) Dow Corning Ltd., British Patent 663,810 (1951).

(7) A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919); **56B**, 1087 (1923).

(8) R. O. Sauer, U. S. Patents 2,647,136 (1953), 2,730,540 (1956); A. J. Barry and J. W. Gilkey, British Patent 642,630 (1950), U. S. Patent 2,647,912 (1953); B. A. Bluestein, U. S. Patent 2,717,257 (1955); G. H. Wagner and M. M. Burnham, U. S. Patent 2,746,980–3 (1956); Baeyer Farbenfabriken, British Patent, 671,880 (1952); D. L. Bailey and G. H. Wagner, U. S. Patent 2,732,281 (1956); E. M. Soshestnenskaya, *J. Gen. Chem.* (*USSR*), **26**, 247 (1946); B. N. Dolgov, S. N. Borsov and M. G. Voronkov, *ibid.*, **27**, 709, 2062, 2692 (1957); *Doklady*, **114**, 93 (1957); J. L. Speier and R. E. Zimmerman, THIS JOURNAL, **77**, 6395 (1955); C. E. Erickson and G. H. Wagner, U. S. Patent 2,627,451 (1953).

(9) (a) G. Calingaert, H. Soroos and V. Hnizda, THIS JOURNAL, **62**, 1107 (1940); (b) R. O. Sauer and E. M. Hadsell, *ibid.*, **70**, 3590 (1948);

Three mechanisms have been suggested for the disproportionation of substituted silanes in the presence of metal halides. The Whitmore mechanism involves a siliconium ion as an intermediate.[10a]

$$(C_2H_5)_2SiCl_2 + Al_2Cl_6 \rightleftarrows (C_2H_5)_2\overset{+}{Si}Cl + Al_2Cl_7^-$$

$$(C_2H_5)_2\overset{+}{Si}Cl + (C_2H_5)_3SiH \rightleftarrows (C_2H_5)_2SiHCl + (C_2H_5)_2Si^+$$

$$(C_2H_5)_3Si^+ + (C_2H_5)_2SiCl_2 \rightleftarrows (C_2H_5)_3SiCl + (C_2H_5)_2\overset{+}{Si}Cl$$

$$(C_2H_5)_2SiCl_2 + (C_2H_6)_3SiH \overset{Al_2Cl_6}{\rightleftarrows} (C_2H_5)_3SiCl + (C_2H_5)_2SiHCl$$

Calingaert has suggested that analogous reactions of tetraalkyl lead compounds involves the formation of intermediate alkylaluminum compounds.[11] For a substituted silane, the reaction would be formulated as

$$R_3SiR' + Al_2X_6 \rightleftarrows R_3SiX + Al_2X_5R'$$

$$Al_2X_5R' + R_3SiR' \rightleftarrows Al_2X_5R + R_2SiR'_2$$

$$Al_2X_5R + R_3SiR' \rightleftarrows Al_2X_5R' + R_4Si$$

$$2R_3SiR' \overset{Al_2X_6}{\rightleftarrows} R_4Si + R_2SiR_2'$$

Zemany and Price have suggested, on the basis of kinetic evidence, that the disproportionation of alkylchlorosilanes catalyzed by aluminum chlorides at temperatures in the range of 350° should be considered to be a bimolecular reaction between a molecule of chlorosilane and a chlorosilane–aluminum chloride complex.[10c]

$$(CH_3)_2SiCl_2 + (CH_3)_2SiCl_2\cdots AlCl_3 \longrightarrow (CH_3)_3SiCl + CH_3SiCl_3\cdots AlCl_3$$

It was our motivation to ascertain which, if any, of these mechanisms was most consistent with experimental data. Moreover, we have concentrated our efforts on the disproportionation of tri- and tetraalkylsilanes since these reactions have no analogies in the chemistry of hydrocarbons and involve, in some manner, electrophilic substitution on carbon.[12] The present paper presents information on the disproportionation of ethyltrimethylsilane particularly in regard to the catalytic effects of various metal halides, the effects of various additives on the catalytic ability of aluminum bromide, the effects of solvents upon the rate of reaction, the effect of temperature upon rate and equilibrium, the kinetics of the reaction, and the results of experiments designed to detect the intermediates suggested in the mechanisms given previously. In the succeeding paper, the relative rates of disproportionation of ethyltrimethylsilane, trimethylsilane, bromotrimethylsilane and phenyltrimethylsilane are considered.[13a] Other papers of this series discuss the catalytic ability of metal halides in Friedel–Crafts type reaction[13b] and the question of the formation of siliconium ions from substituted silanes.[13c]

Results

Detection of Possible Organoaluminum Intermediates.—A variety of silanes was treated with various metal halides in sealed ampoules. After the desired reaction period the unreacted silanes and any other volatile materials were removed under vacuum and residues hydrolyzed. Gases evolved were collected, measured and analyzed by mass spectra. The results summarized in Table I indicate the occurrence of the reactions

TABLE I

PRODUCTS OF THE REACTION OF METAL HALIDES WITH SILANES[a]

Metal halide, mmoles	Silane	Mole	Mmole hydrolysate	Composition of hydrolysate
$AlCl_3$,[b] 25	$SiHCl_3$	0.073	0.13	H_2
$AlCl_3$, 17	$(CH_3)_4Si$	.042	.06	CH_4
$AlCl_3$, 34	CH_3SiHCl_2	.055	.12	$H_2:CH_4 = 10:1$
$AlCl_3$, 30	$(CH_3)_3SiC_2H_5$	.049	.15	CH_4, trace C_2H_6
$GaCl_3$, 2.8	$(CH_3)_3SiC_2H_6$	.030	.10	CH_4
$AlBr_3$, 1.9	$(CH_3)_3SiC_2H_6$	.030	.07	CH_4
$FeCl_3$,[b,c] 3.1	$(CH_3)_3SiC_2H_5$	.030	< .02	..
$InCl_3$,[b] 2.2	$(CH_3)_3SiC_2H_5$	.030	.04	CH_4
$MgCl_2$,[b] 5.4	$(CH_3)_3SiC_2H_5$	.030	.20	CH_4
$AuBr_3$,[b] 1.1	$(CH_3)_3SiC_2H_5$	.030	< .02	..

[a] 24 hr. at 100°. [b] Heterogeneous. [c] Ferric chloride reduced to ferrous state.

$$\equiv Si\text{-}R + MX_3 \rightleftarrows \equiv Si\text{-}X + MX_2R$$

$$\equiv Si\text{-}H + MX_3 \rightleftarrows \equiv Si\text{-}X + MX_2H$$

However, with the possible exception of ferric chloride, these reactions are either extremely slow or the equilibrium lies far to the left. Further experiments demonstrated the occurrence of cleavage was in no way connected with the disproportionation of ethyltrimethylsilane since completely ineffective catalysts, such as gallium chloride and indium chloride, were as effective in the cleavage of silicon–alkyl bonds as were highly active disproportionation catalysts such as aluminum bromide. Manulkin has also shown that the silicon–ethyl bond of tetraethylsilane may be cleaved in a similar manner by aluminum, ferric, mercuric and bismuth chlorides.[14]

Equilibrium in the Aluminum Chloride-catalyzed Reaction.—Ethyltrimethylsilane and resublimed aluminum chloride were held at 80, 90 and 100° for various periods of time. The ratios tetramethylsilane/ethyltrimethylsilane and diethyldimethylsilane/ethyltrimethylsilane were determined by gas-liquid chromatography. The results are summarized in Table II.

There is no trend in the tetramethyl/ethyltrimethylsilane ratio with temperature. A slight decrease in the diethyldimethylsilane/ethyltrimethylsilane ratio occurred with an increase in temperature. Over the temperature range 80–100°, the average relative molar concentrations at equilibrium are $Me_4Si:Me_3SiEt:Me_2SiEt_2 = 0.68:$

(c) M. Kumada, *J. Inst. Polytech. Osaka City Univ., Ser. C*, **2**, 131, 139 (1952) [*C. A.*, **48**, 11303 (1954)].

(10) (a) F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, THIS JOURNAL, **69**, 2108 (1947); (b) P. D. George, L. H. Sommer and F. C. Whitmore, *ibid.*, **77**, 1677 (1955); (c) P. D. Zemany and F. P. Price, *ibid.*, **70**, 4222 (1948).

(11) G. Calingaert and H. A. Beatty in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, pp. 1806–1820.

(12) For a possible example of electrophilic attack on a carbon atom of a saturated hydrocarbon, see E. J. Corey and R. W. White, THIS JOURNAL, **80**, 6686 (1958).

(13) (a) G. A. Russell, *ibid.*, **81**, 4825 (1959); (b) **81**, 4831 (1959); (c) **81**, 4834 (1959).

