REDUCTION OF FLUOROGRAPHITE WITH LITHIUM TETRAHYDRIDOALUMINATE

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Fluorographite $(CF_{0.9})_n$ was reduced with LiAlH4 in diethyl ether, tetrahydrofuran, and dioxane, and the reaction products were investigated by the X-ray diffraction method. A mechanism of the reduction is suggested involving intercalation of the reagent within the interlayer space of fluorocarbide, and also formation of an intercalate intermediate. The product of the reduction is carbon possessing a lamelar structure.

Fluorographite is a crystalline substance arising from the reaction of graphite with fluorine[1–3]. Similarly as graphite, fluorographite is by nature a polymeric compound, $(CD_x)_n$. The value of x can be 0·25—1·12, in dependence on the way of preparation; the value of n has not been determined. No unique conclusions have been arrived at concerning the crystal structure. The powder diffraction patterns suggest[4] that the substance possesses a lamellar structure with the hexagonal lattice parameters $a = b = 253$ pm, $c = 576$ pm, $\beta = 118{\cdot}8°$, and a chair arrangement of the hexagonal carbon ring. Based on ^{19}F NMR data, Ebert and coworkers[5] assume that $(CF_x)_n$ is linked in a chain of *cis-trans*-arranged boats. If the (CF) basic cell really exists in the boat arrangement, then the X-ray diffraction patterns can be interpreted in terms of an orthorhombic structure with the parameters $a = 251, b = 513, c = 616$ pm. The introduction of a fluorine atom into the graphite lattice increases the spacing[6] from the initial 335 pm to 576—616 pm, in dependence on the amount of fluorine involved.

The C–F bond energy has been calculated based on the reaction of fluorographite with potassium carbonate[7] and on the decomposition of fluorographite if heated in hydrogen atmosphere[8], and the values of 286·8 and 357·5 kJ mol^{-1} have been obtained. These values are relatively low as compared with the carbon–fluoride bond energies in other fluorinated hydrocarbons[9] (460—486 kJ mol^{-1}).

According to Coulson[10], the C–C bond energy in the graphite layer is intermediate between the energies of the benzene and the single C–C bonds. If the C–C bond in graphite is transformed into a single bond on fluorination, the C–F bond energy would be higher by the difference, 91·7 kJ mol^{-1}. Adding this value to the above-mentioned calculated energies we obtain the values of 375·5 and 499·2 kK mol^{-1}, which approach better the C–F bond energy in fluorinated hydrocarbons.

Wood and coworkers[11] suppose a covalent nature of the C–F bond in fluorographite, with the bonding energy of 481·5 kJ mol^{-1}. The vibration of the C–F bond gives rise to an intense IR absorption band at[7,12] 1 215 cm^{-1}; the corresponding force constant of the C–F bond is $16{\cdot}6 \,.\, 10^2$ N m^{-1}. It is worth noting that the analogous force constant in CF_4 is (ref.[7]) $9{\cdot}15 \,.\, 10^2$ N . m^{-1}, hence, in fluorographite the C–F bond is stronger than in tetrafluoromethane.

In saturated fluorinated compounds the carbon–fluorine bond is usually resistant to the hydride anion; fluorine is substituted by hydrogen only rarely and the yields are low[13,14]. The situation is entirely different with systems containing multiple bonds. The fluorine atom attracts the π-electrons of the bond and so makes the nucleophilic attack by the hydride ion possible. The intermediate anion formed readily releases the fluoride anion in a typical elimination process[15]. This applies also to poly- and perfluoroaromatics, which are susceptible to the nucleophilic attack by the hydride anion owing to the electron deficit in the aromatic ring concerned. After a fluorine atom in the aromatic system has been replaced by hydrogen, a second fluorine is replaced in the order valid for nucleophilic substitutions, *viz. para* > *ortho* ≫ *meta* (ref.[16]). The above facts aroused our interest in fluorocarbide and stimulated our study of the resistance of the C–F bond to the attack by the hydride anions of complex hydrides.

In the present work, the action of $LiAlH_4$ on fluorographite $(CF_{0.9})_n$ is examined in various experimental conditions.

EXPERIMENTAL

Chemicals

Graphite CR 5 (Czechoslovak make) was of natural origin, chemically refined. Fluorographite $(CF_{0.9})_n$ was synthesized[17] by a direct reaction of diluted fluorine with graphite at 400—500°C. Lithium tetrahydridoaluminate was a product of Lachema. Tetrahydrofuran (Apolda, GDR) was dried with KOH and Na and distilled prior to use. Diethyl ether (Lachema) and dioxane (Poland) were dried with Na and distilled prior to use.

Apparatus

The X-ray diffraction patterns were obtained on a Mikromat-Chirana Co/Fe instrument.

