Some New Synthetic Approaches to Graphite–Fluorine Chemistry

By **Richard J. Lagow**,† **Rammachandra B. Badachhape**, **James L. Wood**, and **John L. Margrave**,*
Department of Chemistry, Rice University, Houston, Texas 7700

New methods for synthesising poly(carbon monofluoride) $(CF_x)_n$ and tetracarbon monofluoride C_4F are reported. Pyrolytic graphite has been fluorinated and a new compound, graphite oxyfluoride, has been prepared. Poly(carbon monofluoride) has been prepared in a flow reactor, in a fluidized-bed reactor, and in a high-pressure bomb reactor and tetracarbon monofluoride has been prepared by a high-pressure bomb technique. Some new structural data are presented for poly(carbon monofluoride). Recently, poly(carbon monofluoride) has been found to have a high potential as a solid lubricant and as a cathode material in high-energy batteries.

POLY(CARBON MONOFLUORIDE) $(CF_x)_n$ has been known since 1934, when Ruff *et al.*[1] prepared a grey compound of composition $CF_{0.92}$. In 1947 W. and G. Rüdorff[2] reported a series of compositions, $CF_{0.68}$ to $CF_{0.995}$, varying from black in the case of $CF_{0.68}$ through grey to white in the case of $CF_{0.995}$. Tetracarbon monofluoride (C_4F) was reported by W. and G. Rüdoff[1] in 1947. Reviews of the chemistry of these compounds have been published by Rüdorff[3] and Hennig.[4] Very recently a series of Japanese publications on carbon monofluoride have appeared.[5] The poor reproducibility of these syntheses for carbon monofluoride, although not generally appreciated by fluorine chemists due perhaps to the widespread review of the synthesis, has been noted by several authors.[1,2,4] Indeed it is nearly impossible to obtain significant quantities of white or even light grey carbon monofluoride by employing previous preparations, a grey material of stoicheiometry $CF_{0.68}$ to $CF_{0.8}$ normally being obtained.

Samples of carbon monofluoride from our laboratories have been tested by the Lewis Research Center of the National Aeronautics and Space Administration[6] and by the Frakford Arsenal of the U.S. Army[7] and found to be a superior solid lubricant especially under high temperatures, in oxidizing atmospheres, under heavy loads, *etc.* These tests show that it provides adequate lubrication under conditions where graphite and molybdenum disulphide are totally unsatisfactory. Also, workers at the U.S. Army Electronics Command at Ft. Monmouth, New Jersey, and industrial workers in Japan, have concurrently demonstrated a high potential for carbon monofluoride for use as a cathode material in high-energy batteries.[8] Many other intriguing physical properties and especially the thermal stability of this compound, indicate that it may soon join the not too highly populated group of compounds developed by inorganic chemists which have practical applications.

Poly(carbon monofluoride) is a white compound, often reported to be explosive and unstable, but found in this work to be stable in air to temperatures up to at least 600 °C. It decomposes at 800 °C or under a high vacuum at 420—580 °C to form a series of polyolefinic-fluorocarbons.[9] Compounds with compositions in the range of $CF_{0.68}$ to $CF_{0.8}$ are nearly black, while those of compositions $CF_{0.8}$ to $CF_{0.95}$ and $CF_{0.95}$ to $CF_{1.12}$ are grey and white respectively.

Tetracarbon monofluoride (C_4F), first prepared by Rüdorff,[10] is black with the physical appearance of

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† *Present address:* Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

[1] O. Ruff, D. Bretschneider, and F. Elert, *Z. anorg. Chem.*, 1934, **217**, 1.

[2] W. Rüdorff and G. Rüdorff, *Z. anorg. Chem.*, 1947, **253**, 281.

[3] W. Rüdorff, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 230.

[4] G. R. Hennig, *Progr. Inorg. Chem.*, 1959, 125.

[5] B.P. 1,049,582/1966; N. Watanabe and K. Kumon, *Demki Kagaku*, 1967, **35**, 19.

