spectrum is 3.1, well outside the range found for the other boranes. Any attempt to subtract out B_7H_{11} increased the rmd of the residue. The rmd of B_7H_{12} was 2.1, also outside the range of the boranes. The rmd's therefore lead us to doubt the existence of heptaborane(12) and heptaborane(13).

An attempt was made to find alternate formulas for the composite spectrum. Three possible formulas were developed: $C_2B_5H_{11}$ (rmd 0.88), $B_4H_{14}O_2$ (rmd 0.002), and AlB_5H_8 (rmd 0.93). The first formula was tried because hydrocarbons and alkylboranes are known contaminants of the raw B_4H_{10}. Although these were deliberately removed by the experimenters, they seemed to be possible impurities. A methylcarborane of this formula is known, but its fragmentation pattern is different.[8] The oxygen-containing formula was introduced because of the possibility of air and/or water contamination of the reactant. The formula containing a single oxygen atom had a rmd greater than the simple borane. No compounds with this formula have been found in the literature, but $B_4H_{10} \cdot 2H_2O$ may exist. The simplest possible aluminum-containing compound was tried because two aluminum diaphragms were used in these shock tube experiments.[4] No compound of this formula is known. For several reasons, it is not possible to determine the exact formulas present in the composite spectrum. The spectrum is almost certainly that of two or more compounds, and there are probably more ionic species present than there are experimental measurements to determine them. But the main conclusion stands. The isotope cluster technique supports the existence of heptaborane(11) only.

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[8] J. F. Ditter, F. J. Gerhart, and R. E. Williams, *Advan. Chem. Ser.*, **No. 72**, 191 (1968).

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Synthesis of Poly(carbon monofluoride) in a Fluorine Plasma

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Recently, there has been a large amount of interest, both academic and industrial in poly(carbon monofluoride) $(CF_x)_n$. This interest has been due primarily to the development of some new synthetic techniques at Rice University[1] and to some degree to a process developed in Japan for preparing a similar fluorinated carbon material of low molecular weight from activated charcoals and carbon black.[2] The material, obtained from fluorination of graphite is the most thermally stable polymeric fluorocarbon material known. It is indefinitely stable to 600° and stable for short periods of time to 800°.

Carbon monofluoride of a composition $CF_{0.92}$ was first prepared by Ruff, Bretschneider, and Elert in 1934.[3] In 1959, Rudorff and Rudorff[4] reported a preparation of carbon monofluorides of compositions $CF_{0.68}$ to $CF_{0.98}$ which ranged from black to off-white in color.[4,5] The techniques at Rice University[1] employed both high-temperature and high-pressure syntheses to prepare the first perfluorinated carbon monofluoride which had a stoichiometry of $CF_{1.12}$ and was snow white. These syntheses were adaptable to the production of 40 g quantities of pure white carbon monofluoride and also overcame the disadvantage of poor reproducibility which was characteristic of the previous syntheses.

Recently, excitement about the lubrication properties of solid carbon monofluoride has been generated by lubrication engineers at the Lewis Research Center of the National Aeronautic and Space Administration[6] and at the U. S. Army Frankfort Arsenal.[7] These studies have shown that carbon monofluoride as a solid lubricant under extreme conditions such as high or low temperatures, high pressures, or heavy loads is very much superior to graphite or molybdenum disulfide. In addition, workers at the U. S. Army Electronic Command at Ft. Monmouth, N. J.,[8] and industrial workers in Japan have concurrently demonstrated a high potential for carbon monofluoride for use as a cathode material in high-energy batteries.

A structure which was proposed by Rudorff for carbon monofluoride is shown in Figure 1. This structure has been shown to be approximately correct except for the layer stacking[9] and the fact that carbon atoms on the edges of each layer are divalent and therefore have both axial and equatorial fluorine. As one may determine by examining the carbon/fluorine ratio of the most highly fluorinated graphite, the $CF_{1.1}$ ratio is a result of these axial and equatorial fluorines and the exact stoichiometry varies with the particle size. Therefore only the snow white carbon monofluorides with carbon/fluorine ratios greater than 1 lack the fluorine site deficiencies characteristic of the earlier preparations.

Carbon monofluoride of lower stoichiometry has been normally prepared by the reaction of elemental fluorine with graphite at temperatures in the range 400–600°. It is interesting to observe that graphite does not begin to react with a fluorine atmosphere until 400°, while all carbon compounds containing double bonds will

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[1] R. J. Lagow, R. B. Badachhape, J. L. Wood, and J. L. Margrave, "Some New Synthetic Approaches to Graphite-Fluorine Chemistry," in press.

[2] S. Yoshizawa and H. Watanabe, British Patent 1,049,582 (1966).

