Contribution from the Department of Chemistry,
California State University–San Diego, San Diego, California 92115

Pyrolysis of Silylphosphine and Germylsilane and the Formation of Phosphylene (PH)

L. E. Elliott, Peter Estacio, and M. A. Ring*

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The first step in the homogeneous pyrolysis of Si_2H_6[1,2] and Ge_2H_6[1] involves a 1,2-hydrogen shift (*via* a proposed hydrogen-bridged activated complex) to form SiH_2 (GeH_2) and SiH_4 (GeH_4). The significance of this decomposition route in place of homolytic C-C or Si-Si bond rupture [as in C_2H_6 or $Si_2(CH_3)_6$[3]] is the determining factor in the lower thermal stability found for Si_2H_6 and Ge_2H_6 compared to C_2H_6 and $Si_2(CH_3)_6$ especially since the silicon–silicon dissociation energy in Si_2H_6 is 14 kcal/mol greater than in $Si_2(CH_3)_6$.[3-5]

In order to determine the generality of these 1,2-hydrogen shifts in *non-first-row hydrides* we have investigated the pyrolyses of GeH_3SiH_3 and SiH_3PH_2.

Experimental Section

Germylsilane was prepared by the silent electric discharge decomposition of GeH_4 and SiH_4,[6] and SiH_3PH_2 was prepared by the I_2-catalyzed pyrolysis of SiH_4 and PH_3.[7] The SiH_3PH_2 was purified by normal trap-to-trap distillations while the GeH_3SiH_3 was purified by a low-temperature column distillation. The purity of these reagents was checked by an examination of their infrared and mass spectra which clearly demonstrated the absence of SiH_4, Si_2H_6, GeH_4, and Ge_2H_6 from the GeH_3SiH_3 and the absence of similar compounds from SiH_3PH_2.

1. **Pyrolysis of SiH_3PH_2.** The pyrolysis of SiH_3PH_2 in the presence of $(CH_3)_2SiD_2$ was carried out in a mercury free, grease free, light proof flow pyrolysis system containing a glass bladed rotating pump before the thermal zone and a cold U trap following the thermal zone. The cold U trap set the reactant pressures and removed products, which were less volatile than the reagents, from the stream. The asbestos wrapped thermal zone was heated by a heating tape which surrounded the reaction tube and a thermometer well.

Silylphosphine (0.36 mmol) and $(CH_3)_2SiD_2$ (1.58 mmol) were pyrolyzed for 4 hr at 300°. The U trap was held at −78° which set the vapor phase ratio of silylphosphine to dimethylsilane-d_2 at 1.0/4.8. At the end of the reaction, the entire mixture was removed from the pyrolysis system for analysis. Noncondensable gas produced during the reaction (<0.01 mmol) was identified by its mass spectrum to be hydrogen in an isotopic distribution 0.00/0.06/1.00 (D_2/HD/H_2). The fraction condensed at −196° which passed a trap cooled to −130° was a mixture of SiH_4 and PH_3 (0.07 mmol). The infrared spectrum of this mixture contained no bands in the 1560- or 1525-cm^{-1} regions which demonstrated the absence of P-D or Si-D bonds. The ratio of SiH_4 to PH_3 was found to be 1.0/2.6 from a mass spectrum of the sample and from a mass spectrum of an authentic 1.0/1.0 mixture of SiH_4 and PH_3. The fraction condensed at −78° (0.04 mmol) was analyzed by a mass spectrum that contained peaks between *m/e* 96 and 86 which would be consistent with $(CH_3)_2Si_2H_2D_2$ (*m/e* 86-94[8]) and with $(CH_3)_2SiPHD_2$ (*m/e* 91-96[8]). This mass spectrum did not contain peaks higher than *m/e* 96.

2. **Pyrolysis of GeH_3SiH_3.** The pyrolysis of GeH_3SiH_3 was carried out in a system similar to that used for SiH_3PH_2 except that an automatic Toepler pump was used in place of the glass bladed pump.

A. **Pyrolysis of GeH_3SiH_3 in the Presence of CH_3SiH_3.** The pyrolysis of GeH_3SiH_3 (0.17 mmol) in the presence of CH_3SiH_3 was carried out at 245° for 3 hr with the cold U trap cooled to −78°. The pressure of the GeH_3SiH_3 was 4 mm while that of CH_3SiH_3 averaged 45 mm. Only a trace quantity of hydrogen was obtained. The product fraction passing a −160° bath (0.04 mmol) was a mixture of SiH_4 and GeH_4 in a ratio of 90/1, determined by mass spectroscopy. The mass spectrum of the fraction condensed at −130° demonstrated that this fraction contained $CH_3SiH_2GeH_3$ and $SiGe_2H_8$. The compound $GeSi_2H_8$ was absent. The absence of $CH_3Si_2H_5$ was demonstrated in section 2C.