[6] R. L. Fusaro and H. E. Sliney, NASA Technical Memorandum, NASA TMX-5262Y, 1969.

[7] N. Gisser, M. Petronio, and A. Shapiro, *J. Amer. Soc. Lubric. Eng.*, 1970, May, 61.

[8] K. Brauer, Technical Report ECOM-3322 U.S. Army Electronic Command, Fort Monmouth, New Jersey.

[9] A. K. Kuriakose and J. L. Margrave, *Inorg. Chem.*, 1965, **4**, 1639.

[10] W. Rüdorff and G. Rüdorff, *Chem. Ber.*, 1947, **80**, 417.

graphite. Hydrogen fluoride is always incorporated into the C_4F lattice.[10] C_4F is stable in air to *ca.* 100 °C and at higher temperatures it decomposes into a fluffy black soot. This property makes it impossible to prepare $(CF_x)_n$ from C_4F at low pressures since the decomposition occurs before one reaches the temperature of reaction for $(CF_x)_n$. These two compounds and graphite oxide are among the unusual ' compounds ' of graphite in which there is actually bonding to the carbon atoms.

In the past, it has been reported that $(CF_x)_n$ may be prepared by passing fluorine over graphite at 450—600 °C for several hours.[3] Sometimes hydrogen fluoride is used as a catalyst. The preparation of tetracarbon monofluoride [10] was previously accomplished by passing a fluorine–hydrogen fluoride mixture over graphite at 20—80 °C with 20 °C being the most favourable temperature. In our laboratory this preparation was found to be both difficult to reproduce and time-consuming.

EXPERIMENTAL

Materials.—Graphite powder (325 mesh) supplied by Union Carbide Corp., Carbon Products Division, SP-2 grade, lot number G96, was used in all preparations. The total concentration of impurities in this graphite was less than 1 p.p.m. The fluorine used was supplied by the Allied Chemical Corp., and was typically of 98% purity.

Apparatus.—In the preparations *via* the flow technique, the apparatus consisted of a 1 in × 1·5 ft nickel tube in a Hevi-Duty Electrical Company furnace. The flow rates were measured with a Hastings-Raydist, model LF50, mass flowmeter and model LF50M transducer. A typical fluorine-handling apparatus was used.[11] A prefluorinated nickel boat, 7½ in long and ½ in wide, was used to hold the sample.

A fluidized bed reactor with a ¼ in nickel wall and a conical inlet was also used. It was 10 in in length and had a 2 in i.d. The lid was held in place by nuts and bolts with a Teflon O-ring set in the groove at the base to prevent fluorine leak. At the intersection of the cone and the main cylindrical body, a 250-mesh nickel wire cloth supported by two interlocking nickel rings was used to support the sample. Also a nickel wire cloth was used to cover the outlet opening to keep the sample from escaping. Fluorine was allowed to flow into the cone, through the reactor and to escape through an outlet at the top. The reactor was cooled at the outlet by a water-cooled copper coil which was welded to the reactor. The inlet was cooled by air flow through a nickel jacket and the reactor was heated with an electrical resistance furnace of 2½ in o.d.

For the static-bomb technique, a cylindrical nickel bomb, 8 in long, 2½ in i.d., and with a ½ in wall was used. An Autoclave 30 VM-6075 Monel valve was attached to the top outlet of the bomb and this was cooled by the use of air jets. The reactor was heated with a 3 in i.d. electrical-resistance furnace. In the low-temperature C_4F work, a standard fluorine calorimetric bomb works equally well.

The temperatures in all the reactors were measured with a Pt–10% Rh *vs.* Pt thermocouple in conjunction with a potentiometer or a model JP West temperature controller.

The analyses were done by Schwarzkopf Microanalytical Laboratories, Woodside, New York. Infrared spectra were taken on a Beckman IR-8 using KBr disc samples. The powder *X*-ray patterns were made with a Phillips Electronic, model 12045B/3, *X*-ray spectrometer and with type 52056/0 powder pattern cameras. Copper (1·5405 Å) radiation was used in all *X*-ray spectra.

