

Figure 2.—Data for *p*-nitroacetanilide, corrected for activity, plotted according to eq. 9.

the ionization constants as defined in this investigation for liquid ammonia solutions and those for equilibria established in solvents of high dielectric constant such as water. Perhaps a more meaningful comparison involves the degree of ionization, at the same formal

concentration, observed in these two systems. The degree of ionization in ammonia, *i.e.*, $\alpha = ([X^-] + [NH_4^+, X^-])/[HX]$, can be calculated directly from these spectrophotometric data. Expression of α in this form suggests that the properties of the species under consideration are essentially unaltered when it is involved in ion-pair formation. The value of α for both *o*- and *p*-nitroacetanilide in liquid ammonia at -55.6° is about 25% at $10^{-4} m$, which corresponds to an acid with an ionization constant of *ca.* 9×10^{-6} in aqueous solution.

The dissociation constants for the ammonium salts of *o*- and *p*-nitroacetanilide in liquid ammonia have not been reported previously; however, the constants obtained from this investigation are in reasonable agreement with the data available for similar structural types. The equilibrium constant for *o*-nitrophenol in liquid ammonia at -33° is 3.90×10^{-4} as determined by a conductivity method.⁷ Preliminary observations⁸ on the spectra of liquid ammonia solutions of *o*-nitrophenol suggest that it is completely ionized, thus the reported equilibrium constant corresponds to K_a . Assuming the ion-size parameter for ammonium *o*-nitrophenolate and the ammonium salts of *o*- and *p*-nitroacetanilide are similar, and taking into account the temperature difference between the two measurements, the agreement between the dissociation constants is satisfactory.

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Photochemical Synthesis of Volatile Hydride Derivatives

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Mercury-sensitized photolysis techniques have been applied to the synthesis of volatile hydride derivatives of carbon, silicon, and germanium. Methylsilane, germysilane, and germyl methyl ether have been prepared by the mercury photosensitized decomposition of methyl iodide-silane, germane-silane, and methanol-germane mixtures, respectively. Some physical properties of the new compound germyl methyl ether are described.

Introduction

Although extensive kinetic and synthetic photochemical studies have been carried out on the carbon hydrides and their derivatives,² only a few studies have been reported that deal with the lower members of the group IV hydrides. Recently, several articles dealing

exclusively with kinetic aspects of the mercury-sensitized photolysis of silicon^{3,4} and germanium⁵ hydride systems have appeared in the literature. From the results reported therein this technique was deemed a promising approach to the synthesis of various mixed

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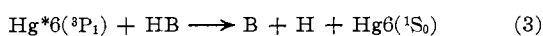
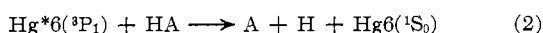
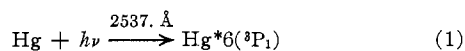
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group IV hydrides, some of which have not been prepared by more conventional synthetic methods.

The formation of the compound AB from the simultaneous photodecomposition of compounds HA and HB depends primarily on the production of the appropriate radicals. Frequently the two reactants, HA and HB, which must be photodecomposed simultaneously do not absorb radiation in the same wave length region, or one of the reactants absorbs only weakly. Under these conditions it becomes difficult to produce an appreciable concentration of the radicals A and B. Hence, the number of mixtures that can be studied becomes very limited. In many such cases these difficulties can be circumvented by the use of a sensitizer such as mercury which will absorb the radiation and decompose the reactants *via* collisions of the second kind. The primary reactions of such a mercury-sensitized photochemical decomposition can be represented by eq. 1, 2, and 3. The ultimate products formed by the radicals



A and B will be determined by various combination and/or abstraction reactions.

In the synthesis of compound AB, it is usually desirable to choose conditions which will lead to the formation of equal concentrations of the radicals A and B in the system. This, of course, is done to maximize the rate of AB formation relative to the rates of AA and BB formation. Although the steady-state concentration of a radical in a particular system is dependent on several factors, the relative concentration of radicals A and B can be estimated from a knowledge of the quenching cross sections of the parent molecules for excited mercury atoms if it may be assumed that these radicals disappear by all paths at approximately equal rates. Quenching cross sections are available for many compounds.^{6,7}

The object of the present work was to investigate the feasibility of using mercury-photosensitized decompositions to prepare various hydride derivatives of the group IV elements. We have investigated the major products formed through the mercury-sensitized photolysis of three two-component systems, *viz.*, CH₃I-SiH₄, SiH₄-GeH₄, and CH₃OH-GeH₄.