(14) Z. M. Manulkin, *J. Gen. Chem.* (*USSR*), **16**, 235 (1946); **18**, 299 (1948); **20**, 2004 (1950).

TABLE II

EQUILIBRIUM IN THE DISPROPORTIONATION OF ETHYLTRIMETHYLSILANE[a]

Temp., °C.	Time, hr.	Me_4Si/Me_3SiEt	Me_2Et_2Si/Me_3SiEt
80	24	0.675	0.515
80	48	.675	.525
80	72	.655	.515
80	120	.685	.52
90	24	.705	.52
90	48	.685	.50
90	72	.71	.51
90	96	.71	.51
100	24	.67	. . .
100	48	.65	.485
100	72	.69	.475

[a] Equilibrium studies involved *ca.* 0.5 g. of aluminum chloride in the presence of 5 ml. of ethyltrimethylsilane.

1.00:0.051. Since the over-all ratio of methyl to ethyl groups is 3, it can be calculated that if the concentration of tetraethylsilane is negligible then triethylmethylsilane will be present at equilibrium to the extent of 0.09 mole per mole of ethyltrimethylsilane. On a completely statistical basis, as would be expected when ΔH of disproportionation is 0, the ratio $Me_4Si:Me_3SiEt:Me_2SiEt_2:MeSiEt_3:Et_4Si$ is calculated to be 0.75:1.00:0.50:0.11:0.01, probably within experimental error of the observed ratios. Since $\Delta H = 0$ and a nearly statistical ratio of products is obtained, this disproportionation fits the Calingaert definition of a redistribution reaction.[11,15,16]

Disproportionations of mixtures of tetraethylsilane and tetra-*n*-propylsilane have given random equilibrium mixtures[9a] while the alkylchlorosilanes have yielded equilibrium mixtures which in certain cases deviate considerably from the statistical mixture.[9b] Random distribution of products has been observed in the disproportionation of various halo, alkoxy and isocyanosilanes.[9c,5b] The methylsilanes also yield a nearly statistical mixture of disproportionated products.[13a]

Effect of Catalyst Structure on Rate.—Although under equilibrium conditions tetramethylsilane and dimethyldiethylsilane are not formed in equivalent amounts in the disproportionation of ethyltrimethylsilane, they are formed in equivalent amounts during the initial stage of the reaction. Furthermore, as has been demonstrated in Table III, during the early stages of the disproportionation the rate of product formation is a linear function of time, at least up to the point where 3.4% of the ethyltrimethylsilane has been disproportionated.

TABLE III

RATE AND PRODUCTS OF ALUMINUM BROMIDE-CATALYZED DISPROPORTIONATION OF ETHYLTRIMETHYLSILANE AT 80°[a]

Reaction time, hr.	Me_4Si/Me_3SiEt	Me_2SiEt_2/Me_3SiEt	Reaction,[b] %	$-\Delta[Me_3SiEt]$[c]
4	0.0045	0.0050	0.89	0.0515
8	.00935	.0085	1.835	0.1065
16	.0165	.00155		
16	.020	.00185	Av. 3.38	0.196
16	.016	.0014		

[a] 5.8 M Me_3SiEt, 0.1585 M Al_2Br_6. [b] Me_3SiEt disproportionated $\times$ 100/Me_3SiEt (initial) = $2(Me_4Si/Me_3SiEt)100/[1 + 2(Me_4Si/Me_3SiEt)]$. [c] Mole l.$^{-1}$.

From a graph of the data of Table III, the rate of the disproportionation of pure ethyltrimethylsilane containing 0.1585 M aluminum bromide at 80° is found to be 3.48×10^{-6} mole l.$^{-1}$ sec.$^{-1}$.

The catalytic abilities of other metal halides, usually determined on the basis of a single experiment, are summarized in Table IV.

TABLE IV

DISPROPORTIONATION OF ETHYLTRIMETHYLSILANE BY METAL HALIDES[a]

Metal halide	Concn., mole $\times 10^4$	Temp., °C.	Time, hr.	Reaction,[b] %	Rate $\times 10^6$, mole l.$^{-1}$ sec.$^{-1}$
None		80	500	<0.02	<0.0007
None[c]		250	125	0.041	. . . .
Al_2Br_6	9.35	80	0–16	0–3.4	3.48[d]
Al_2Br_6	1.11	80	16	0.27	.284
Al_2Cl_6	1.11	80	16	.18	.189
Al_2I_6	1.11	80	90	.25	.047
Al_2Cl_5Et[e,f]	9.35	80	2	.30	2.42
Ga_2Br_6	9.35	80	90	.12	.021
Ga_2Cl_6	9.35	80	90	< .01	< .002
$TiCl_3$[e]	18.7	100	16	.031	.033
BCl_3	18.7	80	500	.025	.0007
Fe_2Cl_6[e]	9.35	80	500	.0039	.0001
AlF_3[e]	67	100	24	< .02	< .004

[a] 34.3 mmoles of Me_3SiEt used. [b] Calculated as in Table III. [c] Vapor at about 1 atm. pressure. [d] From Table III. [e] Heterogeneous. [f] From stoichiometric amounts of Al_2Cl_6 and $ZnEt_2$.

Less than 0.02% reaction during 24 hr. at 100° was observed using the following substances as catalysts: boron fluoride, aluminum chloride etherate, sodium chloroaluminate, aluminum ethoxide, aluminum chloride hexahydrate, aluminum hydride, triethylaluminum, diethylmercury, tetraethyllead, diethylzinc, cuprous chloride, auric bromide, stannic bromide, zirconium tetrabromide, indium trichloride, tellurium dichloride, zinc chloride, iodine, titanium tetrachloride, vanadium dichloride, antimony pentachloride, antimony trichloride, magnesium chloride, sodium borohydride, lithium aluminum hydride, oxygen, α,α'-azodiisobutyronitrile, ethylenediamine, piperidine, potassium *t*-butoxide, benzoyl peroxide, N,N-dimethylcyanamide, adiponitrile, *p*-toluenesulfonic acid and type S-90 Houdry isomerization catalyst.

The catalytic abilities of the metal halides tested were in the order $Al_2Br_6 > Al_2Cl_6 > Al_2I_6 > Ga_2Br_6 > Ga_2Cl_6$, BCl_3, Fe_2Cl_6. This sequence is probably a good representation of the acidic character of these materials. The catalytic sequence of $Al_2X_6 >$

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(15) G. Calingaert and H. A. Beatty, THIS JOURNAL, **61**, 2748 (1939); see also A. E. Stern, *ibid.*, **62**, 1630 (1940).

(16) As defined by Calingaert[15] a redistribution reaction is one "in which all radicals or atoms of one kind, present in a mixture in which they are linked to one or more central groups or atoms of another kind, are interchanged between all the central groups present—the composition of the resultant mixture can be calculated from that of the reactants on the basis of random distribution of the interchanged radicals or atoms." Randomness appears to be a poor criterion for classification of reactions and H. A. Skinner has redefined a redistribution reaction as one in which bonds change in relative position but not in total number or formal character.[17]

(17) H. A. Skinner and T. F. S. Tees, *J. Chem. Soc.*, 3378 (1953); H. A. Skinner and N. B. Smith, *ibid.*, 2324, 3930 (1954); H. A. Skinner, *Rec. trav. chim.*, **73**, 991 (1954).

$Ga_2X_6 > Fe_2X_6, BX_3$ is also observed in the isomerization of hydrocarbons, the alkylation of benzene and other reactions.[13b]

The ethyl derivatives of aluminum, zinc, mercury and lead were ineffective catalysts for the disproportionation. Other results will show that methylaluminum bromides are also ineffective catalysts. Surprisingly, none of the organometallics employed reacted with ethyltrimethylsilane to a significant extent, even at 100°, since dimethyldiethylsilane was not obtained.

Few significant side reactions were observed under the reaction conditions of Table V. However, of particular interest was the observation that ferric chloride and antimony pentachloride were reduced with the formation of alkyl chlorides and chlorosilanes. Antimony pentachloride and ethyltrimethylsilane at 100° gave methyl chloride and ethyl chloride in an approximately 2 to 1 ratio, a result qualitatively consistent with the data of Table I. On the other hand, with ferric chloride, large amounts of ethyl chloride were formed, but only traces of methyl chloride could be detected. The products of the reaction of 1.5 mmoles of Fe_2Cl_6 and 70 mmoles of ethyltrimethylsilane (100°, 24 hr.) gave upon distillation 1.4 mmoles of ethyl chloride and 0.35 mmole of an ethylene–ethane mixture. Less than 0.05 mmole of methyl chloride was present. The recovered metal halide had been reduced to the ferrous state and a chlorosilane was found in the recovered ethyltrimethylsilane. Apparently the reaction

$$Fe_2Cl_6 + Me_3SiEt \longrightarrow 2FeCl_2 + Me_3SiCl + EtCl$$

occurs readily. The occurrence of this reaction possibly explains why ferric chloride is a less efficient catalyst than boron chloride in the disproportionation reaction whereas ferric chloride is usually observed to be the better Friedel–Crafts catalyst.[13b]

The results in regard to cleavage of silicon–alkyl bonds by metal halides, summarized in Table V, present a surprising pattern.