Reaction of Fluorine with Graphite to Produce Poly(carbon monofluoride) $(CF_x)_n$

(A) *Flow Method.*—Graphite (1·0—10·5 g) was spread uniformly over the bottom of the nickel boat. The furnace was allowed to warm to 200 °C for *ca.* 1 h while helium was passed over the sample at a rate of 4 ml/min in order to drive oxygen and moisture from the sample and reaction chamber. At the end of this period the furnace was raised to a temperature of 627 ± 3 °C and fluorine was passed over the sample at a flow rate of 3—4 ml/min. The flow was continued at that temperature for at least 12 h. Then the furnace was cooled and the fluorine was shut off while helium was again passed over the chamber to drive the fluorine out. The white product was then removed from the nickel boat [Found: (*a*) C, 36·0; F, 63·55; (*b*) C, 36·0; F, 61·1%. Calculated empirical formula: $CF_{1\cdot12 \pm 0\cdot03}$].

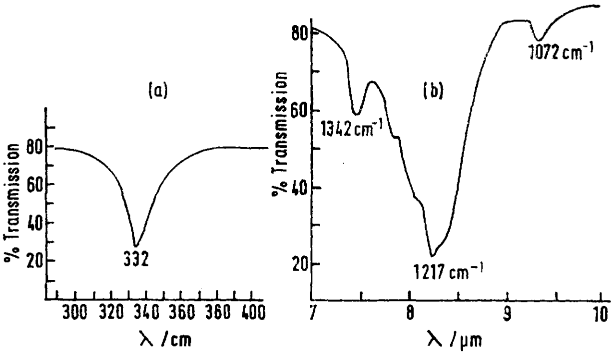

FIGURE 1 (a) Absorption spectrum at fluorinated graphite in the far-i.v. region (410—290 cm^{-1}) as a Nujol mull. (b) Absorption spectrum of fluorinated graphite (in KBr disc) in the C–F vibration frequency region

The infrared spectra of such white samples, recorded with a Beckmann IR-8 spectrometer, showed a broad strong absorption band at 1215 cm^{-1}, corresponding to that reported by Rüdorff and Brodersen.[12] A high-resolution infrared spectrum shows more detail (Figure 1).

The strongest band occurred at 1217 cm^{-1} and may be assigned to the C–F stretching vibrations for tertiary carbon atoms. Two medium bands were observed at 1342 and 1072 cm^{-1}, presumably due to asymmetric and symmetric stretching vibrations, respectively, of the peripheral CF_2 groups. At 332 cm^{-1} a far-infrared band was observed and is probably due to bending in CF_2 groups. A trace of residual CH groups was indicated by a very weak band at 2950 cm^{-1}. Also broad, very weak unassigned bands were noted at 2300, 900, and 890 cm^{-1}.

X-Ray powder pattern analysis with copper radiation yielded interplanar *d* spacings of 5·80, 2·89, 2·23, and 1·29 Å. These lines were somewhat diffuse but pressing in a tetrahedral anvil at 200 °C and 50 kbar for 3 h sharpened the original lines and brought out some weak lines at interplanar spacings of 3·24, 2·57, 2·22 and still fainter lines at 1·86, 1·72, and 1·64 Å. Interplanar spacings of 6·0, 2·23, and 1·30 Å have been previously reported by Palin and

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[11] J. Gordon and F. L. Holloway, *Ind. and Eng. Chem.*, 1960, **52**, 5, 63.

[12] W. Rüdorff and K. Brodersen, *Z. Naturforsch*, 1957, **126**, 595.