Experimental Section

Apparatus.—Gas manipulation was carried out using a Pyrex glass vacuum system. Stopcocks and ground-glass joints were lubricated with Apiezon N grease. The reaction vessel for the preparative work was a cylindrical Vycor tube (36-mm. i.d., 150-mm. length) with ground-glass joints attached at each end. The vessel was connected to the vacuum line and suspended vertically inside the coils of a Hanovia SC 2537 low-pressure mercury lamp. The lower part of the vessel was attached to a tube which contained a small amount of mercury. The apparatus was surrounded by a wooden enclosure for personnel protection. Dry nitrogen was passed through the enclosure during ir-

radiation in order to prevent the accumulation of ozone around the lamp and to maintain the temperature at approximately 35°. Mass spectra were obtained by means of a Consolidated Electrodynamics Model 21-103C mass spectrometer. Infrared absorption spectra were recorded using a Perkin-Elmer 137B Infracord spectrophotometer with the gaseous sample confined at room temperature in a 10-cm. cell fitted with 6-mm. KBr windows. Proton nuclear magnetic resonance data were obtained using a Varian Associates A60 spectrometer. The spectrum was obtained using a NMR Specialties microtube with the sample dissolved in cyclohexane (15–20% solution, by volume; τ C₆H₁₂ = 8.56).

Materials.—Germane (mol. wt. found 76.7, calcd. 76.6; confirmed by its infrared⁸ and mass spectra) was prepared from GeO₂ and NaBH₄.^{9,10} Silane and CH₃SiH₃ were obtained from Professor Alan G. MacDiarmid, Department of Chemistry, University of Pennsylvania. Purity was verified by infrared^{11,12} and mass spectrometry. Analytical grade CH₃OH (dried over BaO) and CH₃I were used after degassing on the vacuum line.

Photolysis Experiments.—All photolysis experiments were performed in the gas phase in the presence of a drop of mercury. Quantities of reactants were calculated from pressure measurements using a bulb of known volume and temperature. Mass spectra of the mixtures were determined before and after photolysis. In every case evidence for reaction products was found in the mass spectrum of the mixture only after irradiation.

Formation of CH₃SiH₃ and GeH₃SiH₃.—Methylsilane and GeH₃SiH₃ were formed by the mercury-sensitized photolysis of a CH₃I-SiH₄ mixture and a GeH₄-SiH₄ mixture, respectively. They were identified by comparing the relative intensities of the peaks of the parent ions as they appeared in the mass spectra of the irradiated mixtures with the spectra of the pure compounds.¹³ In view of the isotopic distribution of the substances chosen, these identifications were unequivocal. The relative yield of product as a function of irradiation time and concentration ratios is given in Table I. The yields were only measured in terms of the number of divisions of a particular peak in the spectrum. Some Si₂H₆ was observed in the products of the CH₃I-SiH₄ reaction and some Ge₂H₆ and Si₂H₆ were observed in the products of the GeH₄-SiH₄ reaction. In both experiments a deposit (presumably polymers of silicon and/or germanium subhydrides) appeared on the inside wall of the reaction vessel.

TABLE I
RELATIVE YIELDS OF METHYLSILANE AND GERMYLSILANE AS A
FUNCTION OF IRRADIATION TIME AND CONCENTRATION RATIOS

Ratio SiH ₄ :GeH ₄	Irradiation time, min.	No. of arbitrary divisions m/e = 108
1	1	22
1	20	18
4	1	18
2	1	34
2	5	32

Ratio CH ₃ I:SiH ₄	Irradiation time, min.	No. of arbitrary divisions m/e = 44
1	1	10
1	5	54

Synthesis of GeH₃OCH₃.—Germyl methyl ether was prepared by the gas phase mercury-photosensitized decomposition of a mixture of CH₃OH and GeH₄. Satisfactory yields were obtained using a 4:1 mole ratio of CH₃OH:GeH₄, with a total cell

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(13) The spectrum of pure CH₃SiH₃ was obtained in our laboratory using an independently prepared sample; that of GeH₃SiH₃ was obtained from the Doctoral Dissertation of E. J. Spanier, University of Pennsylvania, Philadelphia, Pa., 1964.

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pressure of approximately 80 mm. The mixture was irradiated for 5 min. and the products were accumulated from a large number of static experiments. The reaction cell had to be cleaned after every two such experiments to remove the opaque deposit from the inside wall of the cell. Volatile products were removed from the CH_3OH by allowing them to distil through a trap at -64° into a trap at -196° . Germane and Ge_2H_6 (tentatively identified by their infrared spectra^{8,14}) were removed from the mixture by allowing them to distil through a trap at -112° into a trap at -196° . The crude GeH_3OCH_3 (~ 10 mg., identified by its unique mass spectrum; identification supported by infrared spectrum) that remained in the trap at -112° was further purified by allowing it to distil from a trap at -86° into a trap at -196° . Trace amounts of CH_3OH , $(\text{GeH}_3)_2\text{O}$, and Ge_2H_6 (tentatively identified by their infrared^{15,16} and/or mass spectra) could not be removed from the sample by repeated distillations of this type.