Reduction of Fluorographite with Lithium Tetrahydridoaluminate

A) *Reduction in diethyl ether.* Lithium tetrahydridoaluminate (7·6 g, 200 mmol) was dissolved in diethyl ether (150 ml) two days before use, and prior to the reaction, filtered in a dry box. A suspension of fluorographite (2·75 g, 94 mmol) in diethyl ether (70 ml) was placed in a 500 ml three-necked flask fitted with a drooping funnel, a reflux condenser, and a stirrer, the filtered lithium tetrahydridoaluminate was added dropwise to the suspension, and the reaction mixture was stirred on oil bath at 30—35°C for 3 h. After this procedure, the mixture was decomposed with HCl (1 : 1). The product was separated by filtration, multiply washed with dilute (1 : 1) HCl, and then washed with hot distilled water until all chloride was removed. After a successive washing with methanol and ether, the substance was dried in vacuum.

B) *Reduction in tetrahydrofuran.* A suspension of $LiAlH_4$ (3·8 g, 100 mmol) in tetrahydrofuran (100 ml) was placed in the reaction vessel as above, and a suspension of fluorographite (2·3 g, 79 mmol) in tetrahydrofuran (50 ml) was added. The reaction mixture was stirred on oil bath at 60—65°C for 18 h and further proceeded as above.

C) *Reduction in dioxane.* A suspension of $LiAlH_4$ (4·0 g, 105 mmol) in dioxane (100 ml) was placed in the flask as *sub A* and a suspension of fluorographite (2·3 g, 79 mmol) in dioxane (50 ml) was added. The reaction mixture was stirred on oil bath at 95°C for 24 h. Further proceeded as *sub A*.

D) *Reduction in tetrahydrofuran.* A suspension of $LiAlH_4$ (3·6 g, 94 mmol) in tetrahydrofuran (80 ml) was placed in the reaction flask as above, a suspension of fluorographite (2·5 g, 86 mmol) in tetrahydrofuran (40 ml) was added, and the reaction mixture was stirred on oil bath at 55—60°C for 5 h. Further proceeded as *sub A*.

E) *Action of* $LiAlH_4$ *on graphite in diethyl ether.* A suspension of graphite (0·3 g, 25 mmol) in ether (20 ml) was placed in the flask as *sub A*, a suspension of $LiAlH_4$ (0·5 g, 13 mmol) in ether (50 ml) was added, and the mixture was stirred on oil bath at 35—40°C for 5 h. Further proceeded as *sub A*.

RESULTS AND DISCUSSION

The products of reduction of fluorographite with $LiAlH_4$ were studied by the method of X-ray diffraction analysis and by elemental analysis. As the former method revealed, the carbon layer spacing increased on fluorination from 337 pm in graphite to 585 pm in fluorographite. The X-ray diffraction data are summarized in Table I.

Fluorographite was reduced with $LiAlH_4$ in diethyl ether under a slight reflux of the solvent. In this case the hydride solution was added to a suspension of fluorographite (procedure *A*), whereas the reverse approach was applied in the remaining procedures, using tetrahydrofuran and dioxane as solvents. The reaction was accompanied by evolution of heat. Procedures *B* and *D*, both conducted in tetrahydrofuran, differed in the reaction period, *viz.* 18 h for *B* and 5 h for *D* under a solvent reflux. The X-ray diffraction data of the reaction products are given in Table II.

TABLE I

X-Ray diffraction patterns of natural graphite CR-5 and fluorographite $(CF_{0,9})_n$. Relative intensities: s strong, m medium, w weak, vw very weak

hkl	*d*, pm, for graphite	*d*, pm, for fluorographite
002	337 (s)	585 (s)
100	213 (w)	222 (m)
111	206 (vw)	
101	202 (m)	
	194 (vw)	
102	179 (vw)	
004	167 (m)	
103	154 (w)	
110	123 (m)	128 (m)
112	115 (m)	
114	99 (w)	

The patterns are similar for all of them, containing the same number of lines as those of the initial $(CF_{0\cdot9})_n$ (Table I). Only the principal, most intense 002 line characterizing the layer spacing decreased from 585 pm to 342–346 pm, still remaining above the value for graphite, 337 pm. Several causes of this increase in spacing are conceivable: the presence of residual C–F bonds (1–53·5% F, Table III), C–H bonds (see below as to the reaction mechanism), or residual intercalation.