Wadsworth.[13] It has been noticed that the lines change slightly with fluorine content and a detailed study on the structure as a function of the fluorine content is in progress.[14]

(B) *Bed Method.*—The graphite powder was placed on the screen at the conical intersection of the bed and the reaction chamber was then closed. Helium was passed at 10 ml/min through the chamber at 200 °C for 1 h in order to remove air and moisture. Fluorine was introduced at 12 ml/min and the temperature was raised to 625 ± 3 °C. The product, removed after 12 h was found to be nearly white. The products were characterized on the basis of their infrared spectra and *X*-ray powder analyses. The material was identical to that produced in the flow method.

(C) *Static-bomb High-pressure Method.*—(1) *Room-temperature method.* Graphite (3 g) was placed in the bomb and the sample was evacuated to remove air and moisture. Fluorine was then slowly introduced to 20 lbf/in². A slight reduction in the pressure of the gas was noticed after a few minutes, as measured with a common diaphragm pressure gauge. This was due either to surface adsorption or a small preliminary reaction. The pressure was then slowly raised to 200 lbf/in². The next part of the experiment was potentially extremely hazardous. At 225—250 lbf/in² (this varied in the 6 experiments reported here), the fluorine began to react with the graphite, as observed by the pressure drop on a pressure gauge when the fluorine source valve was closed. Special care was taken to add the fluorine slowly and carefully since too rapid addition can give rise to an explosion inside the bomb accompanied by a large energy release. In such experiments, the temperature of the skin of the ½ in thick bomb rose to 110 °C, as measured with a thermocouple, and the pressure gauge was pinned past 700 lbf/in². Fortunately the system was designed to withstand these extremes. When this violent reaction occurs, the product is $(CF_x)_n$ of low fluorine content and CF_4.

After the pressure had been raised to 250 lbf/in² slowly enough to avoid a violent reaction, the fluorine pressure in the bomb was maintained at 250 lbf/in² for 2 h or until no further reaction, *i.e.* pressure drop, was observed. This reaction warmed the jacket of the bomb to 80 °C. The pressure was then raised slowly to 350 lbf/in² at which it was maintained for 12 h. After this time the pressure was released and the bomb evacuated and then refilled with helium at 1 atm; the light grey product was then removed. This had the same infrared absorption at 1215 cm⁻¹ as the $(CF_x)_n$ from other preparations. The *X*-ray powder pattern showed the same lines but they were sharper as in the case of the $(CF_x)_n$ which had been pressed in the tetrahedral anvil.

(2) *Higher temperature methods.* It was found that a combination of high temperature and high-pressure treatments would produce carbon monofluoride at any temperature in the range of 20—627 °C and any pressure in the range of atmospheric to 250 lbf/in². A bomb preparation similar to the room temperature method was used. The conditions are summarized in the Table. The materials produced were characterized by *X*-ray powder pattern lines and infrared spectra which were identical to the $(CF_x)_n$ from other preparations. Exact stoicheiometry varied in different samples from $CF_{0\cdot9}$ to $CF_{1\cdot1}$ but all syntheses will yield $CF_{1\cdot1}$ with careful control.

Critical pressure and temperature chart for carbon monofluoride synthesis

Pressure (lbf/in²)	Temp. (t/°C)
15 (1 atm)	627
60	620
125	610
175	300
215	200
226	20

Reaction of Fluorine with Pyrolytic Graphite

To gain further insight into the nature of the reaction, pyrolytic graphite with *d* spacings of 3·75, 3·42, 2·70, 2·15, 2·07, 2·00, 1·70, 1·239, and 1·18 Å, was allowed to react with fluorine in a procedure identical with that used in the original flow method. A white fluffy powder was obtained. The infrared spectrum was identical with $(CF_x)_n$. The *X*-ray powder pattern revealed that the product had the same *d*-spacings as $(CF_x)_n$. Thus, one concludes that the reaction of fluorine with pyrolytic graphite produced a product which was structurally identical to the product of the reaction with regular graphite.