B. **Pyrolysis of GeH_3SiH_3 in the Presence of CH_3GeH_3.** The pyrolysis of GeH_3SiH_3 in the presence of CH_3GeH_3 was carried out as described in 2A. The pressure of CH_3GeH_3 averaged 32 mm. The product ratio of SiH_4 to GeH_4 was 26/1. The product fraction condensed at −95° was analyzed mass spectroscopically and found to be mainly $CH_3Ge_2H_5$ with some $SiGe_2H_8$ present. The compounds $GeSi_2H_8$ and CH_3GeSiH_5 was absent. The relative intensities of the parent ion envelopes for the ions $CH_3Ge_2H_x^+$ and $SiGe_2H_x^+$ were 7/1 which is a crude estimate of their relative product yields.

C. **Pyrolysis of GeH_3SiH_3 in the Presence of CH_3SiD_3.** The pyrolysis of GeH_3SiH_3 was carried out in the presence of CH_3SiD_3 as described in 2A. The product ratio of SiH_4 to GeH_4 was 69/1. The infrared spectrum of this mixture demonstrated that SiH_3D was absent. The fraction condensed at −95° was analyzed mass spectroscopically. This fraction consisted of $CH_3SiGeD_3H_2$ and $SiGe_2H_8$ in relatively similar quantities. The compound $GeSi_2H_5$ was absent. Methyldisilane has a strong parent peak (*m/e* 76)[9] and the mass spectrum of this fraction had a very weak peak at *m/e* 79 indicating the absence of $CH_3Si_2D_3H_2$.

Results

The results from the pyrolysis of SiH_3PH_2 in the presence of $(CH_3)_2SiD_2$ (stable at 400°)[1] demonstrate that SiH_3PH_2 decomposed by steps 1 and 2 with the ratio, k_1/k_2, equal to

$$SiH_3PH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SiH_2 + PH_3 \qquad (1)$$

$$SiH_3PH_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} SiH_4 + PH \qquad (2)$$

2.6. The diradicals SiH_2 and PH then inserted into the Si-D bond in $(CH_3)_2SiD_2$ and formed $(CH_3)_2Si_2H_2D_2$ [presumably, $(CH_3)_2SiDSiH_2D$] and $(CH_3)_2SiPHD_2$ [presumably, $(CH_3)_2SiDPHD$]. To our knowledge, this is the first chemical evidence for phosphylene (PH).

Alternate decomposition routes can be eliminated. If H atoms were produced by initial rupture of Si-H or P-H bonds, HD and H_2 would have been major products due to H and D atom abstractions from $(CH_3)_2SiD_2$ and SiH_3PH_2. If SiH_3PH_2 decomposed by Si-P rupture to form SiH_3 and PH_2 radicals, the silane and phosphine produced would have contained SiH_3D and PH_2D which were completely absent. In this case, the silane and phosphine would be produced by H or D atom abstraction by SiH_3 or PH_2 radicals from SiH_3PH_2 and $(CH_3)_2SiD_2$. Based on reactions of CH_3 radicals with SiH_4, SiD_4, and CH_4,[10] the abstraction reactions in our system would only be a competition between H atom abstraction from SiH_3PH_2 and D atom abstraction from $(CH_3)_2SiD_2$. The H atom abstraction would be favored in activation energy by about 1 kcal/mol (rate increase of 4 times) while D atom abstraction would be favored by concentration by a ratio of about 2/1. Therefore, the complete absence (<0.5%) of SiH_3D and PH_2D eliminates the primary decom-

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position route of Si-P bond rupture in SiH_3PH_2 to yield SiH_3 and PH_2 radicals.

The results from the pyrolyses of GeH_3SiH_3 in the presence of a 10/1 excess of CH_3SiH_3 and CH_3SiD_3 (stable at 500°)[11] clearly demonstrate that GeH_3SiH_3 decomposed by eq 3 and possibly by eq 4. The absence of molecular hydrogen eliminates primary formation of H atoms by Si-H or Ge-H rupture. The fact that SiH_3D was not formed in the pyrolysis with CH_3SiD_3 eliminates initial homolytic Si-Ge rupture to form SiH_3 and GeH_3 radicals. The low yield of GeH_4 argues similarly.

$$GeH_3SiH_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} SiH_4 + GeH_2 \tag{3}$$

$$GeH_3SiH_3 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} SiH_2 + GeH_4 \tag{4}$$

The fact that no silylene (SiH_2) insertion products were found under conditions where this diradical has been chemically trapped[1,2,12] suggests that step 4 is less significant than expected from the SiH_4/GeH_4 product ratio.