TABLE V

CLEAVAGE OF SILICON–ALKYL BONDS IN ETHYLTRIMETHYLSILANE BY METAL HALIDES AT 100°[a]

Metal halide	Reaction, %	$\frac{\text{Methyl cleavage}}{\text{Ethyl cleavage}}$
Al_2Br_6	3.5	>50[b]
$SbCl_5$	50–100	~2[c]
Fe_2Cl_6	100	<0.01[c]

[a] 0.5 g. of halide in 5 ml. of silane for 24 hr. [b] As methane and ethane after hydrolysis. [c] As methyl and ethyl chlorides.

The preferential cleavage of a methyl group by aluminum bromide is in accord with the known reactivities of methyl and ethyl groups toward electrophilic reagents.[14,18,19] In particular, the reaction of hydrogen chloride, iodine or mercury chloride with ethyltrimethyltin all give predominant methyl cleavage.[14,19] The oxidative cleavage of alkyl and aryl silicon–carbon bonds by ferric and antimony(V) chloride are well known,[20] and it has been suggested that these reactions involve unstable organometallic intermediates.[20b]

$$R_4M + SbCl_5 \longrightarrow R_3MCl + [RSbCl_4] \longrightarrow SbCl_3 + RCl$$

$$R_4M + Fe_2Cl_6 \longrightarrow R_3MCl + [RFe_2Cl_5] \longrightarrow 2FeCl_2 + RC$$

However, on this basis it is hard to see why aluminum bromide or gallium chloride attacks only the methyl group, ferric chloride attacks only the ethyl group and antimony pentachloride attacks both the methyl and ethyl groups of ethyltrimethylsilane.

Kinetics.—Table VI and Fig. 1 present evidence that the rate of disproportionation of ethyltrimethylsilane is dependent on the aluminum bromide concentration to the first power.

TABLE VI

EFFECT OF ALUMINUM BROMIDE AND ETHYLTRIMETHYLSILANE CONCENTRATIONS ON THE RATE OF DISPROPORTIONATION AT 80°

$[Al_2Br_6]$[a]	$[Me_3SiEt]$[a]	Time, hr.	Reaction,[b] %	Rate × 10^6, mole l.$^{-1}$ sec.$^{-1}$
0.1585	5.84	0–16	0–3.4	3.48
.0668	5.99	16	1.70	1.77
.0197	6.08	16	0.266	0.280
.156	0.230[c]	89	7.15	.0514
.151	.425[c]	42	4.29	.1205
.143	.742[c]	20	2.385	.246
.186	2.495[c]	16	5.55	2.40

[a] Mole l.$^{-1}$. [b] As defined in Table III. [c] Cyclohexane diluent.

In Fig. 2 the data of Table VI for the disproportionation in cyclohexane solution have been presented as a log–log plot. The slope of this plot is 1.5 indicating that the disproportionation reaction is 1.5 order in silane. The over-all kinetic equation for the aluminum bromide-catalyzed reaction is thus

$$-d[Me_3SiEt]/dt = k[Al_2Br_6][Me_3SiEt]^{1.5}$$

This equation has been observed to hold over a 10-fold range in silane concentration, 0.23–2.5 M, and a 8-fold range in aluminum bromide concentration, 0.02–0.16 M.

Effects of Solvent and Temperature on Rate.—In Table VII are summarized the specific rate constants for the disproportionation of ethyltrimethylsilane in cyclohexane and benzene solution and in the absence of any added solvent.

TABLE VII

EFFECTS OF SOLVENT AND TEMPERATURE ON THE DISPROPORTIONATION OF ETHYLTRIMETHYLSILANE

Solvent	Temp., °C.	$[Al_2Br_6]$[a]	$[Me_3SiEt]$[a]	Time, hr.	Reaction,[b] %	10^6k[c]
Me_3SiEt	90	0.156	5.74	7	2.95	3.13
Me_3SiEt	80	.1585	5.84	0–16	0–3.4	1.57[d]
C_6H_{12}	80	0.143–.186	0.230–2.495	16–89	2.4–7.2	2.96[e]
C_6H_6	80	.156	0.238	1	3.79	138.5
Me_3SiEt	70	.161	5.93	16	2.02	0.892
Me_3SiEt	60	.163	6.00	16	0.931	0.417
C_6H_6	60	.156	0.245	4	6.89	61.8
C_6H_6	40	.156	.250	10	6.35	22.7

[a] Mole l.$^{-1}$. [b] As defined in Table III. [c] In l., mole and sec. [d] From Table III. [e] From Fig. 2.

The reaction is about twice as fast in cyclohexane solution as when the silane is used as its own solvent and nearly 100 times faster in benzene solu-

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[18] M. S. Kharasch, *et al.*, THIS JOURNAL, **48**, 3130 (1926); **54**, 674 (1932).

[19] Z. M. Manulkin, *J. Gen. Chem.* (*USSR*), **13**, 42 (1943).

[20] (a) A. Y. Yakubovich and G. V. Motsarev, *ibid.*, **23**, 1414 (1953); (b) **23**, 1059 (1953).

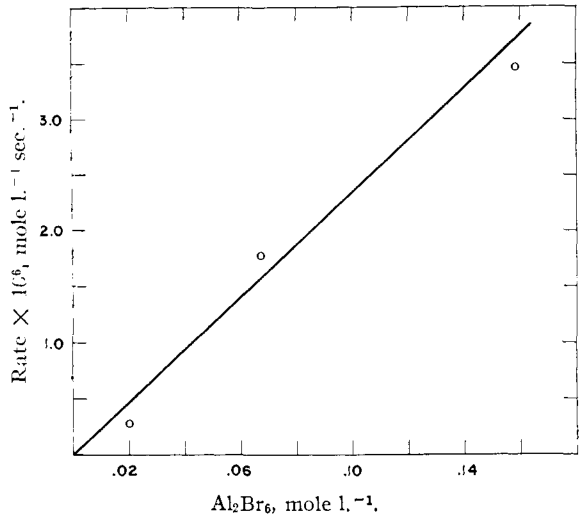

Fig. 1.—Effect of aluminum bromide concentration on the disproportionation of ethyltrimethylsilane at 80°.

tion. The data of Table VII gives an enthalpy of activation of 14.0 and 9.5 kcal. mole^{-1} in ethyltrimethylsilane and benzene solution, respectively. These are surprisingly low energies of activation for reactions which proceed to the extent of only a few per cent. per hour at 80°. The low rate of reactions are due to unusually low *PZ* factors in the Arrhenius equations. In benzene solution, the *PZ* factor is 2.95×10^2 ($\Delta S^{\ddagger}$ −48.6 e.u.) while in ethyltrimethylsilane solution the *PZ* factor is 1.82×10^3 ($\Delta S^{\ddagger}$ −45.0 e.u.).

Co-catalysts and Inhibitors.—The aluminum bromide-catalyzed disproportionation of ethyltrimethylsilane is co-catalyzed by traces of oxygen, moisture and numerous polar materials. Therefore, all kinetic experiments required elaborate and tedious techniques. In Table VIII are presented data on the effect of various additives on the rate of disproportionation. In only one case, trimethylaluminum, was inhibition noticed.

The effects of oxygen, water or hydrogen sulfide were extremely large. Only minimum rate enhancements can be calculated from the data with some of these co-catalysts since the reaction often reached equilibrium before analysis was performed. A similar effect of oxygen or water has also been noted in the aluminum bromide-catalyzed disproportionation of trimethylsilane and phenyltrimethylsilane.[13a] Oxygen was also a powerful promoter for the aluminum bromide-catalyzed reaction in benzene solution. At 40° ethyltrimethylsilane (0.250 *M*) in benzene containing 0.156 *M* aluminum bromide is disproportionated at an initial rate of 0.635%/hr. In the presence of 0.24 mmole of oxygen, 5 ml. of the above solution disproportionated to the extent of 55% in 1 hr. at 40° (equilibrium occurs when 57.6% of the silane has disproportionated). Water had only a small effect on the gallium bromide-catalyzed reaction and water or oxygen did not bring about disproportionation when added to inactive catalysts such as boron chloride, gallium chloride, ferric chloride and numerous other metal halides summarized in Table I.