Reaction of Fluorine with Graphite to Produce Tetracarbon Monofluoride C_4F

A convenient amount of graphite was placed in the reaction bomb and the system was evacuated to remove water and air. Hydrogen fluoride gas was introduced into the bomb to a pressure of 15 lb/sq in and fluorine was then introduced slowly to a pressure of 60 lbf/in². The reaction started immediately upon introduction of fluorine into the bomb and the side of the bomb became noticeably hot to the touch. Although the reaction was essentially complete in 15 min, the pressure was maintained at 60 lbf/in² for 12 h. The bomb was then evacuated and the product removed. The product was placed in a vacuum desiccator in an attempt to remove adsorbed HF.

The infrared spectrum had only a broad band of low intensity in the range 1300—1000 cm⁻¹, with its greatest intensity at 1090 cm⁻¹. Also some bending in the 1600 cm⁻¹ region was noticed. This 1090 cm⁻¹ stretch is assignable as a carbon–fluorine stretching vibration. A small almost unnoticed hump was found at 3510 cm⁻¹, which might be due to adsorbed HF. No infrared data are previously reported. The *X*-ray powder pattern showed *d*-spacings of 5·29 (broad and intense), 2·15 (sharp), 1·24 (weak), and 2·8 (very weak and diffuse) [Found: (*a*) C, 62·85; F, 35·45 ± 5; H, 0·65; (*b*) C, 62·65; F, 32·85 ± 5; H, 0·65%; corresponding to empirical formulas of (*a*) $C_{4\cdot07}F$, 0·50 GF; (*b*) $C_{4\cdot02}F$, 0·49 GF respectively.

Preparation of Graphite Oxyfluoride

Graphite oxide in the dark brown enol form (also known as graphitic acid) was prepared by the reaction of graphite (1 g) with sulphuric acid (25·5 ml), potassium permanganate (3·0 g), and sodium nitrate (0·5 g) for 5 h at 66 °C following Hummers.[15] The product was washed and dried *in vacuo* over P_2O_5 at 40 °C for 3 days.

This brown graphite oxide was then placed in a nickel boat (1 g) and treated in the previously described flow fluorination system. Helium was passed over the sample at 4 ml/min for 1 h to remove the air from the system. Then

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[13] D. E. Palin and K. D. Wadsworth, *Nature*, 1958, **162**, 925.

[14] R. G. Bautista, D. W. Bonnell, and J. L. Margrave, to be published.

[15] W. S. Hummers and R. E. Offerman, *J. Amer. Chem. Soc.*, 1958, **80**, 1339.

fluorine gas was introduced at 4 ml/min for a period of 24 h with the system at room temperature.

The reaction was stopped and the chamber purged with helium. The product was a light grey powder which resembled $CF_{0\cdot 9}$ in appearance. It was reactive and unstable above 50 °C and would decompose to a yellow-brown powder if heated or left standing in air for over 1 day. It reacted with water to evolve hydrogen fluoride gas and giving a muddy green precipitate.

Graphite oxide is an ill-defined compound of empirical formula $C_8O_2(OH)_2$; but it may have variable compositions. The carbon to oxygen ratio of the graphite oxide was found to be 2·2 by elemental analysis. The infrared spectra of graphite oxide consisted of absorption at 3430s,br, 1725s,br, 3620w, 1605m, and 1070vw cm^{-1}, very weak. These same values were reported for graphite oxide by Novak and Hadzi,[16] and in addition they found additional weak bands at 1420, 1365, and 980 cm^{-1}. The 3430 cm^{-1} band is due to the OH stretch and the 1605 cm^{-1} was assigned in their paper to the bending of adsorbed water molecules, however, it appears that this may be due in part to the double-bond stretching of the enol groups or double bonds in the carbon lattice. The infrared spectrum of the fluorinated compound was unchanged except that a strong broad band appeared at 1095 cm^{-1} due to a C–F stretch. This stretch covered the weak stretch at 1070 cm^{-1}. Also the 1605 cm^{-1} feature may have weakened in intensity. Fluorine analysis ranged from 16·25 to 22·4% fluorine content in several samples of the oxyfluoride and the carbon oxygen ratio dropped to a range of 4·4—4·28.

