Bull. Chem. Soc. Jpn., 57, 701—705 (1984)

Preparation of Graphite Fluoride by Vertical Vibrating Reactor

Nobuatsu WATANABE,* Saburo KATOH, and Tsuyoshi NAKAJIMA
*Department of Industrial Chemistry, Faculty of Engineering, Kyoto University,
Sakyo-ku, Kyoto 606*
(Received July 20, 1983)

A study was made of the yield and crystallinity of graphite fluoride using a vertical vibrating reactor, which made it possible to prepare much graphite fluoride. The yield of graphite fluoride decreased beyond 500 °C for natural graphite and petroleum coke heat-treated at 2800 °C, and beyond 300 °C for calcined petroleum coke. The crystallinity of graphite fluoride was improved through the decomposition and refluorination process in these temperature ranges where the yield decreased. It was found that a sublimative solid by-product was formed together with gaseous fluorocarbons. It was a white solid fluorocarbon with 5—9 cyclohexane rings.

There are two kinds of stable graphite fluorides, $(CF)_n$ and $(C_2F)_n$, prepared by a high temperature reaction between a carbon material and fluorine gas. Their formation and yield depend on the crystallinity of the starting carbon material, on reaction temperature, and on fluorine pressure. When natural graphite is used as a raw material, $(CF)_n$ and $(C_2F)_n$ are formed at *ca.* 600 °C and 350—400 °C, respectively.[1] Between these temperatures, a mixture of $(CF)_n$ and $(C_2F)_n$ is obtained.

As the rotary reactor[1] previously reported produces only 1—2 g of graphite fluoride, it is not suitable for the evaluation of the yield of the graphite fluoride. In this study, the yield and crystallinity of graphite fluoride were investigated using a vertical vibrating reactor which made it possible to prepare 5—40 g of graphite fluoride. It has been said that the decrease in the yield of graphite fluoride is due to the formation of gaseous fluorocarbons such as CF_4 and C_2F_6. However, it was found in the present study that solid fluorocarbons with molecular weights of 798—2016 were formed together with the gaseous compounds. The structure of these solid fluorocarbons was also studied.

Experimental

Samples. Starting carbon materials were natural graphite (290—833 and 61—74 μm) and petroleum coke (original and heat-treated at 2800 °C). Fluorine gas of purity, 99.4—99.7% was used for the fluorination of carbon materials. Most of the impurity contained in fluorine gas was nitrogen.

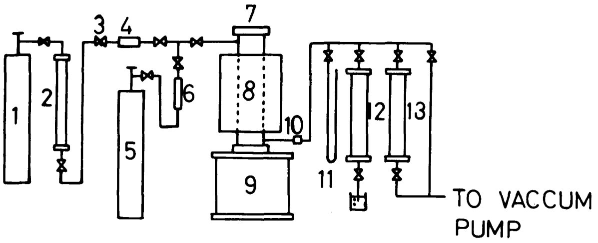

Fig. 1-a. Schematic diagram of vertical vibrating reactor.
1: F_2 cylinder, 2: HF absorber (NaF pellets heated at 110 °C), 3: control valve, 4: mass flowmeter for F_2, 5: Ar gas, 6: flowmeter for Ar, 7: reaction tube, 8: electric furnace, 9: Uras vibrator, 10: safety valve, 11: Hg manometer, 12, 13: F_2 absorber (soda lime pellets).

Vertical Vibrating Reactor. Figure 1-a is the schematic diagram of the vertical vibrating reactor for the production of 5—40 g of graphite fluoride. This vibration system was adopted to achieve the continuous mixing of a carbon material. When the mixing of carbon is insufficient, the explosive decomposition of formed graphite fluoride sometimes occurs due to the lack of supply of fluorine gas. The mixing of

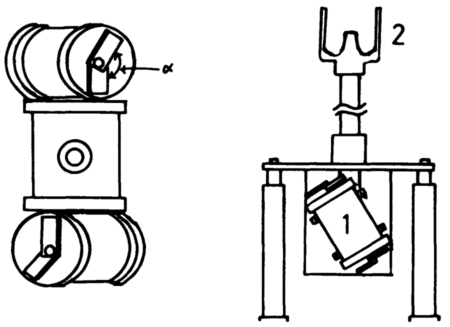

Fig. 1-b. Uras vibrator.
1: Uras vibrator, 2: reaction vessel.

