obvious from this figure that the production of trifluoroacetyl hypofluorite was greatly favored by adding water to the reacting mixture. It also appears that the addition of water beyond a certain limit was of little or no increased value. This limit, about 0.0085 mole/hr. in these experiments, corresponded to relative molar flow rates of fluorine to acid to water of about 5:3:1. (It was not learned whether the yield of the hypofluorite might be increased above about 15% by increasing the concentration of fluorine or lengthening the time of residence in the reactor.)

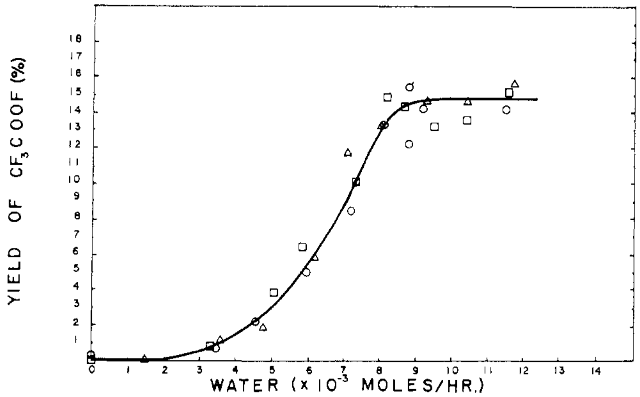

Figure 2.

Discussion

Although the experiments just described clearly indicate that the formation of trifluoroacetyl hypofluorite and of nonexplosive products such as CF_4 and CO_2 is greatly accelerated by water vapor, the exact role of water is still unclear. It may reasonably be assumed that water reacts either with the acid or with fluorine to give an intermediate which then gives the hypofluorite. Such an intermediate may be a gaseous hydrate of the acid or it may be a substance formed by the reaction of fluorine with water. The known products from fluorine and water are hydrogen fluoride, oxygen, and oxygen difluoride. None of these appears to be an intermediate responsible for producing CF_3-COOF. A mixture of oxygen difluoride with trifluoroacetic acid vapor was found to stand at room temperature essentially without reacting. Menefee and Cady[2] have shown that hydrogen fluoride vapor does not accelerate the formation of pentafluoropropionyl hypofluorite from fluorine and pentafluoropropionic acid as does water. Oxygen lacks the presence of fluorine needed to form trifluoroacetyl hypofluorite from trifluoroacetic acid. This state of affairs leaves the authors guessing that an active intermediate is involved in the reaction and that it may be a hydrate of trifluoroacetic acid, atomic fluorine, ·OF radical, HOF molecule, or some other unknown species. It is not clear why increasing the ratio of molecules of water to acid above 1:3 failed to increase the yield of trifluoroacetyl hypofluorite.

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[2] A. Menefee, Thesis, University of Washington, 1953, p. 6.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE RADIATION LABORATORY, BERKELEY, CALIFORNIA

The Synthesis of Disilanylphosphine and Disilylphosphine in a Silent Electric Discharge

BY SUDARSHAN D. GOKHALE AND WILLIAM L. JOLLY

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We previously observed that the two isomers of Si_2PH_7 (disilanylphosphine, $Si_2H_5PH_2$, and disilylphosphine, $(SiH_3)_2PH$) were formed when a mixture of silane and phosphine was passed through an ozonizer-type silent electric discharge tube.[1] These compounds have such similar volatilities that we were unable to separate them by ordinary vacuum-line techniques. Disilanylphosphine was isolated by gas chromatography, but disilylphosphine decomposed on the chromatographic column. In this note, we report silent-electric-discharge methods for preparing both disilylphosphine and disilanylphosphine, each free from the other. Disilylphosphine was prepared from a mixture of silane and silylphosphine, and disilanylphosphine was prepared from a mixture of disilane and phosphine. The methods are based on the fact that, when a stream of molecules passes rapidly through a silent electric discharge, the molecules generally do not undergo drastic fragmentation and rearrangement. Because the molecular fragments more or less retain their original configurations, it is possible to predict the structures of new molecules that are formed by the combination of the molecular fragments. Thus by a suitable choice of starting materials, it is possible to tailor-make molecules.