The *X*-ray powder pattern (Cu radiation) *d* values for the graphite oxide were found to be 8·5 strong; 3·15 medium; and 1·24 weak. The fluorinated graphite oxide had only 3*d* values of 7·6 strong; 3·31 medium; and 2·34 weak.

Oxidation of C_4F *and* $CF_{0\cdot 68}$

Samples of C_4F and $CF_{0\cdot 68}$ were subjected to the same oxidation procedure used to produce graphite oxide from graphite. Both samples were initially black and the products were also black. The experiment was performed in the hope of producing another oxyfluoride of graphite. The powder pattern *X*-ray and infrared spectra revealed that the structure of the product was the same as the starting material (same *d* lines). This result was interpreted to mean the C_4F and $CF_{0\cdot 68}$ had been resistant to this harsh oxidation and that they had remained unchanged.

RESULTS AND DISCUSSION

The synthesis of poly(carbon monofluoride) $(CF_x)_n$ was accomplished by two new methods and the flow method was refined and improved. In the flow method and the fluidized-bed method it was found that to produce the whitest $(CF_x)_n$ of the highest fluorine content, it was necessary to maintain a temperature of 627 ± 3 °C. This 6° range was very critical. In the previous work this was not recognized and consequently the process for production of $(CF_x)_n$ gained a reputation for being irreproducible. $(CF_x)_n$ Is formed from *ca.* 540 to 630 °C. At the 540 °C the empirical formula is $CF_{0\cdot 68}$ and the product is black. One may observe this effect experimentally in the reaction boat. If the furnace has a 'hot' zone within this 6 °C range smaller than the length of the boat, only the central region of the boat produces white $(CF_x)_n$ and on either side the colour ranges from grey to black. At temperatures over 630 °C the compound is unstable in fluorine and burns to produce CF_4 and a black soot. $(CF_x)_n$ Is a solid subfluoride of carbon which is formed only under these critical conditions.

As a result of the discovery of the critical nature of the temperature control, the limiting stoicheiometry of $(CF_x)_n$ has been found to be $CF_{1\cdot 12\,\pm\,0\cdot 03}$. Other maximum values have been reported previously in the $CF_{0\cdot 98}$ region, *i.e.* the *x* in $(CF_x)_n$ approaches one. The poly(carbon monofluoride) produced here is a homogeneous compound as substantiated by the infrared spectra and the structural data.

Rüdorff[10] postulated a structure for $(CF_x)_n$ (Figure 2) in which a fluorine atom was attached to each carbon atom alternately above and below the plane of the original graphite lattice, and an interplanar spacing of 6·6 Å. Further, Rüdorff assumed that the layer stacking was carbon over carbon. After examining 3-dimensional models of the structure, it appears more likely that the stacking would be carbon atom over the hole in the centre of the cyclohexane ring in either an ABAB (hexagonal) or ABCABC (rhombohedral) lattice. A more exact *X*-ray study is in progress.[14] In Figure 2, the individual cyclohexane rings are arbitrarily shown in the chair configuration, due to the thermodynamic stability of this form in cyclohexane. It is also possible to construct all-boat configurations, but these show a more puckered lattice. The boat structures lead to two types of fluorine atoms, *i.e.* the fluorine atoms are not equidistant. Also, one can draw configurations with both chair and boat rings. The several possible structures for CF_x may account for the fact that the *X*-ray powder pattern is not sharply defined until the solid is forced into its most stable configuration using the tetrahedral anvil press.

