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Previous determinations of the heat of formation have been based on indirect measurement, either the heat of combustion of silane or the temperature coefficient of the equilibrium constant for the reaction

$$Si(s) + 2H_2(g) \xrightarrow{} SiH_4(g)$$
 (1)

The first method depends upon the heat of formation of hydrated silica, which is not accurately known.⁶ The second depends upon the establishment of a true equilibrium, and the existence of such an equilibrium is questionable.² Also, the values obtained for the heat of formation of silane, namely, -8.7^{1} , -13.7^{2} and $-14.8^{3.6}$ kcal./mole are not consistent with the following observed properties of this compound. Hogness, Wilson and Johnson (ref. 4) allowed finely divided silicon and hydrogen to remain in contact for several days at temperatures up to 480° and a total pressure of one atmosphere. No pressure drop was observed; no silane could be detected. Measurements made in this Laboratory⁵ show that, when silane and excess hydrogen are mixed at 425° and a pressure of 100 atmospheres, complete decomposition of the silane takes place. However, if the values for the heat of formation listed above are combined with the free energy functions (obtained from heat capacity or spectrographic measurements) for silicon, hydrogen and silane,⁷⁻⁹ calculated values of the equilibrium constant for reaction 1 require large equilibrium mole percentages of silane under the conditions used by Hogness, Wilson and Johnson or by Brant-ley and Smist. In view of these contradictory results, a direct determination of the heat of formation of silane seemed necessary.

The heat of formation was measured by a standard calorimetric procedure,¹⁰ purified silane being decomposed to crystalline silicon and hydrogen at 680°. The calorimeter was designed to operate at 550° but a temperature of 680° proved necessary to ensure complete decomposition of the silane. At 680° there was considerable thermal lag in the calorimeter system. Also the ratio of electrical energy to silane decomposition energy was 60:1 in contrast to 35:1 at 550°. These facts probably account for the large average deviation in the measurements. The value obtained, based on five calibration runs and four runs in which silane was decomposed, was $+7.8 \pm 3.5$ kcal./mole. The heat of formation is positive in contrast to the negative values reported previously. Because of the limited data and large average deviation in the calorimetric experiments, the sign of the heat of formation was checked by another method.

A 1-inch quartz tube was fitted with gas inlet and outlet tubes, a gas flow meter in the inlet side, and a thermocouple in the center of the quartz tube about 3 cm. downstream from the inlet tube. This assembly was placed in a tube

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furnace and heated to 600° . The system was flushed with hydrogen and was then allowed to come to temperature equilibrium with no gas flowing through the system. Hydrogen was then allowed to flow through the system and the thermocouple registered a large temperature drop (about 10°). The thermocouple returned to its original equilibrium value when the hydrogen flow was stopped. Next, silane was allowed to flow at the same rate, and the thermocouple registered an increase in temperature (about 2°). The system returned to equilibrium when the silane flow was stopped. This procedure was repeated several times with the same results. The temperature of the furnace was then set at 320° and the same experiments performed. At this temperature, which is well below the temperature at which silane decomposes rapidly, a flow of either silane of hydrogen resulted in a decrease in the temperature of the thermocouple (about 4° for silane, 10° for hydrogen). The temperature increase observed during the silane flow at 600° must then result from the exothermic decomposition of this gas.¹¹

Calculated values of the equilibrium constant for reaction (1) based on $\Delta Hf^{\circ} = +7.8$ kcal./mole and the data from references 7, 8 and 9 are: $K_{\rm p} =$ 1.9×10^{-10} at 25° and $K_{\rm p} = 1.4 \times 10^{-7}$ at 450°. The amount of silane present at equilibrium at 450° is therefore extremely small, about 1.4 × 10^{-5} mole % in the gas phase at one atmosphere pressure and about 1.4×10^{-3} mole % at a pressure at 100 atmospheres. This explains the failure of Hogness, Wilson and Johnson to form silane and the essentially complete decomposition of silane under the conditions employed by Brantley and Smist. The stability of silane at room temperature must be attributed to a very slow rate of decomposition rather than to a favorable equilibrium.

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(11) Mr. E. G. Caswell of this Laboratory carried out these confirming experiments.

THE METHYL IMINO RADICAL¹

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The thermal decomposition of methyl azide has been studied² and found to be a homogeneous, unimolecular reaction. Leermakers³ reported the results of a study of the reaction in a static system at temperatures between 200–240° and pressures from 0.078 to 46.6 cm., and suggested that the methylimino radical forms, and then undergoes a rearrangement to methyleneimine. Our experiments were designed to stabilize the methylimino radical or other active species by freezing the products of the thermal decomposition in a high speed flow system.⁴

(1) This work was supported in part by the United States Atomic Energy Commission, contract No. AT-(40-1)-1305.

(2) H. C. Ramsperger, J. Am. Chem. Soc., 51, 2134 (1929).

(3) J. A. Leermakers, ibid., 55, 3098 (1933).

(4) For a description of the technique see F. O. Rice and M. Freamo, *ibid.*, **73**, 5529 (1951).

⁽⁶⁾ T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press Inc., New York, N. Y., 1954, p. 241.

⁽⁷⁾ Calculated from data given by K. K. Kelley, Bur. Mines Bull., 371 (1934).

⁽⁸⁾ N.B.S.-N.A.C.A. Tables of Thermal Properties of Gases, Tables 7.10 and 7.11.

^{(9) (}a) C. Cerny and E. Erdos, Chem. Listy. 47, 1742 (1953);
(b) A. P. Altschuler, J. Chem. Phys., 23, 361 (1955).

⁽¹⁰⁾ See, for example, W. H. Johnson, R. G. Miller and E. J. Prosen, N.B.S. Report No. 3257, January 15, 1953.