Experimental

Reagents.—Disilane was prepared from silane by a previously described silent-electric-discharge process.[2] Silylphosphine was prepared by circulating a 1:1 mixture of silane and phosphine through an ozonizer tube at −78° and a product-collecting trap at −112°.[3] The crude product was distilled into a series of traps at −95, −130, and −196°. A mixture of silylphosphine and disilane collected in the −130° trap; the disilane was preferentially vaporized from the trap by pumping into a −196° trap as the trap gradually warmed up. The latter fractions, whose infrared spectra showed them to consist of pure silylphosphine, were saved, and the earlier fractions were subjected to a second fractionation. Traces of trisilane in the silylphosphine were removed by passage through a −112° trap. By this procedure, about one-third of the silylphosphine in the original product mixture was isolated with a purity estimated at greater than 99%.

Electric Discharge Reactions.[3]—The discharge tube was kept at 0° and the product-collecting trap at −45°. The volume of the discharge system was 1.5 l. At the end of each run, the contents of the discharge apparatus was fractionally condensed in traps at −95 and −196°. The material which collected in

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[1] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **3**, 1141 (1964).

[2] E. J. Spanier and A. G. MacDiarmid, *ibid.*, **2**, 215 (1963).

[3] For a discussion of the ozonizer-type discharge, see J. E. Drake and W. L. Jolly, *J. Chem. Soc.*, 2807 (1962), and W. L. Jolly, Chapter 5 in "Technique of Inorganic Chemistry," Vol. 1, H. B. Jonassen and A. Weissberger, Ed., 1963, p. 179.

the −95° trap (Si_2PH_7 plus higher molecular weight products such as Si_3H_8) was then distilled into an n.m.r. tube containing a known amount of tetramethylsilane. The yields of Si_2PH_7, Si_3H_8, and (when present) P_2H_4 were determined by integration of the n.m.r. peaks. The Si_2PH_7 was isolated by fractional condensation of the material in the n.m.r. tubes in traps at −63, −83, and −196°. The fraction which collected in the −83° trap was fractionally vaporized by gradually warming the trap; the middle fraction consisted of pure Si_2PH_7.

A mixture of 6.2 mmoles of SiH_3PH_2 and 12.4 mmoles of SiH_4 was circulated through the discharge apparatus until 3.5 mmoles of the SiH_3PH_2 and 1.3 mmoles of the SiH_4 had been consumed. $(SiH_3)_2PH$ (0.5 mmole) and Si_3H_8 (0.5 mmole) were the only products detected by n.m.r. analysis. In another run, 16.9 mmoles of SiH_3PH_2 was circulated through the discharge apparatus until 10.6 mmoles had been decomposed. Again, only $(SiH_3)_2PH$ (0.4 mmole) and Si_3H_8 (0.3 mmole) were detected by n.m.r. analysis. In each of these cases, we can say that less than 0.02 mmole of $Si_2H_5PH_2$ was formed.

A mixture of 18.2 mmoles of Si_2H_6 and 36.4 mmoles of PH_3 was circulated through the discharge apparatus until 10.8 mmoles of Si_2H_6 and 15.4 mmoles of PH_3 had been consumed. The products consisted of $Si_2H_5PH_2$ (0.9 mmole), Si_3H_8 (1.3 mmoles), P_2H_4 (0.8 mmole), and an undetermined amount of SiH_3PH_2. No $(SiH_3)_2PH$ was detected; our limit of detection was about 0.02 mmole.

Characterization of Disilylphosphine.—The 0° vapor pressure of the $(SiH_3)_2PH$ was found to be 28 ± 1 mm. The infrared spectrum, as obtained with Perkin-Elmer Infracord spectrophotometers (NaCl Model 137B and KBr Model 137) showed bands at the following frequencies (cm.$^{-1}$): 2300 (w), 2166 (s), 2080 (vw), 943 (m), 934 (m), 930 (m), 893, 881, 880 (s), 837 (w), 830 (w), 825 (w), 801 (w), 798 (m), 790 (m), 783 (m), 780 (m), 773 (m), 766 (m), 756 (w), 742 (w), 736 (w), 732 (w), 724 (w), 700 (w, br), 693 (w), 690 (w), broad bands from 620 to 670 (vw), 550 to 580 (vw), 452 to 470 (w).