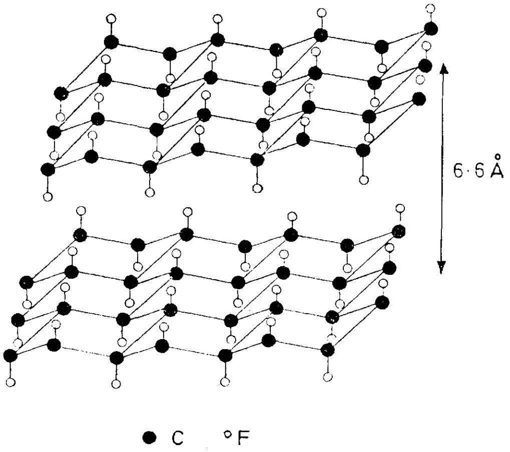

FIGURE 2 Rüdorff $(CF_x)_n$ structure

The stoicheiometry obtained in this study, $CF_{1\cdot 12\,\pm\,0\cdot 03}$,

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[16] D. Hadzi and A. Novak, *Trans. Faraday Soc.*, 1955, **51**, 1614.

implies extra fluorine atoms and these fluorines occur as CF_2 groups around the edge of the ring. Rüdorff's $CF_{0\cdot95}$ empirical formula does not provide evidence for these peripheral-CF_2 groups and even indicates some fluorine deficiencies on the tertiary carbon atoms in the graphite plane. It is also possible that Rüdorff's particle size may have been large enough to make this excess negligible stoicheiometrically. The peripheral CF_2 groups would have fluorine atoms in axial and equatorial positions. The side bands at 1342 and 1072 cm^{-1} are probably due to the asymetric and symmetric stretching of these groups and provide evidence of their presence. Also, the strong band at 1217 cm^{-1} is characteristic of the C–F stretch. In the infrared spectrum of perfluorocyclohexane, Thompson and Temple [17] observed three similar bands at 1200, 1270 (strongest), and 1320 cm^{-1} and made the same assignment.

In the fluidized-bed preparation it was possible to make larger quantities of poly(carbon monofluoride) per run than in the flow method. The major problem was to keep unchanged graphite particles from sticking to the walls of the bed, out of the ' hot ' zone, and eventually contaminating the product. This was partially overcome by sandwiching the reactant between the base screen and a screen placed at the upper limit of the 6 °C zone.

The first bomb method is unique in that the process is spontaneous at room temperature. It is also adaptable to large quantities. Its disadvantage is the danger involved in the synthesis. The second bomb method constitutes a nearly complete investigation of pressure–temperature relation for the reaction and allows the preparation of carbon monofluoride over a wide range of pressures and temperatures.

The room-temperature bomb preparation of carbon monofluoride may be more than just a trivial alternative synthesis with some potential economic advantages. It is certainly unusual that fluorine does not begin to react with graphite at atmospheric pressure until a temperature of >450 °C has been reached. In contrast, all other known carbon–carbon $sp^2\sigma$ bonds are very reactive, often giving rise to explosive reactions with fluorine under ambient conditions and temperatures. The fact that temperatures of *ca.* 600 °C are needed to prepare carbon monofluoride efficiently, is an indication that a kinetically significant population of atomic fluorine may be necessary to initiate this attack. The higher pressure room-temperature reaction occurs spontaneously even though the atomic fluorine concentration is lower. This is perhaps due to the rapid regeneration of a kinetically significant population of fluorine atoms at the surface of the graphite layer from the increased molecular collision frequency at the higher pressure.

The pyrolytic graphite experiment may have indicated that the structure of the graphite starting material has little effect on the product's structure owing to the expansion of the interplanar lattice parameter. The method for making tetracarbon monofluoride in the bomb is far superior to the previous method because it is adaptable to large quantities and the time involved is much shorter; the reaction is essentially complete in 15 min. In our sample as in Rüdorff's original sample, HF was adsorbed on the surface of the compound. It appears impossible to remove this impurity completely and, consequently, the fluorine due to HF must be subtracted from the carbon/fluorine analysis. This is done by analysing for hydrogen as well. Also it was assumed that the carbon and hydrogen analyses were more reliable than the fluorine analysis. The analyses come to totals of 98·92 and 95·97% and the discrepancy was assumed to be a deficiency in the fluorine analysis.