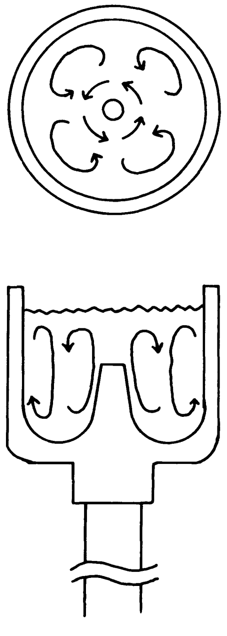

Fig. 1-c. Aspect of movement of carbon material by vibration.

carbon is therefore very important for the fluorination of large amounts of carbon. Vibration caused by a Uras vibrator (Fig. 1-b) installed at the bottom of the nickel reactor is transmitted through a nickel rod to a reaction vessel. The adjustment of vibration is made by changing the angle (α) between two unbalanced weights attached to the Uras vibrator. The aspect of movement of a carbon material in the reactor is schematically shown in Fig. 1-c.

Fluorination Reaction and Analyses of the Product. After pumping at room temperature, the reactor containing the starting carbon material was heated to a temperature between 300 and 600 °C; this was followed by further pumping for several hours. The reactor was then filled by argon gas at 1 atm, and a mixture of argon and fluorine gases was supplied to the reaction system (gas flow rate, F_2: 80 ml/min for natural graphite or 60 ml/min for petroleum coke, Ar: 70 ml/min). Unreacted fluorine gas was made to react with soda lime. After fluorination, the graphite fluoride prepared was analyzed by X-ray diffractometry (by Cu $K\alpha$) and elemental analysis. In addition to these analytical methods, the structure of the solid by-product was investigated by IR, ^{19}F-NMR, ESCA, and mass spectroscopies.

Results and Discussion

Yield of Graphite Fluoride. Figure 2 shows the yield of $(CF)_n$ and the time required for the completion of fluorination reaction as a function of the amount of each carbon material. The yield was decreased with increasing amounts of natural graphite, because it took a much longer time for fluorination with any increase in raw material and the decomposition of graphite fluoride to gaseous fluorocarbons occurred at the same time.

Figure 3 is the change of yield for the fluorination of a fixed amount of natural graphite as a function of reaction time and temperature. No unreacted graphite was detected under any condition. As seen in the figure, the yield decreased with increasing time and temperature. The decrease in yield started at *ca.* 500 °C for natural graphite and at *ca.* 300 °C for the original petroleum coke. The remarkable decrease in yield was observed especially in the latter case.

Composition and Crystallinity of Graphite Fluoride Prepared from Natural Graphite. Figure 4 is the composition and crystallinity of $(CF)_n$ prepared from natural graphite at 600 °C. The interlayer spacing and half width of the (001) diffraction line (d_{001}, β_{001}) decreased with increasing time, which means the improvement of crystallinity of graphite fluoride, while the chemical composition, F/C was almost unchanged. The improvement of crystallinity would be attained by eliminating the disordered parts among crystallites of graphite or $(CF)_n$. The disordered parts are easily attacked by fluorine gas to give gaseous fluorocarbons such as CF_4 and C_2F_6.[1,2]

The change in composition and cystallinity of graphite fluoride prepared from the flaky natural graphite

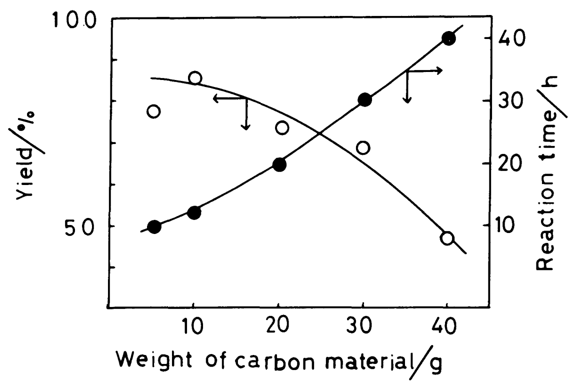

Fig. 2. Dependence of yield of $(CF)_n$ and reaction time on weight of starting carbon material.
Carbon material: natural graphite (290—833 μm). Reaction temperature: 600 °C.

