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).

Contribution from the Chemical Technology Division,
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The Effect of Tungsten on the Hydrolysis of Uranium Dicarbide[1]

By Mildred J. Bradley and Leslie M. Ferris

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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).

hydrogen from uranium dicarbide. In our earlier experiments we assumed that the trace of tungsten, an impurity from the electrodes used to arc-melt our specimens, did not significantly affect the hydrolysis reaction. Studies with thorium dicarbide contaminated with 6 wt. % tungsten[4] indicated that this assumption was not necessarily valid. Therefore, some additional work on the effect of tungsten on the uranium dicarbide hydrolysis was needed.

Experimental

Carbides.—Essentially tungsten-free uranium dicarbide (specimen UC_2-19A, Table I) was prepared by arc-melting high purity uranium metal (less than 400 p.p.m. total impurities) and spectroscopic grade carbon, using a graphite electrode in a helium atmosphere. The electrode reacted with the melt, thus increasing the carbon concentration from 8.8 wt. % in the original uranium metal–graphite mixture to 10.6 wt. % in the final carbide. The combined-C:U atom ratio was 1.86, which is about the maximum obtainable by arc-melting.[2] Uranium dicarbide is always substoichiometric, the most common composition being $UC_{1.8}$.[5] Metallographic examination of specimen UC_2-19A showed single-phase uranium dicarbide with large amounts of excess graphite. The X-ray diffraction powder pattern was that of uranium dicarbide possibly contaminated with a trace of the monocarbide since the 2.87 Å. line of the latter was faintly visible. Specimen UC_2-20A (Table I) was prepared by arc-melting a mixture of tungsten, uranium, and carbon, using a tungsten electrode in an argon atomosphere. Metallographic examination of this specimen showed grains of single-phase uranium dicarbide, some graphite, and a lower melting phase at the grain boundaries which presumably contained the tungsten. Uranium dicarbide and WUC_2[6] were detected by X-ray diffraction analysis. Assuming that all the tungsten was present as WUC_2 (see Results and Discussion), the composition of the dicarbide phase in specimen UC_2-20A was $UC_{1.68}$. Both specimens were also analyzed for oxygen (<0.05%) and nitrogen (<30 p.p.m.).

TABLE I

COMPOSITION OF URANIUM DICARBIDES (WT. %)

	Specimen	
	UC_2-19A	UC_2-20A
Uranium	89.4	83.8
Total C	10.58	8.62
Free C	2.20	0.62
Tungsten	0.002	6.20

Hydrolysis and Analytical Procedures.—Carbide specimens (3–4 g.) were hydrolyzed with 50 ml. of water at 80° following the procedure described earlier.[2] The evolved gases were collected and then analyzed by gas chromatography.[7] This method for determining the total carbon in the gas is accurate within 10%.[2] Specimen UC_2-19A was analyzed by the standard methods[2]; however, the analysis of specimen UC_2-20A was different. One portion was burned in oxygen and the carbon collected as CO_2. The uranium was then leached from the combustion ash with nitric acid and this solution analyzed. Tungsten was determined gravimetrically by allowing a second portion to react with 14 *M* HNO_3, collecting the residue by filtration, burning the carbon (the free graphite in the original carbide) from this residue, and weighing as WO_3. Free carbon was determined as CO_2 by dissolving the carbide in 10 *M* HNO_3, filtering off the carbon (and tungstic oxide), and burning the carbon to CO_2.

Results and Discussion

Tungsten, as an impurity in uranium dicarbide, had a pronounced effect on the hydrolysis reaction. For example, the hydrogen concentration in the gas increased from 33 to 75 vol. % as the W:U atom ratio increased from essentially 0 to 0.1 (Table II). With the same change in W:U ratio, the amount of free hydrogen increased from 0.3 g.-atom per g.-atom of uranium to 1.1, the amount of gaseous C_2 to C_8 hydrocarbons decreased from 33 to 20% of the combined carbon, and the amount of wax increased from 20 to 52% of the combined carbon. The ratios of the various hydrocarbon isomers were the same as reported earlier.[2] Specimens with W:U atom ratios of 0.002 yielded approximately the same quantities of the various products as the essentially tungsten-free carbide (Table II). Dissolving the hydrous uranium oxide products in HCl gave solutions of uranium(IV) chloride in all cases. Based on chemical and X-ray analyses, 70% of the original tungsten in specimen UC_2-20A was collected as finely divided WUC_2 after hydrolysis of the specimen and HCl dissolution of the $UO_2 \cdot xH_2O$. Additional black solids which probably also contained WUC_2 stuck to the surface of the reaction vessel and could not be removed by washing with water, HCl, acetone, or ether. No tungsten was found in the solutions from the hydrolysis or HCl dissolution.

The effect of a tungsten impurity in catalyzing the polymerization of the C_2 units to wax during the hydrolysis of uranium dicarbide is very similar to its effect on the thorium dicarbide hydrolysis[4] and further emphasizes the importance of carefully characterized materials for carbide studies.

TABLE II

EFFECT OF TUNGSTEN IMPURITY ON THE REACTION OF URANIUM DICARBIDE WITH 80° WATER

	Specimen UC_2-19A	Av. for all UC_2 specimens in ref. 2	Specimen UC_2-20A
		W:U atom ratio	
	0.00003	0.002	0.096
Vol. of gas evolved, ml. (STP)/g. of carbide	39	42	51
Gas composition, vol. %			
Hydrogen	33	41	75
Methane	17	15	7
Ethane	35	28	10
Propane	1.0	1.0	0.4
Butanes	4.4	4.6	1.2
C_5 to C_8 alkanes	0.8	1.1	0.5
Ethene	1.8	1.6	1.1
Butenes	4.6	4.7	2.1
C_5 to C_7 alkenes	1.5	2.0	1.2
Alkynes	0.8	0.6	1.0
Unidentified unsaturates	1.0	1.2	0.9
Carbon distribution in hydrolysis products[a]			
Methane	4	4	3
C_2 to C_8 gaseous hydrocarbons	33	34	20
Wax	20	27	52
Unaccounted for	43	35	25

[a] % of carbon present as $UC_{1.85 \pm 0.03}$ (excluding WUC_2 and free C).