[3] O. Ruff, D. Bretschneider, and F. Elert, *Z. Anorg. Allg. Chem.*, **217**, 1 (1934).

[4] W. Rudorff and G. Rudorff, *Z. Anorg. Chem.*, 217 (1947).

[5] W. Rudorff and G. Rudorff, *Chem. Ber.*, **80**, 417 (1947).

[6] R. L. Fusaro and H. E. Sliney, *NASA Tech. Memo.*, NASA TMX-S262Y (1969).

[7] H. Gisser, M. Petronio, and A. Shapiro, *J. Amer. Soc. Lubric. Eng.*, 161 (May 1970).

[8] K. Braeuer, Technical Report FCOM-3322, U. S. Army Electronics Command, Fort Monmouth, N. J.

[9] R. G. Bautista, D. W. Bonnell, and J. L. Margrave, "The Structure of Carbon Monofluoride," to be submitted for publication.

burn in fluorine under identical conditions. Examination of the thermodynamics of fluorine addition to normal double bonds reveals that this reaction is exothermic by approximately 68 kcal/mol of carbon–fluorine bonds formed.

The π electrons in graphite are probably the most extreme case of carbon electron delocalization known since there is an equal probability of finding a given π electron in any of three adjacent rings around each carbon atom. It would be expected that the "stabilization energy" from this delocalization is very high since the "delocalization energy" of benzene is known to be 36 kcal/mol. It is probable that the reaction of fluorine molecules with graphite does not occur readily due to the extra activation energy required to attack the very stable π-electron system and that the dissociation energy of fluorine must be provided to facilitate the reaction. A Boltzman calculation reveals that at 400° there are only a marginal number of fluorine atoms available while at 600° the fluorine atomic population becomes kinetically significant. It is also possible that the activation energy for the reaction may be such that electronically excited fluorine atoms are required. It would appear that a glow discharge in elemental fluorine is ideally suited for preparing carbon monofluoride at low gas temperatures. A high degree of dissociation of fluorine atoms may be achieved under appropriate plasma conditions and the likelihood of electronically excited fluorine atoms is also high. A fluidized bed reactor configuration was chosen to provide maximum surface contact of graphite particles with fluorine.

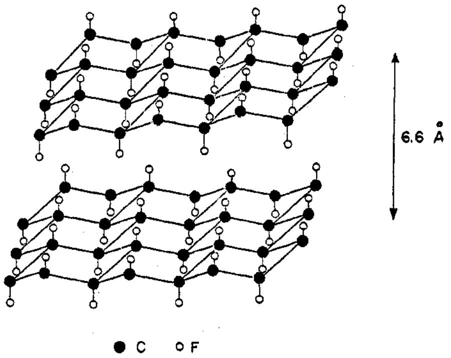

Figure 1.—Rüdorff $(CF_x)_n$ structure.

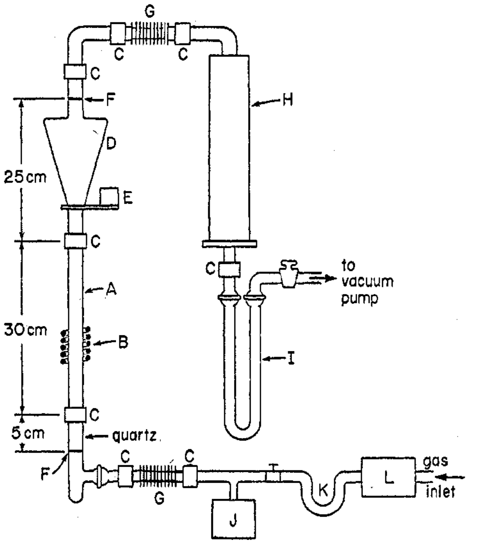

Figure 2.—Fluidized bed reactor.

Experimental Section

Materials, Analyses, and Physical Measurement.—The starting material was flake graphite (60 mesh 99%) which was selected to facilitate the particle fluidization and minimize particle losses. Fluorine was purchased from Allied Chemical Corp. (98%). The elemental analysis was done by Schwarzkopf Laboratories of Woodside, N. Y. Infrared spectra were obtained with a Beckman IR-20A spectrometer. KBr disk samples were used. Powder pattern X-rays were obtained on a Philips Electronics Model 12045B/3 X-ray generator using type 520 56/0 powder cameras. Copper (1.5405 Å) radiation was used in all X-ray spectra.