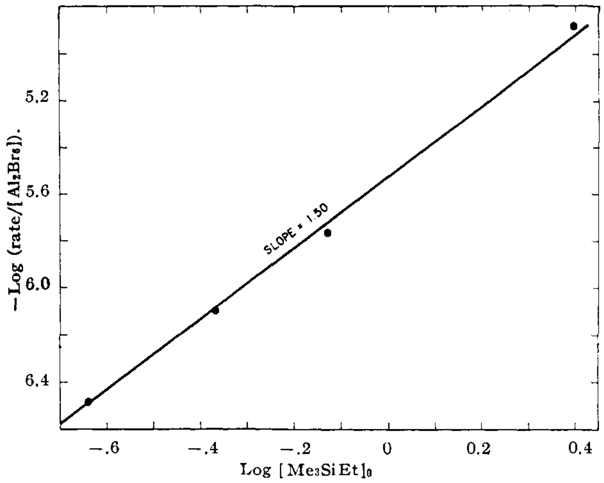

Fig. 2.—Correlation between rate and ethyltrimethylsilane concentration for the aluminum bromide-catalyzed disproportionation in cyclohexane solution.

Aluminum oxybromide, a possible product of the reaction of either water or oxygen with aluminum bromide, was synthesized and found to be equally as effective as mixtures of aluminum bromide with water or oxygen. A pronounced oxygen effect was also observed in aluminum chloride-catalyzed reactions. Because of the low solubility of aluminum chloride in the silane these reactions were heterogeneous. In Fig. 3 are presented results obtained by adding, under anhydrous conditions, 0.50 g. of powdered aluminum chloride to 5.0 ml. of ethyltrimethylsilane. In series A the contents of the ampoule were frozen in liquid nitrogen and evacuated to 1 mm. for 5 minutes. In series B the solutions were degassed by several freeze-thawings at 1 mm. It is estimated that series A contained approximately 0.02 mmole of oxygen or one part of oxygen per thousand parts of ethyltrimethylsilane. The data of Fig. 3 should not be compared with the quantitative data of Tables III–VIII.

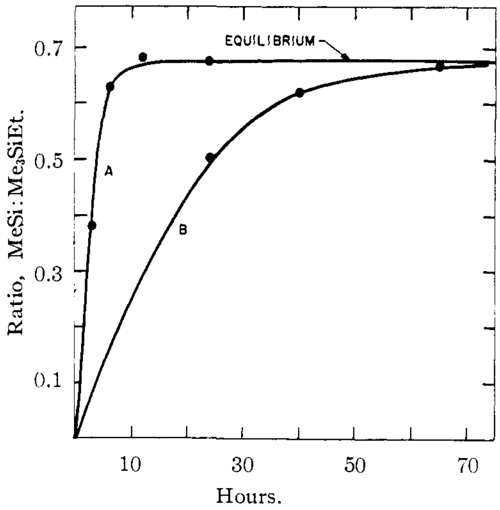

Fig. 3.—Aluminum chloride-catalyzed disproportionation of ethyltrimethylsilane at 100°: A, not degassed; B, degassed.

TABLE VIII

CO-CATALYSIS IN THE DISPROPORTIONATION OF ETHYLTRIMETHYLSILANE AT 80°[a]

Co-catalyst[b]	Time, hr.	Reaction,[c] %	Rel. rate
	Aluminum bromide catalyst		
None	16	3.38	1.0
Al_2Me_6	16	1.29	0.4
$ZnEt_2$[d]	2	0.55	1.3
Me_3SiBr	16	6.12	1.8
HCl	16	6.92	2.2
HBr	16	7.40	2.2
Et_2S	16	14.9	>4.4
i-PrBr	16	14.7	>4.4
MeBr	2	2.38	5.6
MeOH	2	2.12	5.0
EtOH	2	2.28	5.4
Et_2O	16	18.7	>5.5
Me_3N[d]	16	20.8	>6.2
Me_3N + HBr[d]	16	23.8	7.0
NH_3	16	25.2	>7.5
Me_2NCN	16	34.2	>10
Me_3SiOMe	2	6.04	14
H_2S[d]	2	36.2	> 86
H_2O	2	49.0	>116
O_2[e]	2	3.56	8.4
O_2[f]	2	58.0	>137
$O_2 + I_2$[g]	2	59.0	>140
"AlOBr"[d,h]	2	50.0	>118
Equilibrium	...	57.6	...
	Gallium chloride catalyst		
H_2O	500	<0.02	
O_2	500	< .02	
MeCl	16	< .02	
i-PrCl	16	< .02	
	Boron chloride catalyst		
H_2O	16	< .02	
i-PrCl	500	< .02	
	Gallium bromide catalyst		
None	90	0.12	1.0
H_2O	90	0.27	2.2

[a] 34 mmoles of Me_3SiEt, 1.87 mmoles of catalyst as MX_3. [b] 0.286 mmole. [c] As defined in Table III. [d] Heterogeneous. [e] 0.0125 mmole, 20 mm. oxygen pressure in ampoule. [f] 600 mm. oxygen pressure (0.30 mmole). [g] Aluminum iodide catalyst. [h] Containing 1.87 mmoles of aluminum and 0.29 mmole of oxygen atoms.

TABLE IX

EFFECT OF ETHYLMETALLICS ON PRODUCTS OF THE DISPROPORTIONATION OF ETHYLTRIMETHYLSILANE AT 80°[a]

Ethylmetallic[b]	Time, hr.	Reaction,[c] %	Product composition Me_2SiEt_2/Me_4Si
None	16	3.38	0.92
$ZnEt_2$[d]	2	0.55	3.0
$HgEt_2$[d]	2	0.30	2.6
Al_2Et_6	2	0.48	1.3
$PbEt_4$[d]	2	1.20	2.0

[a] 34 mmoles of Me_3SiEt, 1.87 mmoles of $AlBr_3$. [b] Approximately 0.3 mmole. [c] As defined in Table III. [d] Heterogeneous.

Although aluminum, zinc, lead or mercury alkyls did not react with ethyltrimethylsilane at 100°, reaction was observed at 80° in the presence of aluminum halides, although in general the organometallics did not promote the rate of disproportionation.

$$ZnEt_2 + Me_3SiEt \xrightarrow{Al_2Br_6} Me_2SiEt_2 + MeZnEt$$

Table IX summarizes pertinent data.

Discussion

Evidence against Carbonium Ion Intermediates.—George, Sommer and Whitmore have presented data that isopropyl groups do not rearrange in the disproportionation of substituted silanes.[10b] This is a convincing argument that the reaction does not involve a carbonium ion intermediate, *e.g.*

$$R^+ + R_3SiR' \longrightarrow R_4Si + R'^+$$

Additional evidence against a carbonium intermediate is the fact that benzene, a carbonium ion trap,[21] does not retard the aluminum bromide-catalyzed disproportionation and that isomerization of cyclohexane to methylcyclopentane does not occur when cyclohexane is used as a solvent for the disproportionation.[13c] Furthermore, alkyl halides have but a small accelerating effect upon the aluminum bromide-catalyzed reaction. That this small effect is not due to carbonium ion formation is indicated by the fact that methyl bromide is as effective a co-catalyst as isopropyl bromide. In the presence of Lewis acids isopropyl bromide is known to be more effective than methyl bromide as a source of carbonium ions.[13b] Finally, mixtures of ethyl bromide, tetramethylsilane and aluminum bromide at 80°, under conditions where the ethyl bromide was completely destroyed, gave no indication of the formation of ethyltrimethylsilane.

Evidence against Organoaluminum Intermediates.—Conclusive evidence against the Calingaert mechanism[11] is furnished by the observation that trialkylaluminum compounds are ineffective catalysts for disproportionation and that alkylaluminum halides are not as effective as catalysts as the aluminum halides. Moreover, water, oxygen and other materials, which would be expected to destroy an organoaluminum intermediate, are actually powerful co-catalysts in the disproportionation of ethyltrimethylsilane. Thus, although organoaluminum compounds can be detected from the reaction of a tetraalkylsilane with aluminum chloride, these materials are not intermediates in the disproportionation reaction.

