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Effect of Ultraviolet Ray on Graphite Fluoride in Organic Solvents

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Graphite fluoride, $(CF)_n$, was photolyzed in alcohols and hydrocarbons. Hydrogen fluoride was formed in each case. Alcohols were partially converted into the corresponding carbonyl compounds by the reaction $2(C\text{–}F)+RR'CHOH \xrightarrow{h\nu} 2(C)+2HF+RR'C{=}O$. ESCA measurement revealed that the fluorine at the surface decreases more rapidly than that of the inner region of $(CF)_n$ particle, the inner region being also photolyzed. Results of DTA measurement indicate that the irradiation reduces the thermostability of $(CF)_n$.

Graphite fluoride, $(CF)_n$, is prepared by the reaction of fluorine gas with various carbon materials at high temperature. The crystalline structure consists of condensed cyclohexane-like carbon rings with fluorine atoms occupying the fourth coordination site of the sp^3-hybridized carbon atom.[1–3] Recently, the compound has been used as a superior lubricant[4–6] under extreme conditions of high temperature and high vacuum. It has also been found to be a cathodic depolarizer in high energy density batteries.[7–9] However, little is known about its chemical reactivity towards organic compounds. This paper deals with the effect of ultraviolet irradiation on graphite fluoride in various hydrocarbons and alcohols.

Experimental

Graphite fluoride with a F/C molar ratio of 1.16 was prepared by the direct fluorination of petroleum coke,[10] fine white powder with particle size greater than 400 mesh being obtained. All organic solvents were of reagent grade and used without further purification. Graphite fluoride dispersed in the solvent was irradiated at room temperature in a 500 ml photochemical reactor (Ushio Denki Co.) with a high pressure mercury lamp of 100 W (UM-102) put into a water cooling jacket made of Pyrex glass. The lamp emits ultraviolet rays (the output is indicated in parentheses) 3132 Å (2.10 W), 3650—3663 Å (3.08 W), 4047—4078 Å (1.26 W), and other rays with smaller power. The suspension was stirred with a magnetic stirrer during the course of irradiation. The oxygen dissolved in the solvent was removed by bubbling nitogen for half an hour before irradiation. After the irradiation, $(CF)_n$ was separated from the solvent by centrifugation, and then dried in a vauum. The sample was analyzed by means of X-ray photoelectron spectroscopy (ESCA), X-ray diffraction, and differential thermal analysis (DTA). The content of carbon, hydrogen and fluorine was determined by the usual method.[11]

Results and Discussion

Photochemical Decomposition of $(CF)_n$. The F/C molar ratio of $(CF)_n$, which was allowed to stand in MeOH without irradiation for more than six months remained almost unchanged. On the other hand, by ultraviolet irradiation for several hours, the color of $(CF)_n$ in organic solvent turned black or brown from white, the F/C ratio decreasing with increasing irradiation time. Thus, the decomposition of $(CF)_n$ by ultraviolet irradiation would proceed only in a solvent, considering the fact that $(CF)_n$ is photochemically stable in the air.

Since the F/C ratio decreased by irradiation, the photolysis of $(CF)_n$ may lead to the cleavage of a C–F bond rather than a C–C bond. In thermal decomposition of $(CF)_n$ in a vacuum or in inert gas, the initial step of the reaction may be the rupture of C–C bonds rather than C–F bonds.[12]

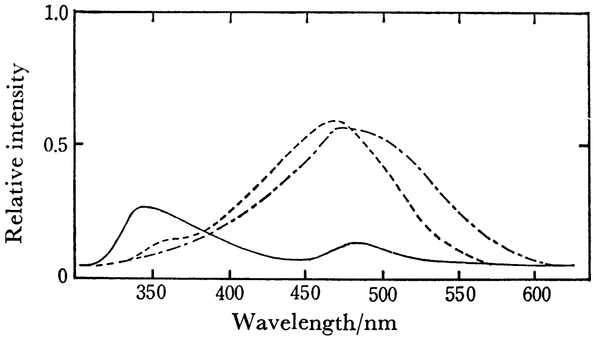

Fig. 1. Emission spectra of $(CF)_n$. Exciting wavelength is 290 nm. ——: in air, ----: in paraffin, –·–: in MeOH.