Apparatus.—The apparatus is illustrated in Figure 2. Fluorine flow was monitored with a Hastings-Raydist Model LF 50M transducer. The fluorine flow was controlled with a Monel needle valve. A sodium fluoride trap (L), placed after the needle valve, was used to remove hydrogen fluoride from the fluorine and a −78° copper U-trap (K) was used to remove the last traces of hydrogen fluoride. The internal pressure was measured with a Hastings Model Sp-1 vacuum thermocouple gauge (T) which was isolated with a Monel valve which is not depicted. Cajon 1 in. Ultra Torr fittings were used as coupling at all connections labeled (C) in the diagram. Viton O-rings which were coated with Fluorolube stopcock grease were used as seals. The Cajon couplings above and below the reactor were water cooled by soldering a piece of $^1/_4$ in. copper tubing to them and passing water through the tubing to keep the O-rings cool. The items labeled (G) are Cajon stainless steel flexible bellows. The glass items in the system were fabricated of Vycor. Nickel screens (150 mesh) were used to support and contain the graphite particles at the locations indicated in the diagram (F). These screens were held in place with Teflon washers. The reactor used was a 1 in. o.d. alumina (Al_2O_3) tube (A). Even quartz tubes will not withstand a fluorine plasma for more than several hours. A five-turn $^1/_4$ in. copper coil was used in conjunction with a 2 kW Raybond radiofrequency generator as a source for plasma generation. A 20-MHz operating frequency was selected. A particle return (D) was fabricated from a Vycor erlenmeyer flask and a vibrator was used (E) to prevent graphite particles from adhering to the walls. This vibrator was connected to an electrical circuit which pulsed the vibrations periodically. A particle trap was inserted after the particle return to catch the fine white carbon monofluoride powder produced. Unreacted fluorine was removed from the effluent gases with an alumina trap (H) (8–14 mesh activated alumina, $Al_2O_3 + F_2 \rightarrow 2\ AlF_3 + {}^3/_2O_2$). A liquid-nitrogen trap (I) was used to protect the vacuum pump which was attached as indicated in the diagram.

Experimental Procedure.—About 1 g of flake graphite was placed on a lower nickel screen (F). The system was then sealed and evacuated to at least 0.1 mm. The alumina must be dry or such vacuum is not possible. A fluorine flow of 30 cm^3/min is then introduced into the system and the pumping speed is adjusted to give an internal pressure of 2–5-mm. This fluorine flow fluidizes the particles between the upper and lower nickel screens (F). The fluidized particles are returned with the aid of the vibrator by sliding down the walls of the particle return (D). Thus the particles pass continually through the plasma reactor (A) to ensure maximum surface contact with the plasma. The water flow in the Cajon joints (C) above and below the reactor (A) is then initiated. The radiofrequency generator is then activated at a power output of 480 W. This value was obtained by measuring the voltage across the coil and the current between the blocking and tank capacitors. A highly reactive fluorine plasma is produced as the power is applied. The fluorine plasma is brilliant pink and turns to violet if any air leaks are present. The particles are then fluidized through the plasma for a 12-hr period. As the carbon monofluoride formation occurs, breakup of the graphite flakes is observed. Some of the snow white powder of stoichiometry $CF_{1.1}$ which is formed is deposited on the upper part of the erlenmeyer particle return and the majority of this carbon monofluoride passes through the upper screen (F) into the particle trap. After 12 hr the plasma is terminated, the reactor is dismantled, and the white carbon monofluoride is removed from the particle trap and the uppermost walls of the particle return.

The amount of snow white carbon monofluoride produced averaged 0.2–0.3 g per run. The material remaining on the lower nickel screen (F) was found to be carbon monofluoride of lower stoichiometry $\sim CF_{0.68}$ as determined by its infrared spectra and X-ray powder pattern. If finely powdered graphite is substituted for the flake graphite, more surface contact with the plasma occurs and as expected, the reaction proceeds more rapidly. However, it is difficult to keep the finer particles fluidized with the 30 cm^3/min fluorine flow because they stick to the upper screen (F) out of the plasma region. If this new synthesis is run on a larger industrial scale, finer particles will be used and the apparatus will be appropriately adapted. One other change would be necessary to perfect this system. The Vycor particle return (D) and the Vycor inlet to the reactor tube (A) is attacked by the fluorine plasma to such an extent that they may only be used for two or three runs. This attack removes a very significant amount of fluorine atoms from the plasma and this efficiency loss results in longer reaction times. Fabrication of these parts of alumina, although expensive, would completely eliminate this problem.

Carbon Monofluoride.—The total yield of carbon monofluoride was 80% based on a mass balance study of the system. The major by-product, carbon tetrafluoride, was recovered in the U-trap. A 10% yield of the snow white carbon monofluoride of composition $CF_{1.19}$ was obtained. This white material was recovered in the particle trap as previously indicated. Carbon tetrafluoride is the principal by-product and accounts for essentially all of the remaining 20%. *Anal.* Found: C, 34.2; F, 64.75. Calculated empirical formula: $CF_{1.19\pm0.04}$.