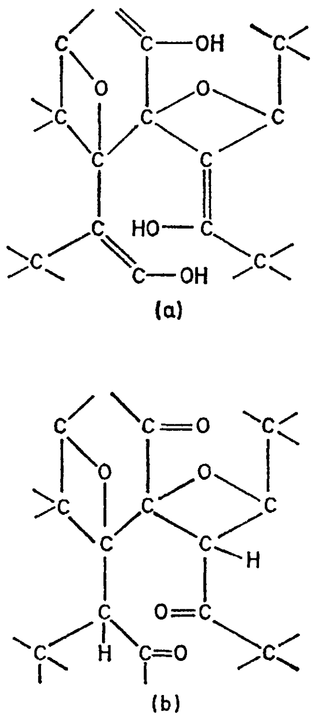

FIGURE 3 Hofmann's graphite oxide structure, (a) enol form, (b) keto form

Graphite oxide is a very ill defined compound. The *X*-ray powder pattern of graphite oxide has only 3 lines and the infrared spectrum is not definitive. Its structure is probably best represented as in the diagram of Hofmann *et al.*[18] (Figure 3). This structure leads to an idealized empirical formula of $C_8O_2(OH)_2$. Graphite oxide is most suitably characterized by the carbon/oxygen ratio.[3] The graphite oxide produced in this work was found to have a carbon oxygen ratio of 2·2 by elemental analysis. This corresponds to a highly oxidized sample since it has been reported that carbon oxygen ratios of 2·4—2·9 represent well oxidized preparations and ratios lower than 2·0 have not been attained.[3]

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[17] H. W. Thompson and R. B. Temple, *J. Chem. Soc.*, 1948, 1432.

[18] A. Clauss, R. Plass, H. P. Boehm, and U. Hofmann, *Z. anorg. Chem.*, 1957, **291**, 205.

There is evidence of carbonyl, enol, and epoxy group absorptions in the infrared spectrum. The ' enol and keto forms ' of Hofmann are interconvertible and the enol is probably the most stable since the keto rearranges to this form both when heated and with time. This is accompanied by a colour change from light tan or yellow to a dark brown (enol form). However, both in our infrared spectrum of graphite oxide and that of Hadzi and Novak weak absorption at 1725 cm^{-1} (CO stretch) was present together with absorption at 3430 cm^{-1} (strong enol stretch). The obvious conclusion from this information and the variable stoicheiometry of graphite oxide is that this compound is not of uniform structure, but an array of enol, keto-, and epoxy-groups randomly dispersed in the graphite lattice in a manner similar to the diagrams of Hofmann.

The new oxyfluoride exhibits a carbon fluorine stretch at 1095 cm^{-1} indicating the formation of carbon–fluorine bonds. In accordance with the discussion of the graphite oxide structure, the fluorine content of 16·25—22·4% of the oxyfluoride, and the reduced oxygen content of the oxyfluoride indicated by a change in the carbon/oxygen ratio from 2·2 to the range 4·4—4·20, one is able to postulate the structure of the new compound. The fluorine probably replaces all hydrogen on the tetrahedral carbons in the keto-form with fluorine, adds to most of the enol-type double bonds in the enol form, and replaces at least some of the enol, hydroxy-groups, keto, carbonyl, and epoxy-type oxygen with fluorine. It is possible that oxygen–fluorine bonds may be formed initially in reactions with these groups, but this bond is usually unstable and would easily decompose. The addition of the carbon–fluorine bonds to the system changes the interplanar spacings as evidenced by the changed powder pattern lines. The graphite oxyfluoride appears to be an interesting new composition, but is a compound only to the extent that one considers graphite oxide to be a compound. Its reactivity may prove of use as a fluorinating agent.

Financial support for this work from the U.S. Army Research Office, Durham, North Carolina is gratefully acknowledged.

[3/1823 *Received, 3rd September, 1973*]