

### Short Communication

## Synthesis of graphite hydrofluoride by hydrofluorination of graphite at room temperature

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#### Abstract

Madagascar natural graphite, when treated with pyridinium poly(hydrogen fluoride) in the presence of a metal fluoride catalyst at room temperature, yields a grey hydrofluorinated product in about 10 days. The product, graphite hydrofluoride, has been characterised by IR, XRD, SEM and conductivity measurements.

**Key words:** Room temperature hydrofluorination, graphite, graphite hydrofluoride, hydrogen fluoride.

### 1. Introduction

Graphite fluorides possess unique physicochemical properties and have a wide variety of industrial uses. They are covalent compounds of graphite; however, they can be regarded as graphite intercalation compounds because of their layered structures derived from graphite by insertion of covalently bonded fluorine atoms. They are usually prepared by direct reaction of elemental fluorine on graphite. Effects of diluting with inert gases, oxygen and hydrogen fluoride on the formation of graphite fluoride have also been reported<sup>1,2</sup>, but no mention has been made of hydrogen fluoride as a fluorinating reagent. This work reports the first attempt of the reaction of graphite with modified hydrogen fluoride at room temperature. The product has been characterised as graphite hydrofluoride. This is also the first synthesis report of the formation of covalent C-H and C-F bonds at room temperature with graphite carbon.

### 2. Experimental procedure

Madagascar natural graphite (200-250 mesh) was treated with 20 ml of pyridinium poly(hydrogen fluoride) (70:30) in the presence of a metal fluoride catalyst at room temperature (range: 20-30°C) for 10 days, in a polyethylene container under continuous stirring. At the end of this period, the treated graphite was separated, washed free of hydrogen fluoride and finally dried under vacuum. Spectral studies were done on a dry sample.

Infrared absorption spectra of the graphite hydrofluoride (KBr pellet) were recorded on a Hitachi model no. 270-50 spectrophotometer, X-ray powder diffraction patterns on Philips 1050 70 X-ray diffractometer using  $\text{CuK}_\alpha$  radiation for the Madagascar natural graphite, and  $\text{Co-K}_\alpha$  radiation for the synthesised graphite hydrofluoride. Scanning electron micrographs of treated and untreated graphite were recorded on a JSM 840 A scanning electron microscope and the surface resistivity of a pelletised graphite hydrofluoride was recorded using a constant current source Keithley instrument.

### 3. Results and discussion

The IR absorption spectra (fig. 1 and Table I) show absorptions due to aliphatic  $-\text{CH}_3$ ,  $(\text{CH}_2)_n$  and  $>\text{CF}_2$  group and  $\text{CF}_2$  wagging bands in  $\text{CF}_2$  chains as a series of sharp regularly spaced bands in the region  $1000-400\text{ cm}^{-1}$ . These assignments have been made based on the pattern followed for ethyl and methylene groups<sup>3</sup>. Since the intensities of the bands due to stretching vibrations of carbon-fluorine are much less than that of carbon-hydrogen it is inferred that carbon-hydrogen bonds are predominantly present in the peripheral positions and C-F bonds are the result of fluoride permeation into the basal plane to form  $>\text{CF}_2$  chains. Further, in graphite fluoride  $[(\text{C}_2\text{F})_n$  and  $(\text{CF})_n]$  C-F stretching vibration of tertiary carbon atom is observed as strong absorption bands at  $1221\text{ cm}^{-1}$  and  $1219\text{ cm}^{-1}$ , respectively<sup>2</sup>. This is found to be absent in the present sample indicating the absence of peripheral  $-\text{CF}_3$  groups and the predominant presence of  $-\text{CH}_3$  groups.

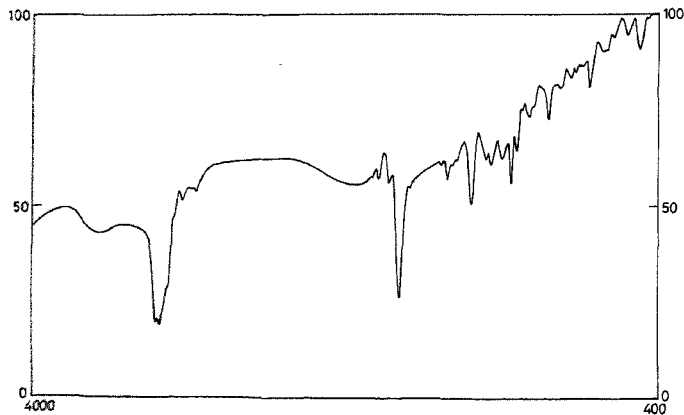


FIG. 1. IR Spectral data of graphite hydrofluoride.