The infrared spectra of the samples consisted of a strong carbon–fluorine stretch at 1217 cm^{-1} and two medium bands at 1342 and 1072 cm^{-1} which are due to asymmetric and symmetric stretching vibrations of the peripheral CF_2 groups. A 332 cm^{-1} far-infrared band was observed and is due to bending in CF_2 groups.

The X-ray powder pattern contained nine lines. The observed "*d*" spacings (Å) were 5.80 vs, br; 3.4 w; 2.85 diffuse, m; 2.55 w; 2.2–2.25 vs, br; 1.83 w; 1.71 w; 1.66 w; and 1.289 s.

Results and Discussion

The plasma technique provides a new synthesis for poly(carbon monofluoride) $(CF_x)_n$. The infrared spectrum is in substantial agreement with that reported by Rudorff and Brodersen[10] and by workers at Rice University.[1] The X-ray powder pattern "*d*" spacings are in agreement with those of workers at Rice University[1] and in rough agreement with the spacings of 6.0, 2.23, and 1.30 Å reported by Palin and Wadsworth.[11] We have noted that the lines change slightly with fluorine content. The elemental analysis is consistent with the carbon monofluoride structure and corresponds to a stoichiometry of $CF_{1.19}$. This new synthesis for poly(carbon monofluoride) has several advantages over previous high-temperature syntheses. A much lower temperature was used. Measurement revealed that the gas temperature of the plasma is less than 150°. The amount of energy required to generate the plasma (480 W) is much less than is required to maintain a furnace of corresponding size in the 600° temperature range. Also it may prove easier to generate a larger plasma than to keep a large reactor uniformly in the rather narrow temperature range required for the thermal synthesis of the snow white $CF_{1.1}$. The fluidized bed method also avoids the necessity for batch processing since graphite may be continually added or withdrawn from the system.

This synthesis provides an example of the use of a fluidized bed plasma reactor design to prepare an industrially important material. This synthesis also demonstrates some of the advantages of a fluorine plasma in preparative fluorine chemistry.

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Benzene Clathrates with a Novel Kind of Metal Complex Host Lattice. $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ and $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$

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Two new benzene clathrate compounds, $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ (I) and $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$ (II), have been prepared, which appear to have a new kind of host structure. These clathrates were prepared as colorless crystals by contacting benzene with an aqueous solution of $Cd(en)_3Cl_2$ mixed with a solution of $K_2Cd(CN)_4$ or $K_2Hg(CN)_4$. *Anal.* Calcd for $C_{18}H_{20}N_6Cd_2$: C, 39.66; H, 3.70; N, 15.41; Cd, 41.23. Found: C, 39.68; H, 3.65; N, 15.30; Cd, 40.40. Calcd for $C_{18}H_{20}N_6CdHg$: C, 34.13; H, 3.18; N, 13.27; Cd, 17.75; Hg, 31.67. Found: C, 34.09; H, 3.15; N, 13.55; Cd, 17.89; Hg, 32.1. The chemical composition is analogous to that of the known clathrate Cd(en)Ni-

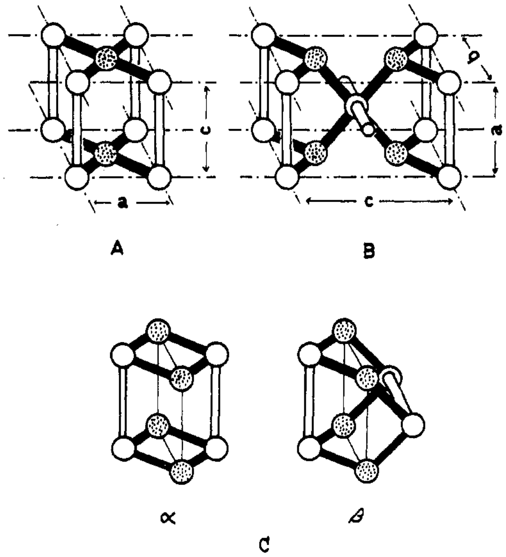

Figure 1.—(A) The tetragonal unit cell of $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$, (B) the proposed pseudotetragonal (orthorhombic) unit cell of $Cd(en)M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg), and (C) cavities for guest molecules: open circles, octahedral Cd; shaded circles, square-planar Ni and tetrahedral Cd or Hg; open columns, en; solid columns, CN. For $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ a = 7.675 and c = 8.056 Å.[2]

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[10] W. Rudorff and R. Brodersen, *Z. Naturforsch.*, **126**, 595 (1957).

[11] D. E. Palin and K. D. Wadsworth, *Nature (London)*, **162**, 925 (1948).

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