Figure 1 shows the emission spectra of $(CF)_n$ in the air, MeOH, and in liquid paraffin. The peak areas of the spectra both in MeOH and in paraffin were 3 times greater than those in the air. The coloration of $(CF)_n$ turns slightly dark when it is put into MeOH and paraffin, *viz.* solvatochromism takes place. The absorption spectrum of a solution changes with solvent without chemical reaction between solute and solvent. In the case of $(CF)_n$, the main peak in its emission spectra shifted to lower wavelength with increasing solvent polarity. Compounds which show such bathochromic effect are, in general, more polar in excited state than in the ground state.

Parry[13] calculated the band structure of $(CF)_n$ on the basis of the self-consistent semi-empirical LCMO method, and found that the direct band gap at the center of the Brillouin zone for a layer of $(CF)_n$ is 8.4 eV, *viz.*, 147.6 nm. The emission spectra were not in line with his results. This may be attributed to the $(CF)_n$ we prepared which has mechanical distortions and crystal defects such as exfoliation and crack, being far from Parry's ideal crystal.

The F/C ratio and decomposition ratio (α) of $(CF)_n$ after photolysis in various alcohols and hydrocarbons for 24 h are given in Table 1. The decomposition ratio,

Table 1. F/C ratio and decomposition ratio of graphite fluoride photolyzed for 24 h in various alcohols and hydrocarbons

Solvent	F/C[a)]	Decomposition ratio/%	Dielectric constant
MeOH	0.94	7.3	32.6
n-PrOH	0.97	6.3	20.1
i-PrOH	0.99	5.5	18.3
n-BuOH	1.01	4.9	17.8
t-BuOH	1.08	2.5	10.9
Hexane[b)]	1.09	2.3	1.9
Cyclohexane[b)]	1.07	2.8	2.0

a) Value of original $(\mathrm{CF})_n$ 1.16. b) Irradiation time 20 h.

α, is defined by

$$\alpha = \frac{F_0-F}{F_0} \times 100,$$

where F_0 and F are the fluorine content of original sample and that of the sample photolyzed, respectively. Graphite fluoride was decomposed to a greater extent in alcohols than in hydrocarbons. α is proportional to the dielectric constant of the solvent. Thus, $(\mathrm{CF})_n$ seems to be polar at the transition state of the reaction. This is supported by the solvent effect of the emission spectra, if the excited state is the transition state of the reaction.

Photochemical Reaction in Alcohols. When photolysis was carried out for a longer time, the reaction mixture became acidic by the formation of hydrogen fluoride. When it was neutralized with aqueous sodium hydroxide, precipitation of sodium fluoride took place. This was confirmed by means of X-ray diffraction. The amount of hydrogen fluoride coincided with the net decrease of fluorine in $(\mathrm{CF})_n$.

The solvent was subjected to gas chromatography with Porapak R (Water Associates Inc.) as a separating packing. In *i*-PrOH and *n*-BuOH, the corresponding carbonyl compounds, acetone and butyraldehyde, respectively, were detected. From the results, photochemical decomposition of $(\mathrm{CF})_n$ in alcohols can be presented by

$$2(\mathrm{C{-}F}) + \mathrm{RR'CHOH} \xrightarrow{h\nu} 2(\mathrm{C}) + 2\mathrm{HF} + \mathrm{RR'C{=}O},$$

where R and R′ are either hydrogen or alkyl group.

ESCA Measurement. ESCA measurement was made on $(\mathrm{CF})_n$ photolyzed in MeOH for 27, 72, and 96 h (Fig. 2). The spectra show, in addition to the main peak at 290 eV (A_1), a broad shoulder at 292.4 eV (A_2) and a low intensity tail at *ca.* 294.4 eV (A_3), which are assigned to the carbon having $\rangle\mathrm{CF}$, $>\mathrm{CF_2}$, and $-\mathrm{CF_3}$ bonds, respectively.[14,15)] After photolysis, the peaks became smaller, while a new peak appeared at *ca.* 286 eV (A_4), which may be the carbons having no C–F bond.[16)] The peak at 285 eV is due to hydrocarbon contamination, and regarded to have approximately the same intensity in each run.

The relative peak area of these peaks, the F/C ratio calculated from above relative peak area, and that determined by elemental analysis are given in Table 2.