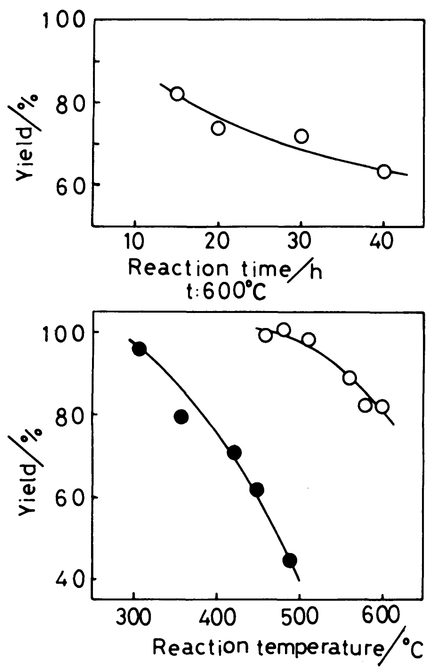

Fig. 3. Dependence of yield of graphite fluoride on reaction time and temperature.
○: Natural graphite (290—833 μm, 20 g), ●: petroleum coke (10 g).

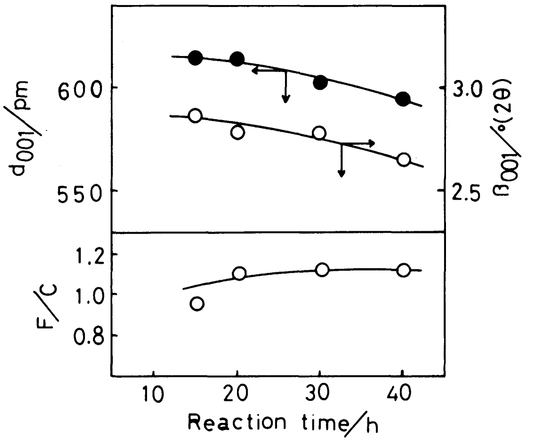

Fig. 4. Dependence of crystallinity and composition of $(CF)_n$ on reaction time.
Carbon material: natural graphite (290—833 μm). Reaction temperature: 600 °C.

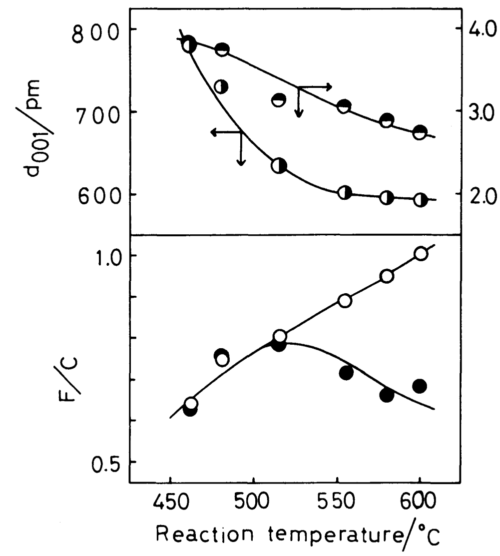

Fig. 5. Dependence of crystallinity and composition of graphite fluoride on reaction temperature.
Carbon material: natural graphite (61—74 μm), F/C: ○; from elemental analysis, ●; from weight increase.

is shown in Fig. 5 as a function of temperature. $(CF)_n$ was prepared at around 600 °C with d_{001} of 585—590 pm and F/C of 1. An F/C value of more than unity is attributable to CF_2 and CF_3 groups at the edge of the crystallite. As $(C_2F)_n$ was mainly formed at 450—500 °C, the d_{001} and F/C approached 900 pm and 0.5, respectively, with decreasing temperature. As shown in the lower part of Fig. 5, the F/C calculated from the weight increase of a carbon material started to deviate from that obtained by elemental analysis at around 500 °C, and their difference was caused by the decomposition of graphite fluoride to gaseous fluorocarbons. No decomposition of graphite fluoride occurred in the temperature regions where $(C_2F)_n$ was preferentially formed.

Composition and Crystallinity of Graphite Fluoride Prepared from Petroleum Coke. When graphite fluoride was prepared from the original petroleum coke, the d_{001} and β_{001} decreased remarkably in a temperature range higher than 350 °C, while the F/C was between 1.1 and 1.2 at 350—500 °C (Fig. 6). Graphite fluoride prepared at 300—500 °C had larger d_{001} and β_{001} values than $(CF)_n$ prepared from the natural graphite. This is not because of the simultaneous formation of $(C_2F)_n$ but is attributed to the formation of $(CF)_n$ with low crystallinity. It is known that only $(CF)_n$ is formed from a carbon material with low crystallinity under any condition and F/C is much greater than unity because of CF_2 and CF_3 groups on the surface.[2] The crystallinity of graphite fluoride has also a close relation with that of a raw material. With increasing temperature, the crystallinity of $(CF)_n$ was remarkably improved by the decomposition of amorphous parts to gaseous fluorocarbons, the d_{001} and β_{001} approaching those of $(CF)_n$ prepared from natural graphite. The F/C obtained from weight increase decreased monotonously with increasing temperature, corresponding to the decrease in the yield.