Mass Spectrum of GeH_3OCH_3 .—The mass spectrum of GeH_3OCH_3 consisted of peaks corresponding to the fragment ions which are expected for this compound. The observed distribution and intensities of peaks in the m/e 98–110 region could be correlated very well with the known relative abundances of isotopes of germanium. The intensities of the peaks in this region relative to the base peak at m/e 105 are as follows (m/e , relative intensity): 98, 0.59; 99, 0.02; 100, 3.2; 101, 19.5; 102, 11.6; 103, 76.4; 104, 32.5; 105, 100.0; 106, 46.8; 107, 99.1; 108, 26.7; 109, 18.1; 110, 8.2. The monoisotopic spectrum of GeH_3OCH_3 is given in Table II. Even though the CH_3O^+ and CH_3^+ fragment ions were observed, they are not reported here because of the presence of a small amount of methanol impurity. The absence of Ge–C ion peaks in the mass spectrum of the irradiated mixture prior to product separation suggests that no Ge–C bonds were formed during photolysis.

TABLE II
MONOISOTOPIC MASS SPECTRUM OF $\text{GeH}_3\text{OCH}_3^a$

Positive ion	Relative intensity	Positive ion	Relative intensity
H_6GeOC^+	22.6	H_2GeO^+	0.4
H_4GeOC^+	100.0	HGeO^+	24.2
H_4GeOC^+	14.5	GeO^+	4.9
H_3GeOC^+	39.3	GeH_3^+	89.4
H_2GeOC^+	5.0	GeH_2^+	11.1
HGeOC^+	0.5	GeH^+	46.9
GeOC^+	1.2	Ge^+	35.2
H_3GeO^+	2.4		

^a Isatron temperature 250° . Sensitivity at m/e 43 for *n*-butane = 37.57 divisions/ μ . Ionizing voltage 70 v. Sensitivity at m/e 105 for CH_3OGeH_3 = 7.39 divisions/ μ .

Infrared and Proton N.m.r. Spectra of GeH_3OCH_3 .—The infrared absorption spectrum of gaseous GeH_3OCH_3 was measured at a pressure of 6 mm. The absorption maxima are as follows (cm^{-1}): 2950 (w), 2890 (w), 2109 (sh), 2096 (sh), 2084 (s), 1458 (vw), {1089 (s), 1076 (s)} d, {866 (vs), 855 (vs)} d. Weak bands were observed at 1042, 802, and 795 cm^{-1} and can probably be attributed to trace amounts of CH_3OH and $(\text{GeH}_3)_2\text{O}$ in the sample.^{15,16}

The proton n.m.r. spectrum of GeH_3OCH_3 consisted of two single absorptions of equal intensity at τ 6.51 and 4.88. By analogy with other germyl and methyl compounds,^{17–20} the absorption at τ 4.88 is assigned to the GeH_3 protons and the absorption at τ 6.51 is assigned to the CH_3 protons. No ^{73}Ge , H coupling was observed.

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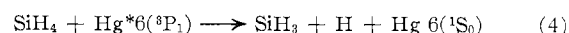
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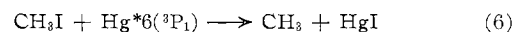
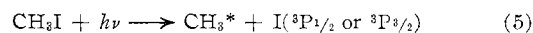
Results and Discussion

It has been postulated that the reaction of $\text{Hg}^*6(^3\text{P}_1)$ atoms with SiH_4 produces SiH_3 radicals according to the primary process^{3,4} shown in eq. 4. The main products