Experimental

Methyl azide was prepared by allowing dimethyl sulfate to react drop by drop with an alkaline solution of sodium azide heated on a steam-bath. The evolved gases were passed over anhydrous calcium chloride and collected at -78° . The crude material was distilled through a Vigreux type column and fractions of the distillation proceeded. The main impurity was found to be the lower boiling dimethyl ether which was removed by a careful fractionation. The pure methyl azide obtained in this manner boiled between 20 and 21°, and was stable indefinitely when stored in the dark at -80° . The mass spectrum of the methyl azide was obtained before each experiment and did not vary from day to day.

Methyl azide was allowed to expand into an evacuated reservoir of known volume, fitted with a manometer. In a typical experiment about 10^{-2} mole of methyl azide was passed through a quartz tube heated to about 900°. The rate of flow was adjusted by means of a suitable capillary so that the pressure at the inlet end of the furnace was about 0.1 mm. The products of the reaction which were condensable at -196° were frozen out onto a surface cooled with liquid nitrogen, located about 2.5 cm. from the exit end of the furnace. The non-condensable gases which were formed at this stage of the reaction were removed from the reaction chamber by means of a high speed pumping system, and were passed into a gas measuring buret. Use was then made of the mass spectrometer as an analytical tool for the determination of the composition of these gaseous products.

Anal. N₂, 76.5, 80.0; H₂, 22.6, 18.5; CH₄, 0.9, 1.4.

The other products condensed on the cold finger at -196° in the form of a clear colorless glass. When the liquid nitrogen was removed from the finger, the deposit almost immediately underwent a rapid transition to a white opaque solid. The change was quite vigorous and was accompanied by a slight "ping" with small pieces of the deposit being shot off the tube. No hydrogen or other gas was produced during this phase of the reaction. This transition was not observed in a blank experiment where all conditions were the same except that the furnace was not heated.

When the deposit was finally warmed to room temperature, the pressure in the system increased and a thick sirup remained on the glass surface. The vapor phase was analyzed on the mass spectrometer and found to consist practically entirely of ammonia and hydrogen cyanide. Anal. NH₂, 55%; HCN, 45%. Under our conditions ammonium cyanide is completely dissociated. Table I gives the amounts of the gaseous products formed per mole of methyl azide used.

TABLE I

Analysis of Gases (moles) Formed during the Thermal Decomposition of Methyl Azide

	Expt. 1	$\frac{\text{Expt.}}{2}$
Methyl azide used	1.00	1.00
Nitrogen	0.98	0.96
Hydrogen	0.23	0.28
Methane	trace	trace
Ammonia	0.27	0.29
Hydrogen cyanide	0.22	0.23

Under the conditions of the experiment essentially all of the methyl azide was decomposed. Each mole of methyl azide which decomposed yielded on the average 1.25 moles of permanent gas, of which one mole was nitrogen and 1/4mole was hydrogen. For each mole of methyl azide consumed there was also produced 1/2 mole of products, which condensed at -196° but were gases at room temperature. This result may be slightly low due to the solubility of some of the gases in the condensed phase at room temperature. These gases consisted of about 0.28 mole of ammonia and 0.23 mole of hydrogen cyanide for each mole of methyl azide decomposed.

aziae decomposed. The only other product was the polymeric material whose empirical formula could be calculated by difference since the quantities of all other products were known. This calculation gave an empirical formula of $C_5N_3H_9$. The calculated analysis of $C_5N_3H_9$ is: C, 54.1; N, 37.8; H, 8.1. The actual analysis for the material gave: C, 55.12, 55.27; N, 35.19, 35.04; H, 9.48, 9.64. Extensive attempts to sublime this material in order to obtain a crystalline product failed. It did not sublime in a vacuum when heated to 100°. When heated *in vacuo* for extended periods at temperatures near 150°, it turned brown but only minute amounts of a tan sirup appeared on the condenser. Leermakers identified both ammonium azide and hexamethylenetetramine in the white crystalline solid which formed during the thermal decomposition of methyl azide in a static system. The polymeric material formed in our experiments did not contain ammonium azide these would certainly sublime from the condensate during the extensive attempts to sublime it.

Discussion

A mechanism which is consistent with the results of the analysis of the product is

$CH_3N_3 \longrightarrow$	$\mathrm{CH}_{8}\mathrm{N}$	$+ N_2$	(1)
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 $0.25 \text{CH}_3 \text{N} \longrightarrow 0.25 \text{HCN} + 0.25 \text{H}_2 \qquad (2)$

$$0.75 \mathrm{CH}_{3}\mathrm{N} \longrightarrow 0.3 \mathrm{NH}_{3} + 0.15 \mathrm{C}_{5}\mathrm{N}_{3}\mathrm{H}_{9} \qquad (3)$$

The $C_5N_3H_9$ represents the empirical formula of the material required to complete the mass balance.

Reaction 1 involves the formation of the methylimino radical (CH₃N) by the elimination of a mole of nitrogen. The radical can decay at least in part, according to (2). This reaction takes place exclusively during the initial stage of the reaction and does not occur in the solid at -190° . This reaction probably only goes with an appreciable rate at the elevated temperature in the furnace, since neither hydrogen nor hydrogen cyanide is found in products of the thermal decomposition at 200-240°. If some of the methylimino radicals are stabilized on the cold finger at -190° , then (3) is the reaction which occurs at liquid air temperatures and is accompanied by the physical transition.

It is possible that the methylimino radical is not stabilized but rather rearranges to methyleneimine, either in the vapor phase or on contact with the cold surface. Then CH_2 ==NH is the active species stabilized and this polymerizes on slight warming. This polymerization may be initiated by some isolated methylimino radicals that are trapped in the deposit.