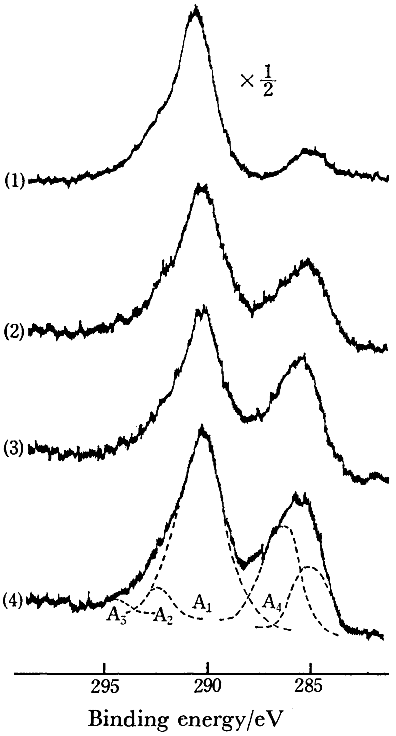

Fig. 2. The change in ESCA spectra of C_{1s} photoelectron of $(\mathrm{CF})_n$ photolyzed for various times in MeOH. (1) Original sample, (2) 27 h, (3) 72 h, (4) 96 h.

Table 2. Influence of time on the relative peak area of C_{1s} and F/C ratio of $(\mathrm{CF})_n$ photolyzed in methanol

Irradiation time	C_{1s} peak/%				F/C ratio	
h	A_1	A_2	A_3	A_4	(a)	(b)
0	79.4	16.0	4.6	0	1.33	1.16
27	67.3	5.0	4.6	23.1	0.91	0.93
72	59.5	4.4	3.8	32.3	0.80	0.86
96	60.9	3.6	2.7	32.8	0.76	0.84

a) Determined by means of ESCA spectrum. b) Determined by chemical analysis.

In the original $(\mathrm{CF})_n$, the F/C ratio calculated from the ESCA spectrum is higher than that from elemental analysis. This indicates that there are many $>\mathrm{CF_2}$ and $-\mathrm{CF_3}$ groups at the surface of the $(\mathrm{CF})_n$ particle. Since the electron escape depth for C_{1s} photoelectron is *ca.* 10 Å,[17)] and the $(\mathrm{CF})_n$ particle has a diameter of several micrometers, only the surface region of solid can be examined by ESCA. By photolysis, the amount of fluorine at the surface decreased more rapidly than that of the inner region of the particle (Table 2). However, after photolysis for even 96 h, many fluorine atoms remained undecomposed at the surface as shown in Fig. 2, the F/C ratio at the surface no differing from that of the total particle. The reaction may proceed not only at the surface but also in the inner region of the solid, especially at cracks and mechanically distorted parts where the solvent can permeate.

Effects on the Structure of $(CF)_n$. No remarkable changes of the structure of $(\mathrm{CF})_n$ due to photolysis

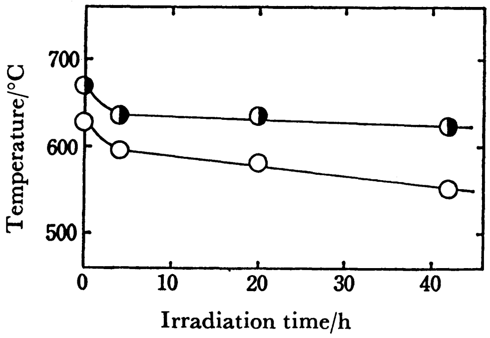

Fig. 3. The variation of the starting temperature, T_s, and of the peak maximum temperature, T_m, with the irradiation time.
○: T_s, ◑: T_m.

were observed by means of X-ray diffraction. A DTA curve of $(CF)_n$ prepared from flaky natural graphite showed an exothermic peak at *ca.* 670 °C. Figure 3 shows variation of the peak starting temperature, T_s, and of the peak maximum temperature, T_m, with irradiation time. Photolysis was carried out in MeOH, the DTA being measured in a vacuum. Both T_s and T_m decreased linearly, the peak being broadened with increasing irradiation time. The irradiated sample undergoes thermal decomposition at lower temperature as compared with the original one. The thermostability of $(CF)_n$ is reduced by irradiation.

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