observed from such a photolysis reaction are H_2 and Si_2H_6 ; the latter being formed through the combination of SiH_3 radicals. A similar mechanism of decomposition has been proposed for GeH_4 .⁵ It has been shown in the present work that the mercury-sensitized photolysis of a mixture of SiH_4 and GeH_4 results in the formation of GeH_3SiH_3 in addition to H_2 , Si_2H_6 , and Ge_2H_6 . Germysilane was identified in the mass spectrum of the irradiated mixture by its characteristic mass spectral pattern.¹³ The relative intensities of the series of strong peaks in the parent ion m/e region 92–98 are compared to those obtained by Spanier as follows (m/e , relative intensity this work, relative intensity according to Spanier¹³): 74, . . . , 100; 98, 12.6, 12.1; 99, 19.4, 17.3; 100, 39.2, 33.3; 101, 42.6, 37.4; 102, 72.1, 73.8; 103, 55.8, 59.0; 104, 79.9, 79.9; 105, 44.3, 48.7; 106, 67.5, 74.0; 107, 26.7, 33.0; 108, 31.6, 36.2; 109, 7.1, 7.7; 110, 5.6, 5.9. On the basis of quenching cross section values ($\text{SiH}_4 = 26 \text{ \AA}^2$, GeH_4 (estimated) = 140 \AA^2),^{7,21,22} one would expect to obtain the maximum yield of GeH_3SiH_3 from a $\text{GeH}_4:\text{SiH}_4$ ratio of 1:5. However, as can be observed in Table I, the maximum yield of GeH_3SiH_3 was obtained using a $\text{GeH}_4:\text{SiH}_4$ ratio of 1:2. This may be attributed either to an error in the estimation of the quenching cross section of GeH_4 or to a much greater rate of disappearance of the GeH_3 radicals as compared to the SiH_3 radicals resulting in a lower steady-state concentration of the former. It should also be noted from Table I that the GeH_3SiH_3 does not accumulate in the mixture but apparently achieves a steady-state concentration after approximately 1 min. (or less) of irradiation. This suggests that GeH_3SiH_3 could be made in larger quantities by using a flow system provided allowance is made for the opaque deposit. Since GeH_3SiH_3 has been prepared and characterized by other techniques,²³ larger quantities were not made.

Mercury-photosensitized decomposition of a mixture of CH_3I and SiH_4 led to the formation of CH_3SiH_3 . Methyl iodide was chosen for the source of CH_3 radicals rather than CH_4 since it has a much larger cross section for quenching $\text{Hg}^*6(^3\text{P}_1)$ atoms.⁷ Because CH_3I has a strong absorption band at about 2500 \AA ., two primary processes must be considered in its mercury-sensitized photolysis,^{24 viz.}



The CH_3 radicals produced in (5) are known to be

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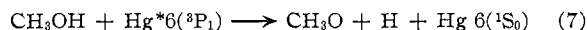
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hot.^{25,26} They may abstract a hydrogen atom from CH_3I or SiH_4 or be deactivated to thermal radicals. The over-all effect of the CH_3I absorption in the present system is to produce more CH_3 radicals than would be expected from the quenching cross section value of CH_3I . The ratio of reactants was arbitrarily set at 1.0. Methylsilane was identified in the mass spectral pattern of the irradiated mixture in the m/e 40–46 parent ion region. Disilane was also detected in the mass spectrum. Since CH_3SiH_3 can be conveniently prepared in large quantities by standard chemical procedures,²⁷ no attempt was made to prepare it on a large scale by this technique.

Methanol is known to undergo the primary process²⁸ shown in eq. 7. Carrying out this reaction in the pres-



ence of GeH_4 has produced the compound GeH_3OCH_3 . Since this compound has not been reported in the literature, a number of static photolysis experiments were performed in order to accumulate enough material for further study. An opaque deposit which formed on the inside walls of the reaction vessel during irradiation suggested the use of a flow system. Since sufficient product was obtained by static photolysis a more elaborate apparatus was considered unnecessary.

Germyl methyl ether was characterized by its mass, infrared, and proton n.m.r. spectra. The infrared spectrum was similar in many respects to that of an impure product obtained by Onyszchuk on reaction of GeH_3Cl with NaOCH_3 .²⁹ The chemical shift of the CH_3O protons (τ 6.51) is remarkably close to that reported for the same group in SiH_3OCH_3 (τ 6.58).¹⁷

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As expected, the GeH_3 proton resonance is at a lower field than the proton resonance of GeH_4 and is similar to that of the simple chloro derivative.¹⁸

Considering the low quenching cross section for CH_3OH (8 \AA^2),²⁸ the formation of GeH_3OCH_3 should be favored by a high $\text{CH}_3\text{OH}:\text{GeH}_4$ ratio. However, some preliminary experiments indicated that a $\text{CH}_3\text{OH}:\text{GeH}_4$ ratio of 4:1 gave a larger yield of GeH_3OCH_3 than a ratio of 10:1. Furthermore, it should be noted that a 1:1 ratio did not improve the yield of GeH_3OCH_3 . In the latter study, a considerable amount of Ge_2H_6 was observed among the products. Additional studies are required to explain these observations.

The GeH_3OCH_3 product was found to reach a "steady-state" concentration after the first 5 min. of irradiation. Presumably, the accumulation of the opaque deposit (polymer?) on the walls of the cell lowered the light flux sufficiently to inhibit the rate of photodecomposition. The formation of opaque deposits in this instance and in the other systems reported here makes the preparation of these compounds in large quantities time consuming in static photolysis experiments. While this is a serious drawback in large-scale applications of the proposed photochemical technique, it was merely annoying in the small-scale preparation reported here.

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