Evidence against Siliconium Ion Intermediates.—Some of the arguments advanced in regard to carbonium ion intermediates can also be used as evidence against the occurrence of siliconium ion intermediates. Unfortunately these arguments are somewhat clouded by the fact that the reactivity of a siliconium ion is relatively unknown. If a siliconium ion has a reactivity similar to a carbonium ion, then the absence of isomerization of cyclohexane, the lack of retardation by benzene, and the absence of silylation products of benzene[13c] argue against the formation of siliconium ion intermediates. A siliconium ion could possibly be less reactive than a carbonium ion thus eliminating the argument based on the lack of cyclohexane isomerization. However, since a carbonium ion will attack benzene in preference to tetramethylsilane,[13c] the lack of retardation by benzene and the absence

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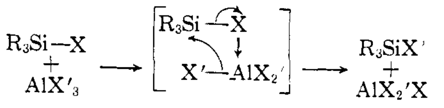
(21) H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **71**, 749 (1949); **72**, 4055 (1950).

of silylation products in benzene solution is still pertinent evidence against a free siliconium ion. Further evidence against the siliconium ion is furnished by a consideration of co-catalysis. Bromotrimethylsilane and ethoxytrimethylsilane would be expected to yield a siliconium ion by interaction with aluminum bromide much more readily than would ethyltrimethylsilane. Although these materials did promote the rate of the aluminum bromide-catalyzed disproportionation of ethyltrimethylsilane, the promotion was small, at least when compared with the effect of an alkyl halide on aluminum halide-catalyzed hydrocarbon isomerization.[13b,22] The addition of bases, such as trimethylamine or ammonia, to the aluminum bromide-catalyzed disproportionation of ethyltrimethylsilane resulted in an increase in the rate of reaction. These materials certainly would act as traps for siliconium and carbonium ions, or even ion-pairs, and their effect upon the disproportionation reaction is additional evidence against a siliconium ion intermediate.[23] One of the best siliconium ion traps, stable in the presence of aluminum bromide, would be a negatively charged ion. The disproportionation of ethyltrimethylsilane in the presence of aluminum bromide, trimethylamine and hydrogen bromide therefore was investigated. Trimethylamine plus hydrogen bromide actually promoted the reaction.



$$R_3Si^+ + R_3N: \longrightarrow R_3Si^-\overset{+}{N}R_3$$

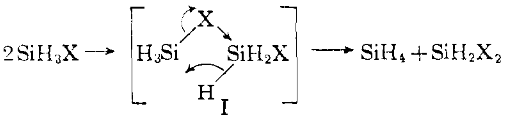
$$R_3N + HBr + Al_2Br_6 \longrightarrow R_3NH^+Al_2Br_7^-$$

$$R_3Si^+ + Al_2Br_7^- \longrightarrow R_3SiBr + Al_2Br_6$$

Moreover, the promotion was greater than would have been expected for a similar quantity of trimethylbromosilane. Again, these facts argue against the occurrence of free siliconium ions.

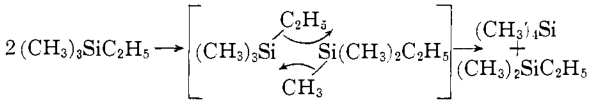
Proposed Mechanism.—Any proposal in regard to the mechanism of the metal halide-catalyzed disproportionation of substituted silanes must be in accord with the facts: (a) The reaction will occur slowly at elevated temperatures in the absence of catalysts; (b) the ability of metal halides to catalyze the reaction is proportional to their strength as Lewis acids; (c) the reaction is not autocatalytic; (d) the reaction has an extremely low *PZ* factor; (e) the reaction occurs more readily in benzene than in cyclohexane solution; (f) there is no reaction with solvent in either benzene or cyclohexane solution; (g) the reaction is first order in aluminum bromide and one and one-half order in ethyltrimethylsilane; (h) traces of many polar substances accelerate the reaction although in large amounts these materials may completely destroy the activity of the catalyst; (i) oxygen, water and hydrogen sulfide are powerful accelerators for the aluminum bromide-catalyzed reaction; (j) exchange between two electronegative groups occurs easily; other things being equal hydrogen and phenyl groups migrate more readily than alkyl groups[13a]; (k) carbonium ions, siliconium ions and organoaluminum compounds can be eliminated as reaction intermediates.

The observations cited above appear to be best explained by the Zemany–Price mechanism of disproportionation.[10c] This mechanism bears a close resemblance to the suggested mechanism of thermal disproportionation of halosilanes.[24]



I

In the case of ethyltrimethylsilane we have demonstrated that the vapor in Pyrex glass ampoules will disproportionate, albeit slowly, at 250° under conditions where no other reaction products can be found. Here we believe disproportionation involves a four-centered transition state similar to I.



The reaction is pictured as occurring with electrophilic substitution on carbon and nucleophilic substitution on silicon. Nucleophilic substitution on silicon can occur *via* a transition state wherein the entering and leaving groups are oriented at approximately 90° to each other.[25]

Similar transition states have been suggested for the disproportionation of certain mercury compounds[26] and for the disproportionation of trialkylboranes.[27] Analogous reactions are known for compounds aluminum,[28] tin,[29a] lead[29b,11] and zinc.[29c] These thermal disproportionations usually occur more readily than the analogous reaction in the silicon series, possibly because in some cases the organometallic reagent is a Lewis acid and can serve as its own catalyst. In the case of aluminum com-

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[22] Aluminum halides and halosilanes do readily undergo halogen exchange [C. Eaborn, *J. Chem. Soc.*, 2755 (1949)]. However, this process does not necessarily involve the formation of a siliconium ion since a cyclic process or a concerted process are easily visualized.

[23] This argument is weakened by the fact that the amine was present as the aluminum bromide complex and that we have no data indicating that the amine could not have been consumed rapidly at the beginning of the reaction period.

[24] A. G. MacDiarmid, *Quart. Revs.*, **10**, 208 (1956).

[25] L. H. Sommer and O. F. Bennett, THIS JOURNAL, **79**, 1108 (1957); L. H. Sommer, O. F. Bennett, P. G. Campbell and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957).

[26] S. Winstein, T. G. Traylor and C. S. Garner, *ibid.*, **77**, 3741 (1955); S. Winstein and T. G. Traylor, *ibid.*, **77**, 3747 (1955); **78**, 2597 (1956); D. E. Applequist and J. D. Roberts, *Chem. Revs.*, **54**, 1065 (1954). Recently it has been reported that alkyl groups maintain their configuration in the disproportionation of alkylmercury compounds [F. R. Jensen, L. O. Whipple, O. K. Wedegaertner and J. A. Landgrebe, THIS JOURNAL, **81**, 1262 (1959)].

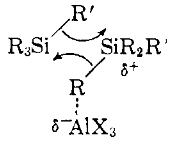
[27] T. D. Parsons and D. M. Ritter, *ibid.*, **76**, 1710 (1954); T. D. Parsons, M. B. Silverman and D. M. Ritter, *ibid.*, **79**, 5091 (1957); G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *ibid.*, **79**, 5192 (1957).

[28] (a) A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940); (b) K. S. Pitzer and H. S. Gutowsky, THIS JOURNAL, **68**, 2204 (1946).

[29] (a) K. A. Kozeschkow, *Ber.*, **62**, 996 (1929); **66**, 1661 (1934); G. J. M. van der Kerk and J. G. A. Luiften, *J. Appl. Chem.*, **6**, 49 (1956); W. C. Davies, S. T. Bowden, C. Edwards, V. E. Davis and L. H. Thomas, *J. Chem. Soc.*, 1947 (1946); (b) P. R. Austin, THIS JOURNAL, **54**, 3287 (1932); (c) Krause and Fromm, *Ber.*, **59**, 931 (1926)

pounds electron-deficient bonding is such that structures similar to I are stable.[28b]

In the presence of a Lewis acid the transition state for disproportionation of a substituted silane can be drawn as[30]



II

In a non-polar medium a transition state similar to II would be expected to give an unusually low *PZ* factor in the Arrhenius equation since low *PZ* factors are generally observed for reactions proceeding through intermediates or transition states which involve considerable ionic character in a non-polar media.[31]

The 100-fold rate increase noted in going from cyclohexane to benzene as solvent may thus be explained as due to increased solvation of the transition state. This increase in rate occurs even though benzene, a base, must cause a decrease in the acidity of aluminum halides. Moreover, the increases in rate observed when small amounts of polar substances, such as ethers, alcohols, amines or nitriles are added to the aluminum bromide-catalyzed reaction may also result from solvation of this transition state by the highly ionic complexes formed between these substances and aluminum bromide.