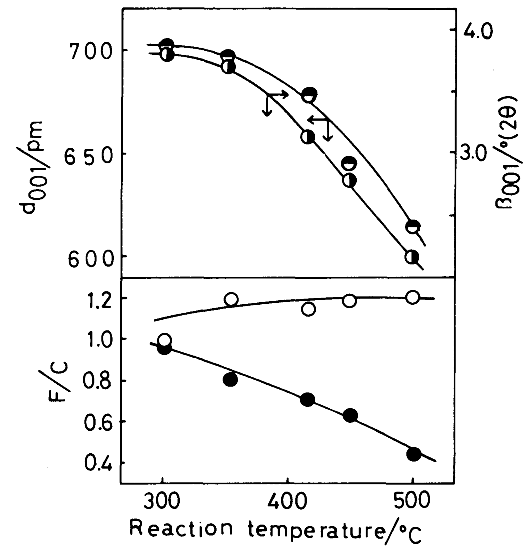

Fig. 6. Dependence of crystallinity and composition of $(CF)_n$ on reaction temperature.
Carbon material: petroleum coke.
F/C: ○; from elemental analysis, ●; from weight increase.

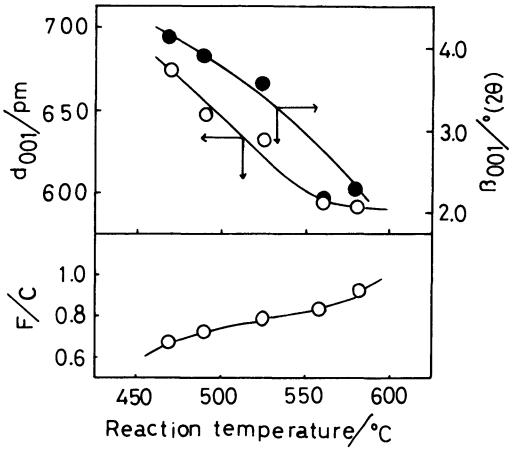

Fig. 7. Dependence of crystallinity and composition of graphite fluoride on reaction temperature.
Carbon material: petroleum coke heat-treated at 2800 °C.

The temperature dependences of the composition and crystallinity of graphite fluoride prepared from the petroleum coke heat-treated at 2800 °C were similar to those from the natural graphite (Fig. 7). The yield started to decrease at 500 °C as in the case of the natural graphite, but, the rate of decrease was larger than that in the natural graphite. The F/C value was much smaller than unity since $(C_2F)_n$ was formed from the graphitized carbon. The d_{001} and β_{001} approached those of $(CF)_n$ with increasing temperature, and only $(CF)_n$ was prepared at 580 °C.

Structure of Solid By-product. It was found that a white solid by-product was formed in the upper part of the reactor when the fluorination of a carbon material was made at a temperature where the yield of graphite fluoride largely decreased. In addition to gaseous

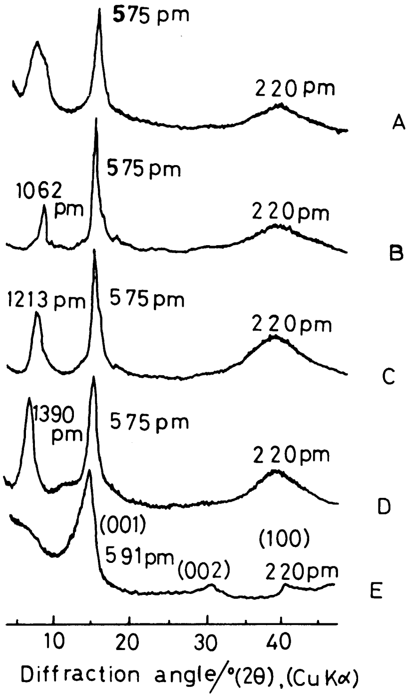

Fig. 8. X-Ray diffraction patterns of by product.
A: Original by-product, B: sublimated at 150 °C, C: sublimated between 200 and 250 °C, D: residue on sublimation at 300 °C, E: graphite fluoride, $(CF)_n$.