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[4] M. J. Bradley and L. M. Ferris, *J. Inorg. Nucl. Chem.*, in press.

[5] B. R. T. Frost, *J. Nucl. Mater.*, **10**, 265 (1963).

[6] H. Nowotny, R. Kieffer, F. Benesovsky, and E. Laube, *Monatsh. Chem.*, **89**, 692 (1958).

[7] A. D. Horton and J. L. Botts, *Nucl. Sci. Eng.*, **18**, 97 (1964).

The effect of the trace of tungsten in the uranium dicarbide specimens used in our earlier hydrolysis studies[2] was only slightly larger than the experimental error (±10% of the value reported for hydrogen, the least accurate analysis). It does not account for the discrepancies between our data and those of others, although variations in the tungsten concentration in our specimens may be responsible for some minor variations in our data. The neutron activation analysis for traces of tungsten was not sufficiently accurate to confirm this.

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CONTRIBUTION FROM THE REACTION MOTORS
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Carborane Phosphate Exocycle

BY JOSEPH GREEN AND ANATOLE P. KOTLOBY

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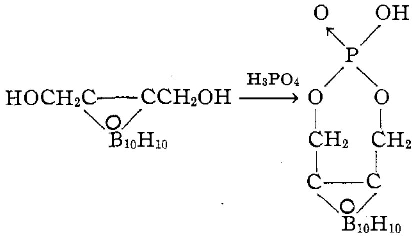
We wish to report the formation of a carborane exocycle prepared from 1,2-bis(hydroxymethyl)carborane and polyphosphoric acid.

Disubstituted carborane compounds have been reported to form 1,2-exocyclic compounds with ease. Numerous examples of the participation of the two carbon atoms of the carborane nucleus in five-membered rings have been reported.[1-4] The formation of six-membered[5] compounds (two carboranes contribute to ring) and a seven-membered[6] exocyclic compound has also been reported. This communication describes the formation of another seven-membered exocyclic compound.

Experimental

A mixture of 5.5 g. (0.03 mole) of 1,2-bis(hydroxymethyl)-carborane and 60 g. of polyphosphoric acid was allowed to react at 100–110° for 12–14 hr. Approximately 300 ml. of water was added to the slurry and then filtered to yield 9.4 g. of a solid. The solid was dissolved in ether and the solution was dried over magnesium sulfate. Evaporation of the ether yielded a white, crystalline solid which was recrystallized from hot benzene to give a solid, m.p. 259–260°. The product was soluble in acetone and hot acetonitrile, slightly soluble in benzene, and insoluble in pentane. The mass spectrum showed the most intense peaks in the m/e 262 to 268 region. The infrared spectrum (Figure 1) of the product contained absorption bands at 2899 (C–H), 2584 (B–H), 1653 (>P(O)(OH)), 1468 (CH_2), 1290 (PO), 1176 ($-CH_2OP$), 1081 (POC), 1026 (BH_2), and 727 cm.$^{-1}$.



Anal. Calcd. for $C_4H_{15}B_{10}O_4P$ (266.25): C, 18.05; H, 5.68; B, 40.61; P, 11.63. Found: C, 18.04; H, 5.62; B, 40.50; P, 11.82.

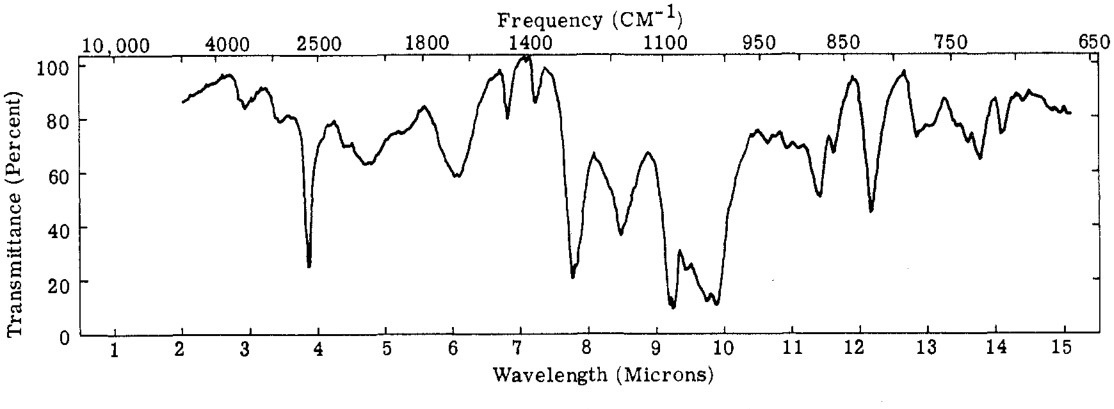


Figure 1.—Carborane phosphate exocycle.

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(1) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

(2) S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).

(3) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963).

(4) D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. Smith, S. Karlen, C. Vogel, and M. M. Fein, *ibid.*, **2**, 1125 (1963).

(5) R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963).

(6) J. Green, N. Mayes, A. P. Kotloby, M. M. Fein, E. L. O'Brien, and M. S. Cohen, *J. Polymer Sci.*, **B2**, 109 (1964).