The fact that hydrogen and phenyl groups migrate more readily than alkyl groups is consistent with II since it is well known that the attack of an electrophile on a silicon compound results in the cleavage of silicon–hydrogen and silicon–phenyl bonds in preference to silicon–alkyl bonds.[13a,32]

The over-all rate expression

$$-d[\text{silane}]/dt = k[\text{silane}]^{1.5}[\text{Al}_2\text{Br}_6]$$

is consistent with a reaction proceeding *via* II if the following reaction sequence is involved.

$$\text{Al}_2\text{Br}_6 + \text{R}_3\text{SiR}' \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{III}}{\text{R}_3\text{SiR}'\text{---Al}_2\text{Br}_6} \quad (1)$$

$$\text{III} + \text{Al}_2\text{Br}_6 \xrightarrow[\text{slow}]{k_2} \underset{\text{IV}}{\text{R}_3\text{SiR}'\text{----AlBr}_3} + \text{Al}_3\text{Br}_9 \quad (2)$$

$$\text{Al}_3\text{Br}_9 + \text{R}_3\text{SiR}' \xrightarrow{\text{fast}} \text{IV} + \text{Al}_2\text{Br}_6 \quad (3)$$

$$2\text{IV} \xrightarrow{k_4} 2\text{R}_3\text{SiR}' + \text{Al}_2\text{Br}_6 \quad (4)$$

Under steady state conditions the concentration of IV will be

$$[\text{IV}] = (2k_1k_2/k_4k_{-1})^{1/2}[\text{Al}_2\text{Br}_6][\text{R}_3\text{SiR}']^{1/2}$$

and the over-all rate expression for the process

$$\text{IV} + \text{R}_3\text{SiR}' \xrightarrow{k_5} \text{II} \longrightarrow \begin{array}{l} \text{R}_4\text{Si} + \text{R}_2\text{SiR}_2'\text{----AlBr}_3 \\ \qquad\qquad \text{or} \\ \text{R}_2\text{SiR}'_2 + \text{R}_4\text{Si----AlBr}_3 \end{array}$$

becomes

$$\text{rate} = (2k_1k_2/k_4k_{-1})^{1/2}k_5[\text{Al}_2\text{Br}_6][\text{R}_3\text{SiR}']^{1.5}$$

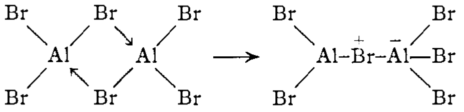
The reaction is formulated as a chain reaction since the following reactions should occur readily

$$\text{R}_3\text{SiR---AlBr}_3 + \text{R}_3\text{SiR}' \xrightarrow{\text{fast}} \text{R}_3\text{SiR} + \text{IV}$$

$$\text{R}_2\text{SiR}'_2\text{---AlBr}_3 + \text{R}_3\text{SiR}' \xrightarrow{\text{fast}} \text{R}_2\text{SiR}'_2 + \text{IV}$$

particularly at the early stages of the reaction when the concentration of $\text{R}_3\text{SiR}'$ is high compared with R_4Si or $\text{R}_2\text{SiR}'_2$.[33]

The conclusion that III does not lead to disproportionation, whereas IV does, is consistent with the interpretation that AlBr_3 is a more acidic species than Al_2Br_6 since for Al_2Br_6 to function as an acid there must be a molecular reorganization or dissociation, *e.g.*



The need for a very strong acid in the disproportionation of ethyltrimethylsilane is indicated by the fact at 80–100° only the strongest of the Lewis acids catalyze the reaction and that even for these materials great differences between catalytic ability were observed.[34] Our interpretation suggests that other kinetic patterns may be observed for other disproportionations. For example, a disproportionation which occurs very readily may not require the formation of IV and may occur *via* a bimolecular reaction between III and the silane.

Further support for a mechanism involving the intermediate IV comes from the fact that the methyl bromide–aluminum bromide complex, a complex which involves only partial ionization of the carbon–bromine bond,[35] has a reactivity similar to that postulated for IV. Both the methyl bromide complex and IV quantitatively attack a molecule of tetraalkylsilane in preference to benzene.[13c]

We prefer to consider IV as having a slightly polarized silicon–alkyl bond due to electron deficient bonding with the Lewis acid. On a resonance basis, IV can be considered to be the hybrid of structures IVa and IVb.

$$\underset{\text{IVa}}{\text{R}_3\text{Si-R}'\text{AlX}_3} \longleftrightarrow \underset{\text{IVb}}{\text{R}_3\text{Si}^+\text{R}'\text{AlX}_3^-}$$

Whether the complex is best described by the sym-

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[30] Transition states similar to II can be formulated for numerous other reactions of alkyl and halosilanes.[13c]

[31] A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., Ch. 7. For example, the entropies of activation for the gallium bromide-catalyzed methylation, ethylation or isopropylation of toluene in toluene solution are in the range of −19 to −22 e.u. [S. U. Choi and H. C. Brown, THIS JOURNAL, **81**, 3315 (1959)].

[32] H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

[33] Zemany and Price[10c] report a somewhat different kinetic order for the aluminum chloride-catalyzed disproportionation of dimethyl dichlorosilane at 350°, $-d[\text{silane}]/dt = k[\text{Al}_2\text{Cl}_6][\text{silane}]$. Their interpretation of this rate equation involves the formation of a $(\text{CH}_3)_2\text{SiCl}_2\text{–AlCl}_3$ complex, undissociated at 350°. This is a surprising conclusion since aluminum chloride is only slightly soluble in chlorosilanes and there is no appreciable heat of solution at room temperature. At 350° the equilibrium $\text{Al}_2\text{Cl}_6 \rightleftarrows 2\text{AlCl}_3$ is important and possibly in the presence of any amount of excess silane the equilibrium is driven completely to the right due to the formation of the 1-1 complex.

[34] There is abundant evidence that Lewis acids can complex with chlorosilanes [A. Y. Yakubovich and G. V. Motsarev, *Doklady*, **99**, 1015 (1954)]. Weaker catalysts may be used for reactions which intrinsically occur more readily. Thus interchange of negative groups, such as halogen and alkoxy, is reportedly catalyzed by ferric chloride [R. O. Sauer, U. S. Patent 2,421,653 (1947)] or hydrogen chloride [M. J. Hunter and P. C. Servais, U. S. Patents 2,485,928 (1949), 2,626,273 (1953)].

[35] H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

bolism of IV or as the ion-pair IVb is difficult to determine unambiguously, even if stereochemical evidence were available. Both IV and IVb, as well as III, should show some reactivity toward some of the additives which were found to accelerate the reaction, *e.g.*, hydrogen bromide, amines and alcohols. As pointed out previously these additives may be complexed with aluminum bromide (*e.g.*, amines, ethers, alcohols) and thereby unavailable for reaction or they may react with III or IV during the early stages of the reaction (*e.g.*, hydrogen bromide). In searching for a chemical additive which might destroy the ion-pair IVb but not the complex IV, it was found that iodine is not readily consumed in the aluminum iodide-catalyzed disproportionation of ethyltrimethylsilane and that iodine did not retard the rate of reaction. We cannot conceive of IVb not reacting with iodine.

In those cases where the co-catalyst used could lead to the formation of hydrogen bromide or bromotrialkylsilane the acceleration may involve a series of reactions of the bromosilane.

$$(CH_3)_3SiBr + (CH_3)_3SiC_2H_5 \xrightarrow{Al_2Br_6} (CH_3)_4Si + (CH_3)_2Si(C_2H_5)Br$$

$$(CH_3)_2Si(C_2H_5)Br + (CH_3)_3SiC_2H_5 \xrightarrow{Al_2Br_6} (CH_3)_2Si(C_2H_5)_2 + (CH_3)_3SiBr$$

This process cannot be important in the absence of a promoter, even though there is evidence for formation of the bromosilane

$$R_4Si + Al_2Br_6 \longrightarrow R_3SiBr + Al_2Br_5R$$

because (1) the disproportionation is not autocatalytic, (2) the above equilibrium lies far to the left and (3) the accelerating effect of an appreciable quantity of bromotrimethylsilane is quite small.