fluorocarbons, this solid by-product would also cause the decrease in the yield. In this section, the structure of solid by-product was described.

a) X-Ray Diffraction Patterns: Figure 8 is the X-ray diffraction patterns of the by-product. The by-product obtained gave the pattern A, which has nearly the same peaks as (001) and (100) diffraction lines of $(CF)_n$ except for a broad one at 6—9° in 2θ (Cu $K\alpha$). By sublimation at several temperatures, this by-product was separated into three groups, giving the pattern B (sublimated at 150 °C), C (sublimated at 200—250 °C), and D (residue on sublimation at 300 °C). As seen in B, C, and D, the broad diffraction line at 6—9° was separated into three different peaks. With increasing the sublimation temperature, the separated peak was shifted to a lower angle, corresponding to a larger d spacing.

b) ^{19}F-NMR Spectra: The 2nd moment obtained from the absorption derivative of the by-product was 10.1 G^2; this value is very near that of $(CF)_n$, 10.6 G^2.[1] Poly(tetrafluoroethylene) (Teflon) had the value, 5.0 G^2, which is different from the by-product value. This suggests that the unit structure in the by-product is the same as that for $(CF)_n$.

c) IR Spectra: Figure 9 is the IR spectra measured by the KBr method. The spectra of the by-product was very similar to that of $(CF)_n$. The absorption at 1215 cm^{-1} was ascribed to the CF stretching vibration and those at 1380 and 1110 cm^{-1} were due to the symmetric and asymmetric stretching vibrations of CF_2 bonds, respectively.[3] The latter two absorptions were larger in the by-product than in $(CF)_n$, which indicates that the by-product contains more CF_2 groups than $(CF)_n$ does. It is known from the spectra of Teflon that the absorptions due to the bending vibration of CF_2 appear between 500 and 900 cm^{-1},[4] where many small absorptions were also observed in the by-product.

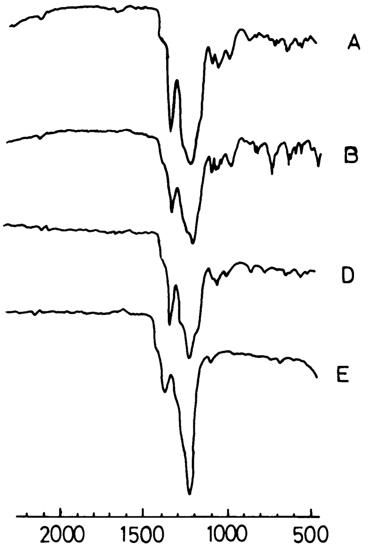

Fig. 9. IR spectra of by-product.
A: Original by-product, B: sublimated at 150 °C, D: residue on sublimation at 300 °C, E: graphite fluoride, $(CF)_n$.

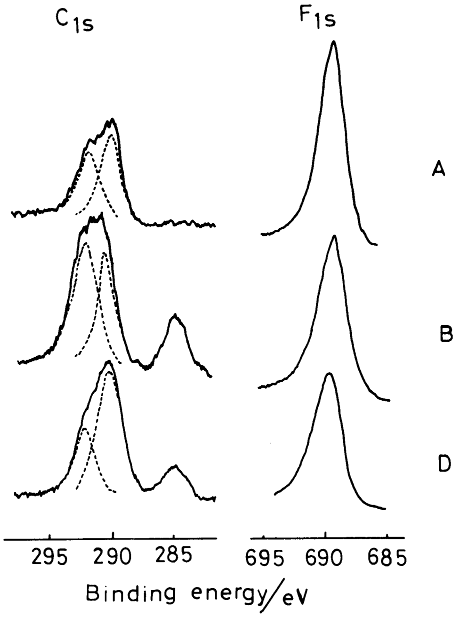

Fig. 10. ESCA spectra of by-product.
A: Original by-product, B: sublimated at 150 °C, D: residue on sublimation at 300 °C.

d) ESCA Spectra: In the C_{1s} spectra of the by-products, two peaks corresponding to CF and CF_2 covalent bonds were observed at 290.5 and 292.4 eV, respectively.[1] These two chemical bonds between carbon and fluorine are the same as those of $(CF)_n$. In $(CF)_n$ powder, a small peak due to CF_3 group is observed at 294 eV in addition to the above two peaks. However, the by-products had only two peaks corresponding to CF