A mixture of 0.098 mmole of $(SiH_3)_2PH$ and 0.147 mmole of water was kept at room temperature for 3 hr. The resulting material was separated by fractional condensation in a series of traps at −95° (0.063 mmole of unreacted H_2O), −145° (0.098 mmole of $(SiH_3)_2O$), and −196° (0.088 mmole of PH_3). The $(SiH_3)_2O$ and PH_3 were identified by their infrared spectra.[4,5]

A mixture of 0.10 mmole of $(SiH_3)_2PH$ and 0.22 mmole of HCl was kept at room temperature for 3 hr. Infrared analysis[6] showed the presence of SiH_3Cl in the products. The mixture of products and unreacted HCl was treated with excess water to convert the SiH_3Cl to $(SiH_3)_2O$, and after a fractionation such as described above, 0.11 mmole of $(SiH_3)_2O$ was isolated. In another experiment, 0.064 mmole of $(SiH_3)_2PH$ and 0.25 mmole of HCl were allowed to react at room temperature for several hours. The resulting mixture was held at −126° in order to render the PH_3 nonvolatile in the form of PH_4Cl, and the SiH_3Cl and excess HCl were pumped off. Treatment of the residue with sodium hydroxide yielded 0.064 mmole of phosphine.

Characterization of Disilanylphosphine.—The physical properties of the $Si_2H_5PH_2$ that was isolated agreed with those observed previously.[1] A mixture of 0.098 mmole of $Si_2H_5PH_2$ and 0.20 mmole of HCl was allowed to react for several hours at room temperature. The resulting mixture was separated by fractional condensation in traps at −95° (0.088 mmole of Si_2H_5Cl) and −196° (0.098 mmole of PH_3, a trace of SiH_3Cl, and excess HCl). The Si_2H_5Cl was identified by its infrared spectrum.[7] The PH_3 was freed of SiH_3Cl and HCl by treatment with sodium hydroxide and identified by its infrared spectrum.[5] The reaction of $Si_2H_5PH_2$ with water has been studied previously.[1]

Discussion

The fact that $(SiH_3)_2PH$, and no $Si_2H_5PH_2$, is formed in the discharge reaction of SiH_3PH_2 with SiH_4 suggests that $(SiH_3)_2PH$ is formed by the combination of silane or one of its fragments with silylphosphine or one of its $SiPH_x$ fragments. A *possible* reaction is

$$SiH_2 + SiH_3PH_2 \longrightarrow SiH_3PHSiH_3$$

The formation of an Si–P bond, rather than an Si–Si bond, is possibly due to the greater electronegativity of phosphorus (and the consequent favored attack by the electron-deficient radical) or to a greater bond energy for the Si–P bond. The fact that an appreciable, although reduced, yield of $(SiH_3)_2PH$ is obtained from the discharge decomposition of SiH_3PH_2 alone suggests that SiH_3PH_2 undergoes some cleavage to fragments such as SiH_2 and PH_2, and that the silane fragment reacts with SiH_3PH_2 to give $(SiH_3)_2PH$.

The fact that $Si_2H_5PH_2$, and no $(SiH_3)_2PH$, is formed in the discharge reaction of Si_2H_6 with PH_3 is consistent with the concept that disilane or one of its Si_2H_x fragments combines with phosphine or one of its fragments. and that there is no tendency for the phosphorus atom to be inserted between the two silicon atoms.

Water and hydrogen chloride react with the isomers of Si_2PH_7 to cleave the Si–P bond.

$$(SiH_3)_2PH + H_2O \longrightarrow (SiH_3)_2O + PH_3$$

$$(SiH_3)_2PH + 2HCl \longrightarrow 2SiH_3Cl + PH_3$$

$$2Si_2H_5PH_2 + H_2O \longrightarrow (Si_2H_5)_2O + 2PH_3$$

$$Si_2H_5PH_2 + HCl \longrightarrow Si_2H_5Cl + PH_3$$

The trace of SiH_3Cl observed among the products of the last reaction is probably due to the decomposition of Si_2H_5Cl in the presence of HCl.[7]

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(4) R. C. Lord, D. W. Robinson, and W. C. Schumb, *J. Am. Chem. Soc.*, **78**, 1327 (1956).

(5) V. M. McConaghie and H. H. Nielsen, *J. Chem. Phys.*, **21**, 1836 (1953).

(6) C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, *ibid.*, **25**, 855 (1956).

(7) A. D. Craig, J. V. Urenovitch, and A. G. MacDiarmid, *J. Chem. Soc.*, 548 (1962).

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The Effect of Tungsten on the Hydrolysis of Uranium Dicarbide[1]

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In an earlier paper we reviewed the work on the uranium dicarbide hydrolysis reaction[2] and found considerable variation in the products reported by different investigators. For example, the concentrations of hydrogen ranged from 14 to 50 vol. % of the evolved gas. Recently Pollard, *et al.*,[3] reported only 0.5%

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) M. J. Bradley and L. M. Ferris, *Inorg. Chem.*, **3**, 189 (1964).

(3) F. H. Pollard, G. Nickless, and S. Evered, *J. Chromatog.*, **15**, 233 (1964).