The Oxygen Effect.—The only observation not yet explained by the proposed mechanism is the powerful acceleration effect observed for water, oxygen and hydrogen sulfide. It is believed that these materials function by the formation of aluminum oxybromide, possibly $Br_2AlOAlBr_2$, or its sulfur derivative. Aluminum oxybromide made by treating aluminum bromide with water followed by removal of the hydrogen bromide[36] proved to be as effective a catalyst as aluminum bromide–water mixtures. In the presence of an excess of aluminum bromide and tetraalkylsilane, the reaction of water or hydrogen sulfide with aluminum bromide should readily go to completion because of the reactivity of the alkylsilane toward hydrogen bromide.

$$Al_2Br_6 + H_2O \rightleftharpoons Al_2Br_4O + 2HBr$$

$$HBr + R_4Si \xrightarrow{Al_2Br_6} RH + R_3SiBr$$

Similarly, oxygen apparently reacts with aluminum halides to form the oxyhalide. This equilibrium evidently lies far to the left except for aluminum

$$Al_2X_6 + {}^1/_2O_2 \rightleftharpoons Br_2AlOAlBr_2 + X_2$$

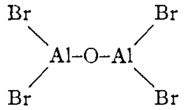
iodide where iodine is formed in significant quantities. In the presence of an alkylsilane the oxidation reaction will be driven to completion by the reaction of halogen with the alkylsilane.

$$X_2 + R_4Si \xrightarrow{Al_2X_6} RX + R_3SiX$$

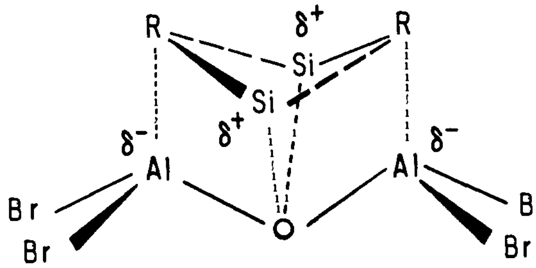
In support of this conclusion the reaction of oxygen, aluminum bromide and trimethylbromosilane at 80° produced methyl bromide in a high yield.[13a]

Oxygen acceleration has been noted in *n*-butane–isobutane and methylcyclopentane–cyclohexane isomerization, particularly in the presence of hydrogen bromide, but in this case the oxygen effect involves oxidation of the hydrocarbon leading to the formation of alcohols or hydroperoxides which can give rise to carbonium ions.[37] In the absence of light, or hydrogen bromide, no effect of oxygen is observed in the methylcyclopentane isomerization.[13b] In silane disproportionation the oxygen effect was observed either in the presence or absence of light. Substitution of various free radical generators for oxygen and aluminum bromide failed to bring about any disproportionation of ethyltrimethylsilane.

There are several possible explanations for the superior catalytic ability observed for aluminum oxybromide and its sulfur derivative. The oxybromide would presumably have the structure



with each aluminum atom in a trigonal configuration since no symmetrical structure with tetrahedral configuration for the aluminum atoms can be written. Since a trigonal aluminum atom should be more acidic than a tetrahedral aluminum atom (as in aluminum bromide) the aluminum oxybromide may be a more powerful Lewis acid than aluminum bromide.[38] In addition, aluminum oxybromide can be a bifunctional acid and its superior catalytic ability in silane disproportionation may result from the formation of the transition state



As pictured, by electron deficient bonding[39] each carbon atom would be in an octahedral configuration, for which there is adequate evidence in other organometallic materials,[40] while each silicon atom would be bonded to five other atoms and would be

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[36] R. C. Wackher and H. Pines, THIS JOURNAL, **68**, 1642 (1946).

[37] (a) H. Pines and R. C. Wackher, *ibid.*, **68**, 599 (1946); (b) H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **72**, 4304 (1950).

[38] Acceleration of aluminum bromide-catalyzed isomerizations by water have been postulated as involving $AlBr_2OH$, a species apparently more acidic than aluminum bromide, since at 25° it apparently can abstract a hydride ion from *n*-butane whereas aluminum bromide cannot [R. C. Wackher and H. Pines, *ibid.*, **68**, 2518 (1946)]. Pines and Wackher prepared samples of aluminum oxybromide from prolonged contact of oxygen with aluminum bromide which would isomerize *n*-butane to isobutane, possibly because of the increased acidity of the catalyst.[37a]

[39] See, for example, P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

[40] R. E. Rundle and J. H. Sturdivant, THIS JOURNAL, **69**, 1561 (1947).

in position to utilize some of the unbonded electrons on the oxygen atom for formation of a sixth bond. As in II, negative charge would be concentrated on the aluminum and carbon atoms and positive charge on the silicon atoms.

Alcohols are much less efficient accelerators of disproportionation than water or oxygen and had an effect approximately equivalent to ethers. Evidently an alkoxyaluminum bromide, which would exist as a bridged structure, is not a particularly stronger acid than aluminum bromide. This conclusion is in agreement with previous conclusions of Pines and Wackher who found no catalytic activity in *n*-butane–isobutane isomerization at 25° for aluminum bromide or $(C_2H_5OAlBr_2)_2$.[36–38]

Experimental

Preparation of Reaction Mixtures.—In the original stages of this work reaction mixtures were prepared by weighing a desired amount of catalyst into a thoroughly dried ampoule in a nitrogen dry-box. Ethyltrimethylsilane was added by pipet and the ampoule evacuated and sealed under reduced pressure. Results summarized in Tables I and II and some of the results of Table IV were obtained in this manner. Although this technique was satisfactory for equilibrium studies and for a rough screening of catalysts, it was woefully inadequate for quantitative results.

The final technique, used for all quantitative rate studies, involved a Stock-type vacuum apparatus containing no greased stopcocks.[41] Reagents were stored over sodium mirrors in the vacuum line for several weeks before their use. Aluminum and gallium halides were prepared by the reactions of hydrogen halides or iodine with the metals in bulbs containing a break-off tip. These bulbs were sealed to the vacuum apparatus and the apparatus thoroughly flamed at 10^{-6} mm. pressure. The apparatus was further pumped at 10^{-6} mm. for 24 hours before the reaction mixtures were prepared. Further flamings, or longer pumping periods, did not affect the measured rates.

Samples were prepared by opening the break-off tip to the bulb used for catalyst preparation. Excess hydrogen halide was removed and the catalyst was sublimed into an ampoule which was an integral part of the original bulb used for catalyst preparation. The catalysts were condensed at 0 to −80°. Samples of ethyltrimethylsilane were measured either by liquid volume (most experiments involve 5 ml. of silane measured at 0°) or as a gas in a bulb of standard volume.

Solvents were measured in the vacuum line according to their liquid volume and the solvent and ethyltrimethylsilane then added to the catalyst ampoule. The contents of the ampoule were degassed by freeze-thawings, non-condensable gases never being detected. The ampoules were sealed and heated for the desired periods of time in thermostated baths. Although the quantities of reagent could be carefully measured, the exact molar concentrations never were measured except for mixtures of aluminum bromide and ethyltrimethylsilane alone. Experimentally, between 60 and 80°, and over the range of aluminum bromide concentrations employed, the volume of mixtures of aluminum bromide and ethyltrimethylsilane followed the equation

$$V_f = V_i + 320 \text{ (mole } Al_2Br_6)$$

where V_f and V_i are final and initial volumes at the same temperature. The density of ethyltrimethylsilane experimentally measured between 0 and 100° followed the equation grams/ml. = 0.701 − 0.00096t, where t is the temperature in °C. For mixtures of aluminum bromide, ethyltrimethylsilane and solvent the final volume of the solution was computed by calculating the volume that the pure solvent and pure ethyltrimethylsilane would occupy at the desired reaction temperature. No volume change in mixing was assumed and the effect of aluminum bromide on the volume of solution was assumed to be the same as its effect on the volume of pure ethyltrimethylsilane. Volume-temperature corrections for cyclohexane and benzene were taken from the "International Critical Tables." The quantities of reagents used and the calculated final volume of the solutions, for the experiments previously summarized in Tables VI and VII, are given in Table X.

TABLE X

SUMMARY OF CALCULATED VOLUMES FOR VARIOUS REACTION MIXTURES

Reactants		Solvent[a]		Calcd. volume	
Me_3SiEt[b]	Al_2Br_6[b]	C_6H_6	C_6H_{12}	ml. and	temp., °C.
4.86	0.935	..	5.0	6.55	(80)
2.635	.935	..	5.0	6.18	(80)
1.43	.935	..	5.0	5.98	(80)
1.43	.935	5.0	..	5.98	(80)
1.43	.900	5.0	..	5.83	(60)
1.43	.890	5.0	..	5.70	(40)
12.55	.935	..	2.46	5.03	(80)
34.4	.935	..	..	5.80	(70)
34.4	.935	..	..	5.90	(80)
34.4	.935	..	..	6.00	(90)
34.4	.383	..	..	5.72	(80)
34.4	.111	..	..	5.64	(80)

[a] Ml. at 10°. [b] Mmole.

Analysis.—After the desired reaction periods the reaction mixtures were frozen in liquid nitrogen and the ampoules broken open. The ampoules were attached to a vacuum system and evacuated at liquid nitrogen temperature. The contents of the ampoule then were allowed to distil to a trap containing 5 ml. of a frozen 10% aqueous sodium hydroxide solution at liquid nitrogen temperature. When the transfer was complete the trap was sealed by stopcocks, and the contents of the trap melted and shaken. The contents of the trap were then allowed to transfer under vacuum through a tube packed with solid sodium hydroxide and were condensed in a liquid nitrogen trap. The tetramethylsilane, ethyltrimethylsilane and diethyldimethylsilane transferred considerably more rapidly than the water. In cases where an accurate measure of the quantity of diethyldimethylsilane formed was needed the sodium hydroxide trap was omitted.