The 100 line has a lower value as compared with that of fluorographite and agrees with the value for graphite (213 pm); only in case *B* the value is lower, approaching

TABLE II

X-Ray diffraction patterns of the products of reduction of $(CF_{0,9})_n$ with $LiAlH_4$ (procedures *A*–*D*) and of the product of action of $LiAlH_4$ on graphite (procedure *E*). Relative intensities: s strong, m medium, w weak, vw very weak

hkl	*d*, pm, for the product of procedure				
	A	*B*	*C*	*D*	*E*
002	344 (s)	346 (s)	345 (s)	342 (s)	337 (s)
100	220 (w)	209 (m)	215 (m)	214 (m)	214 (vw)
101	202 (w)		204 (w)		203 (m)
					195 (vw)
102					179 (w)
004					168 (m)
103					154 (w)
110	122 (m)	122 (m)	122 (m)	122 (m)	123 (m)
112			114 (vw)		116 (m)
006					112 (w)
114					99 (w)

TABLE III

Elemental composition of the reaction products

Procedure	% C	% H	% F
A	92·00	1·60	1·66
B	94·33	1·44	2·18
C	91·10	1·68	3·62
D	92·20	1·37	2·78
E	99·40	0·32	0·00

the 111 line ($d = 206$ pm) for the diamond structure. This suggestion is made particularly with regard to the fact that according to Horita and Watanabe[8], diamond bonding can arise on the fluorination of graphite. The value of the 110 line, which is the same for all the products, *viz* 122 pm, is also lower than for fluorographite and is equal to that for the initial graphite (Tables I and II).

For a comparison, a blank experiment was carried out in which the fluorographite was substituted by graphite, and $LiAlH_4$ was allowed to act on it in diethyl ether (procedure *E*). The data of Tables I and II demonstrate that no changes occurred in the starting graphite.

Thus, in spite of its proclaimed inertness, fluorographite readily undergoes reduction with lithium tetrahydridoaluminate in diethyl ether, tetrahydrofuran, or dioxane under solvent reflux. The product is black, very fine carbon exhibiting a high electrical conductivity and possessing probably a lamellar structure, though with a lower crystallinity degree than in graphite.

Mechanism of the Reduction

Since on the fluorination the graphite macromolecule loses its aromatic character, the mechanism of reduction of fluorinated aromatics does not apply to this case. Therefore, we supposed that the reduction of fluorocarbide with $LiAlH_4$ involves intercalation of molecules of the latter between the parallel layers of the former. This intercalaction brings about an increase in the spacing of the layers and enables formation of C–F bonds bearing an ionic nature. For testing this hypothesis an experiment was carried out similar to procedure *A*, in which, however, the reaction

Table IV

X-Ray diffraction patterns of the intermediate product of reduction of fluorocarbide with lithium tetrahydridoaluminate. Relative intensities: s strong, m medium, w weak, vw very weak

d pm	*hkl*	Assignment	*d* pm	*hkl*	Assignment
412 (s)	004	intercalate	208 (w)	008	intercalate
389 (w)		$LiAlH_4$	200 (m)	200	LiF
297 (w)		$LiAlH_4$	186 (w)	009	intercalate
267 (w)		$LiAlH_4$	180 (w)		$LiAlH_4$
236 (vw)	007	intercalate	176 (vw)		$LiAlH_4$
232 (w)	111	LiF	163 (vw)	0010	intervalate
225 (w)		$LiAlH_4$	151 (vw)	0011	intercalate
217 (m)		$LiAlH_4$	141 (w)	220	LiF
213 (m)	100		139 (w)	00·12	intercalate

mixture was not decomposed with hydrochloric acid, only the solvent (diethyl ether) was distilled off in vacuum. The X-ray diffraction patterns (Table IV) exhibited lines of $LiAlH_4$, LiF, and of the intercalate with a parallel layer spacing of $I_c =$ $= 824$ pm. This warrants the conclusion that molecules or the reagent are intercalated during the first stage of the reaction, whereupon the layer spacing increases from 585 pm to 824 pm, and this increased spacing together with the nucleophilic attack by the hydridoaluminate ion on the carbon imparts an ionic character to the C–F bond and ultimately leads to the releasing of fluoride ions from the fluorographite. The fluoride anions react in turn with lithium cations to give LiF. Hydrogen, after giving up its charge, leaves the reaction mixture in the gas form, or bonds in part to carbon. Aluminium hydride remains intercalated and subsequently is decomposed and washed out of the interlayer space with hydrochloric acid.

The similarity of the powder X-ray diffraction patterns of fluorographite and the reduction products points to the possibility of formation of "hydrographite". This is borne out by the facts that the hydrogen content is five times higher as compared with the blank experiment (Table III) and that the electric conductivity is two times lowered against graphite. Infrared spectra, however, fail to give an unambiguous evidence of the presence of C–H bonds. It is conceivable that the hydrogen is bonded in the reduction product by chemisorption or intercalation.

A CLi_xF_y type intercalate is assumed to be formed if fluorographite is used as the cathode material in lithium batteries with organic electrolytes. Its existence has been proved by Whittingham[18] based on the X-ray diffraction patterns, which included lines $d = 935$, 469, and 312 pm; in the subsequent stage, when the cell is discharged, the intercalate is supposed to disproportionate to LiF and graphite. The formation of CLi_xF_y intercalate (x and y approaching unity) is also assumed by Watanabe[19], who, however, does not consider its successive disproportionation associated with the formation of LiF.

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