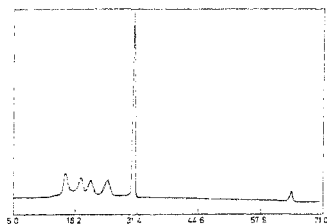


FIG. 2. X-ray Diffraction pattern of graphite hydrofluoride (Target Co-K $\alpha$ ).

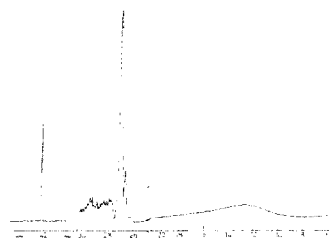


FIG. 3. XRD of graphite. (Target Cu-K $\alpha$ ).

Table I  
IR Spectral data for graphite hydrofluoride  
with assignments

Sl no.	W $\lambda$ (cm $^{-1}$ )	Assignment
1	2956(s)	CH $_3$ Asym str
2	2920(s)	CH $_2$ Asym str
3	2836(m)	CH $_3$ Sym str
4	2728(m)	CH $_2$ Sym str
5	1461(s)	CH $_3$ Asym def CH $_2$ Def
6	1383(w)	CH $_3$ Sym def
7	1080(m)	>CF $_2$ Sym def
8	1000-400(m)	>CF $_2$ Wag vibrations

s: strong, m. medium, w: weak.

Table II  
XRD Data for graphite hydrofluoride

Sl no.	2 $\theta$	hkl Max	d(A)
1	16.2200	20	6.3461
2	19.5200	16	5.2812
3	21.5000	14	4.7998
4	25.1300	16	4.1153
5*	30.8500	100	3.3660
6*	64.4000	14	1.6800

\* due to unreacted graphite (fig. 3).

The X-ray powder diffraction pattern (figs 2 and 3 and Table II) indicates interlayer spacings ('d') at 6.35 to 4.12 Å for (001) type of reflections in graphite hydrofluoride, and at 3.26 and 1.68 Å for Madagascar natural graphite (002) and (004) type of reflections. These values show that the interlayer spacing in graphite has increased on reaction and also products have been formed with different H/F/C ratio. The reported values<sup>1</sup> for graphite fluoride obtained by the reaction with elemental fluorine at intermediate temperature (between 375 and 640°C) vary between 5.85 and 9.0 Å. The present reaction product shows an interlayer spacing in these regions, indicating the intercalation of fluoride and formation of carbon-fluorine covalent bonds. This is supported by IR absorption spectral data discussed above.

The scanning electron micrograph photographs of untreated and treated graphite (fig. 4) show smoothed-out surface for the treated sample and is more compacted with layered nature retained. The smoothed surface indicates reaction at the surface edge and

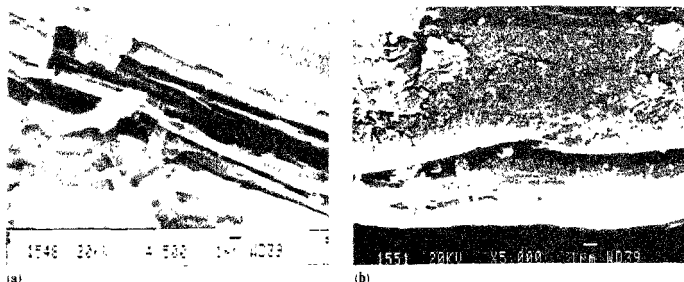


FIG. 4 SEM of (a) untreated graphite, and (b) graphite hydrofluoride.

the distance between the two layers has been considerably elongated indicating intercalation of the fluoride species.

The grey powder, pelletised at 150 bar, shows a surface resistivity of  $1.066 \text{ ohm/cm}^{-1}$  at room temperature.

#### 4. Conclusions

The infrared absorption pattern clearly indicates the covalent bands, C-H and C-F, to be present in the molecule and consequently the XRD pattern shows increased interplanar spacings in graphite.

The interesting feature is that carbon has covalently bonded to hydrogen and fluorine at room temperature and given rise to a covalently bonded carbon, hydrogen and fluoride species. The exact nature of bonding and stacking is under investigation.

SEM and XRD indicate that the crystalline nature of the product has been retained after hydrofluorination as fluorination proceeds mainly along the direction, parallel to the base plane of graphite crystal. The effect of hydrofluorination seems to be felt as an increase in surface tension at the crystal edges and consequently smoothening of the edge surfaces. The product also shows a fairly high conductivity at room temperature. It is of interest to mention that this reagent attacks Teflon at room temperature and cleaves the C-F bonds.

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