The contents of the final trap were melted and stored at −80°. Samples at −80° were injected into a Perkin–Elmer model 154B vapor fractometer using helium carrier gas at 30°. In a 2-m. "A"-column (purportedly di-*n*-decyl phthalate) typical relative retention times were Me_4Si:Me_3SiEt:Me_2SiEt_2 = 1.0:3.1:10.2. Calibration with prepared samples over the concentration range employed gave the equations

$$\frac{\text{mole } Me_4Si}{\text{mole } Me_3SiEt} = (1.13)\,\frac{\text{area } Me_4Si \text{ peak}}{\text{area } Me_3SiEt \text{ peak}}$$

$$\frac{\text{mole } Me_2SiEt_2}{\text{mole } Me_3SiEt} = (1.09)\,\frac{\text{area } Me_2SiEt_2 \text{ peak}}{\text{area } Me_3SiEt \text{ peak}}$$

The calibration factor for tetramethylsilane and ethyltrimethylsilane mixtures is in excellent agreement with thermal conductivity expected on the basis of molecular weight. However, the calibration factor for mixtures of ethyltrimethylsilane and diethyldimethylsilane is not in agreement with thermal conductivity and probably results because the diethyldimethylsilane peak is quite broad compared with the ethyltrimethylsilane peak. Measurement of the mole ratio Me_4Si:Me_3SiEt involved an uncertainty of not more than ±1%.

Reagents.—Ethyltrimethylsilane was prepared by the reaction of ethylmagnesium bromide with purified chlorotrimethylsilane in ethyl ether solution. The material was carefully rectified in a column of about 25 theoretical plates. Constant boiling material, having a constant refractive index and containing no impurity detectable by gas–liquid chromatography, was stored over a sodium mirror in the vacuum system. Two different preparations gave the same kinetic results. Tetramethylsilane was purified by distillation through a low temperature Podbielniak. Its purity was estimated to be greater than 99.9%. Diethyldimethylsilane was obtained by distillation of disproportionated ethyltrimethylsilane. The sample used for calibration of the analytical procedure contained 1% of ethyltrimethylsilane for which a correction was applied. Phillip Petroleum Co. research grade benzene and cyclohexane

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[41] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948

(>99.9% pure) were stored over sodium mirrors in the vacuum line.

Catalysts.—The general technique of preparation of aluminum and gallium halides was described previously. The bulb in which the catalyst was to be prepared and the attached ampoule in which the eventual disproportionation reaction was to be conducted were thoroughly washed with water. The bulb and ampoule were dried under reduced pressure and then thoroughly dried and degassed at 10^{-6} mm. by heating with bunsen burner. Prior to the final degassing, a weighed amount of freshly polished C.P. aluminum wire (Fisher Scientific Co.) or purified gallium (Fisher Scientific Co.) was added to the bulb and, after degassing, a 100% excess of hydrogen chloride or bromide was added. The metal halide was produced by heating with a bunsen burner. The same catalytic efficiency was observed when Fisher C.P. aluminum wire, commercial aluminum foil (Reynolds Wrap) or a special sample of high purity aluminum (containing 0.006% silicon, 0.009% iron and 0.005% copper) furnished by the Aluminum Co. of America was used. Matheson Co. C.P. anhydrous hydrogen bromide and chloride were degassed in the vacuum line and a tensiometrically homogeneous middle fractions used for catalyst preparation. C.P. anhydrous hydrogen bromide and hydrogen bromide prepared from the bromination of tetralin gave identical results as judged from the catalyst efficiency. Aluminum iodide was prepared from the reaction of a weighed amount of C.P. iodine with an excess of aluminum foil. The boron fluoride and chloride were Matheson Co. C.P. grade. Tensiometrically homogeneous middle fractions were used. Resublimed C.P. ferric chloride was weighed and sealed under an inert atmosphere into an ampoule with a break-off tip which was then sealed to the final reaction ampoule which was in turn sealed to the vacuum line. After the vacuum line had been thoroughly dried, the break-off tip was opened and the ferric chloride sublimed into the reaction ampoule. Zirconium tetrachloride was handled in the same manner. Antimony pentachloride was measured by volume and distilled into the reaction ampoule. Most of the other catalysts summarized in Table III were weighed into dried ampoules in a nitrogen dry-box, the ampoule attached to a vacuum line by a greased joint and ethyltrimethylsilane added. This procedure, if used for aluminum bromide, would have resulted in a pronounced acceleration due to traces of moisture.

Co-catalysts.—The co-catalysts were measured by *PVT* relationship in a bulb of standard volume. The co-catalysts were always of C.P. grade or else were specially purified. Where necessary the co-catalysts were dried by sodium mirrors or by lithium aluminum hydride. Oxygen was generated in the vacuum line by heating silver oxide and the quantity added to the reaction ampoule estimated from the free space in the ampoule, the average temperature and the pressure.

Aluminum oxybromide was prepared by treating a sample of aluminum bromide, prepared as described previously, with a measured amount of water vapor. The ampoule was sealed and heated at 89° for 72 hr. The ampoule was reattached to the vacuum line by another break-off tip and the condensable gases removed and measured at 0°. From 1.87 mmoles of $AlBr_3$ and 0.29 mmole of water, there was obtained 0.49 mmole of hydrogen bromide (85%).

The products of the reaction of ethyl bromide, tetramethylsilane and aluminum bromide were carefully examined for the formation of ethyltrimethylsilane. From 34 mmoles of tetramethylsilane, 2.9 mmoles of ethyl bromide and 1.87 mmoles of aluminum bromide (as $AlBr_3$) heated at 80° for 24 hr. less than 0.003 mmole of ethyltrimethylsilane (the limit of detection by gas–liquid chromatography) could be found. Propane and other hydrocarbons were found. Addition of traces of water gave a complex mixture of hydrocarbons, but again ethyltrimethylsilane could not be detected.

Acknowledgment.—The vapor fractometers were operated by Dr. E. H. Winslow and Mr. E. M. Hadsell. Mr. D. E. McBournie assisted in some of the experimental work. Ethyltrimethylsilane was prepared by Dr. J. R. Ladd. Rectifications were performed by Mrs. M. M. Grenoble and Mr. E. M. Hadsell.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Catalysis by Metal Halides. II. The Disproportionation of Trimethylsilane, Phenyltrimethylsilane and Bromotrimethylsilane

BY GLEN A. RUSSELL[1]

RECEIVED JANUARY 29, 1959

The relative rates of disproportionation of compounds of the type Me_3SiR indicate the relative intermolecular migratory tendency in the aluminum bromide-catalyzed reactions as $H > C_6H_5 > C_2H_5$. This migratory sequence is identical with the reactivity of R in Me_3SiR toward electrophilic reagents and supports a disproportionation mechanism involving electrophilic attack on carbon or hydrogen and nucleophilic attack on silicon. Side reactions in the disproportionation of trimethylsilane and phenyltrimethylsilane catalyzed by Lewis acids are discussed. It has been found that trimethylsilane will reduce gallium(III) bromide to gallium(II) bromide or gallium(III) chloride to gallium metal. The effects of oxygen and water on the aluminum bromide-catalyzed disproportionation are discussed and the effect of the polar nature of non-migrating groups in these disproportionations is considered.

The preceding and succeeding communications present data from which the mechanism of the metal halide-catalyzed disproportionation of ethyltrimethylsilane in particular, and substituted silanes in general, can be deduced.[2] Additional support for the suggested mechanism, in terms of relative migratory tendencies of R = H, C_2H_5, C_6H_5 and Br in the reaction

$$2Me_2SiR \xrightarrow{MX_3} Me_4Si + Me_2SiR_2$$

and in the reactivity of R toward electrophilic attack in general, is presented in the present work.

Results

Equilibrium.—The aluminum bromide-catalyzed disproportionation of trimethylsilane was studied at 40 and 60°. Results are summarized in Table I.

Table I indicates that the disproportionation of trimethylsilane yields the four methylsilanes and silane in nearly statistical proportions. The methylsilanes essentially reach their equilibrium ratios rapidly, but silane is formed only slowly and the results in Table I do not necessarily indicate that silane has reached its equilibrium concentration.

There is a small but definite trend for the methylsilane system to yield more of the end-products of disproportionation (tetramethylsilane and silane)

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[1] Department of Chemistry, Iowa State University, Ames, Iowa.

[2] (a) G. A. Russell, THIS JOURNAL, **81**, 4815 (1959); (b) **81**, 4831 (1959).