Table 1. Elemental analysis of by-product

Sample	F(wt%)	C(wt%)
A	67.66	31.66
B	66.60	31.25
C	70.75	29.88
D	66.86	33.92

Table 2. Composition and molecular weight of by-product by mass spectra

Sample	Composition	Molecular weight	Number of cyclohexane ring
B	$C_{19}F_{30}$-$C_{25}F_{38}$	798—1022	5—7
C	$C_{24}F_{36}$-$C_{40}F_{56}$	972—1544	7—13
D	$C_{43}F_{60}$-$C_{54}F_{72}$	1656—2016	14—19

and CF_2 groups and the ratio of CF_2/CF for the by-product was much larger than that of $(CF)_n$. This tendency was more distinctive in the by-products sublimated at a lower temperature.

e) Chemical Analysis and Mass Spectra: The results of chemical analysis are shown in Table 1. Though the fluorine content in a single crystal of $(CF)_n$ is 61.3 wt%, analyzed values are often larger than 61.3 wt% owing to the CF_2 and CF_3 groups on the surface. The highest value hitherto found is 65 wt%. However, the fluorine content in the by-product was 66—70 wt%, much higher than in $(CF)_n$. This is consistent with the presence of more CF_2 groups on the surface of the by-product than there were CF groups in the bulk. Mass spectra revealed that samples B, C, and D separated by sublimation were not a single compound but a mixture of those with different compositions. From the analytical results obtained in the previous sections, the by-product would have a structure in which some cyclohexane rings to which fluorines are bonded are linked with each other. Based on this model, the molecular weight and number of cyclohexane ring were calculated from the result of mass spectra. As shown in Table 2, the raw by-product would be a mixture of fluorocarbons consisting of 5—19 cyclohexane rings with molecular weight of 798—2016. The molecular weight increased in the order of B, C, and D, which is consistent with the fact that the sublimation temperature and *d* spacing obtained from X-ray diffraction pattern increased in the same order.

The analytical results are summarized as follows.

(1) All the by-products separated by sublimation had the same two peaks as (001) and (100) diffraction lines of ideal $(CF)_n$ crystal. The diffraction line at 6—9° in 2θ gave a larger *d* spacing for the sample separated at a higher temperature.

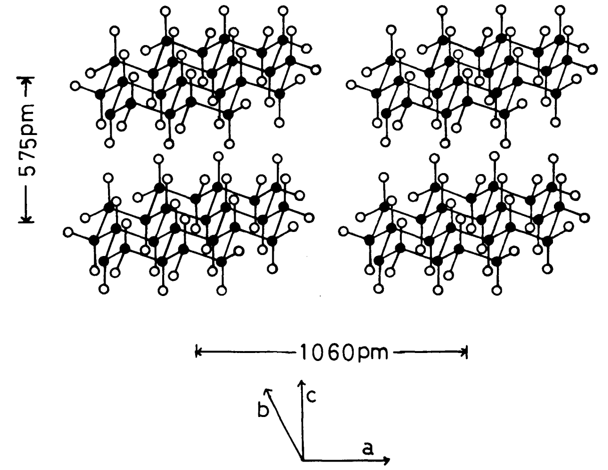

Fig. 11. Crystal structure of $C_{24}F_{36}$.
○: F, ●: C.

(2) IR and ESCA spectra showed that the by-product had the same CF and CF_2 groups as $(CF)_n$ and the ratio of CF_2/CF was much larger in the by-product than in $(CF)_n$.

(3) ^{19}F-NMR spectrum indicated that the unit structure of the by-product was the same as that of $(CF)_n$.

(4) Molecular weight was between 798 and 2016, corresponding to fluorocarbon compounds with 5—19 cyclohexane rings.

From these results, the by-product is regarded as a mixture of low molecular weight fluorocarbons having the same structural unit as that of $(CF)_n$. As an example, the crystal structure of $C_{24}F_{36}$ molecule with 7 cyclohexane rings is shown in Fig. 11, where each molecule is arranged in cubic system. The *d* spacing along the c-axis is 575 pm and the lattice parameter along the a and b-axis is almost the same as that of the diameter of a circular molecule.

References

1) Y. Kita, N. Watanabe, and Y. Fujii, *J. Am. Chem. Soc.*, **101**, 3822 (1979).

2) N. Watanabe, Y. Ashida, and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **55**, 3197 (1982).

3) R. J. Lagow, R. B. Badachhape, J. L. Wood, and J. L. Margrave, *J. Chem. Soc., Dalton Trans.*, **1974**, 1268.

4) C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **25**, 563 (1956).