The homogeneity of these reactions (decomposition and insertion) is uncertain at this time. However, the thermal reactions of SiH_3PH_2 and GeH_3SiH_3 follow the same mechanism as that of the homogeneous[13] thermal decomposition of Si_2H_6 (eq 5 and 6). The alkali metal salt catalyzed decomposition of Si_2H_6 in $CH_3OCH_2CH_2OCH_3$[14] and the Pyrex-catalyzed thermolysis of P_2H_4[15] both appear to follow an intermolecular exchange not observed in the thermal reactions of SiH_3PH_2 and GeH_3SiH_3 with deuteriosilanes. Thus, it appears that the pyrolyses of SiH_3PH_2 and GeH_3SiH_3 are homogeneous over a silicon mirror. In our further discussion, we assume that these decompositions were homogeneous.

$$Si_2H_6 \rightarrow SiH_2 + SiH_4 \tag{5}$$

$$SiH_2 + Si_2H_6 \rightarrow Si_3H_8 \tag{6}$$

It is interesting to note that while 1,2-hydrogen shifts in SiH_3PH_2 take place with similar rates ($k_1 \approx k_2$), GeH_3SiH_3 decomposes primarily by one route ($k_3 \gg k_4$). These results can be understood if one assumes that the forward and reverse (insertion) reactions are reversible, which should be the case. We then have that

$$k_i = K_i k_{-i} \tag{7}$$

where K_i is the equilibrium constant. Since entropies of formation for silicon compounds are fairly additive,[16] one has that

$$\log K_i/K_j = (\Delta H_j^\circ - \Delta H_i^\circ)/2.3RT$$

where ΔH_i° is the heat of reaction for the ith reaction. Although the heats of formation of GeH_2 and PH are not known, one can estimate that K_3/K_4 is probably 10^4 or greater while K_1 and K_2 are probably of the same order of magnitude. Therefore, in GeH_3SiH_3, even with $k_{-4} > k_{-3}$, $K_3 \gg K_4$ so that $k_3 \gg k_4$. In SiH_3PH_2, K_1/K_2 and k_{-1}/k_{-2} are both small numbers so that k_1/k_2 is also a small number.

Data from competitive GeH_2 insertions into Ge_2H_6 *vs.* $(CH_3)_3SiH$ compared to SiH_2 insertions into $(CH_3)_3SiH$ *vs.* $(CH_3)_3GeH$[17] suggest that GeH_2 insertions are greatly favored into Ge-H bonds *vs.* Si-H bonds. This observation is consistent with the results from this study. In the pyrolysis of GeH_3SiH_3 in the presence of CH_3GeH_3 in a 8/1 gas phase excess, the product ratio of $CH_3Ge_2H_5$ to $SiGe_2H_8$ (presumed to be mainly $SiH_3Ge_2H_5$) was on the order of 7/1 which would be due to GeH_2 insertion into the Ge-H bonds of CH_3GeH_3 and SiH_3GeH_3. In the pyrolysis of GeH_3SiH_3 in the presence of CH_3SiD_3 in a 10/1 gas phase excess, the products $CH_3SiGeD_3H_2$ (presumed to be $CH_3SiD_2GeH_2D$) and $SiGe_2H_8$ (presumed to be mainly $SiH_3Ge_2H_5$) were obtained in similar quantities. These products were due to GeH_2 insertions into the Ge-H bond in GeH_3SiH_3 and the Si-D bond in CH_3SiD_3.

Registry No. GeH_3SiH_3, 13768-63-3; SiH_3PH_2, 14616-47-8; PH, 13967-14-1.

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Contribution from the Savannah River Laboratory,
E. I. du Pont de Nemours and Company, Inc.,
Aiken, South Carolina 29801

Quadrivalent Actinide Tetrakis(hexafluoroacetonylpyrazolide) Compounds[1]

W. Andruchow, Jr.,[2] and D. G. Karraker*

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Pyrazole ($HN_2C_3H_3$ or HPz) can react to form polymeric compounds with transition metal ions, lanthanide ions, or actinide ions.[3-5] The probable structure of a polymeric metal pyrazolide (Figure 1a) is stabilized by the resonance both in the pyrazolide ligand and its chelate-type bonding with metal ions. The polymeric metal ion pyrazolides are quite insoluble and inert to dilute acids and bases.

Mahler, at the Du Pont Experimental Station, discovered that hexafluoroacetone (hfa) and some other perhaloketones will react with polymeric pyrazolides to yield compounds with a stability comparable to that of chelates.[5] These compounds are formed by hfa adding between the 1 nitrogen of pyrazole and the metal ion and breaking half the pyrazolide-metal ion bonds (Figure 1b). Mahler prepared and characterized hexafluoroacetonylpyrazolide (hfaPz) compounds with 16 metal ions including Th^{4+} and $UO_2{}^{2+}$. The work reported in this paper includes the synthesis and study of tetrakis(hexafluoroacetonylpyrazolide) compounds of U^{4+}, Np^{4+}, and Pu^{4+} and the tetrakis (hexafluoroacetonyl-3-methylpyrazolide), (hfa-3-MePz)$_4$, compounds of Th^{4+},

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