INTERCALATION OF URANIUM HEXAFLUORIDE INTO GRAPHITE

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Intercalation of UF_6 into graphite, both from the gaseous phase and from the Ledon 113 solution, was studied. The amount of intercalated UF_6 from the gaseous phase was found to be inversely proportional to the size of graphite particles. Intercalation increases with the increasing temperature and surface area of graphite. The contact of gaseous UF_6 with graphite led to the formation of β-UF_5 that is not intercalated. In the Ledon solution, β-UF_5 is not formed. "Passivation" of graphite by elementary fluorine also prevents the formation of β-UF_5 but the amount of intercalated UF_6 decreases.

The intercalation of UF_6 into graphite from the gaseous phase is accompanied by the increase of the distance between the parallel carbon atom layers up to the values of about 884 pm. Ternary intercalates graphite–UF_6–Ledon 113 are formed during the intercalation of UF_6 from the Ledon 113 solutions and the distance between the parallel carbon atom layers is 848–875 pm.

Thermogravimetry in the presence of air revealed that the binary intercalates graphite–UF_6 decompose in a 3-step reaction while the ternary intercalates decompose in a 4-step reaction. In both cases uranium hexafluoride is not released but acts as a fluorination agent on the graphite carbon.

In the published literature only two papers were found dealing with the intercalation of uranium hexafluoride. Binenboym and coworkers[1] prepared the intercalate of graphite with UF_6 at the laboratory temperature, the stoichiometric composition of which was $C_{9.1\pm0.5}UF_6$. In another paper[2], published later, the preparation of an intercalate of the overall formula $C_{13\pm3}UF_6$ has been reported. On the basis of NMR spectra and magnetic susceptibility measurements the authors assume that about 10% of uranium is present in the form of UF_4.

The aim of this study was to investigate the conditions of uranium hexafluoride intercalation into the graphite lattice, both by the direct contact with gaseous UF_6 and by the contact with the solution of UF_6 in Ledon 113 (1,1,2-trichloro-1,2,2-trifluoroethane).

EXPERIMENTAL

Reagents used. Uranium hexafluoride was prepared in this Institute by fluorination of uranium oxides by elementary fluorine[3].

Graphites CR-5 and P are very pure natural graphite powders of Czechoslovak production, chemically refined. Before intercalation, they were dried under vacuum at the temperature of 250–300°C for 24 hours. The graphite specifications are given in Table I.

Graphites $(CR\text{-}5)_f$ and $(P)_f$ are graphites of the types CR-5 and P, respectively, that were exposed to fluorine for 48 hours at the pressure corresponding to the UF_6 vapor pressure at 25°C (16 kPa).

Ledon 113 (1,1,2-trichloro-1,2,2-trifluoroethane), product of "Spolek pro chemickou a hutní výrobu", Ústí n.L., was dried using a molecular sieve.

Analysis and devices. After hydrolysis of the samples by nitric acid, uranium was determined by the previously described method[4]. Mikromat Chirana (Co/Fe) was used for the powder X-ray diffraction analysis and the apparatus Derivatograph 1 500, M.O.M., Budapest, was used for the differential thermal analysis.

UF_6 Intercalation from the Gaseous Phase

1) Monel crucible with a known amount of graphite (0·15—0·2 g) was placed into a vertical monel reactor that was connected by means of vacuum valves to the recipient with UF_6 and also to the oil rotational pump. The apparatus was placed in a glove-box with the nitrogen atmosphere of the dew point $< -60°C$. Before intercalation, the reactor with graphite was evacuated for one hour to the pressure of 1·33 Pa. After evacuation, UF_6 from the recipient was introduced into the reactor. After intercalation, the excess of UF_6 was transferred back to the recipient by cooling it down to the temperature of liquid nitrogen for one hour. During the whole reaction the inner space of the glove-box was kept at a given temperature with the precision of $\pm 1°C$.

2) The vertical reactor, described in the experiment No 1, was replaced by a horizontal nickel reactor of the length of 30 cm, in which the known amount of graphite (4—8 g) was spread in a thin layer over the length of 25 cm. The graphite layer was of about half the thickness used in the experiment No 1. This experiment proceeded like the experiment No 1 with the only difference that the apparatus was not kept in the thermostatic box and the intercalation proceeded at the laboratory temperature, *i.e.*, at 25°C.

Intercalation in the Ledon-113 Solution of UF_6

Ledon-113 solution of UF_6 of a given concentration was added to a known amount of the given type of graphite in a polytetrafluoroethylene vessel (of the volume of 30 ml), *cf.* Table II. The reaction mixture was sealed and kept without stirring in a thermostatic glove-box for a given period of time. After the reaction, the excess solution of UF_6 in Ledon was removed by decantation and the reaction product was dried for 5 hours in the nitrogen atmosphere at 40°C and then for another 3 hours in vacuum (1·33 Pa).

RESULTS AND DISCUSSION

Fig. 1 presents the time dependence of the amount of the gaseous UF_6 intercalated into the graphites CR-5 and P, respectively, at the constant temperature (25°C). The stoichiometry of the produced intercalates was calculated from the weight increase of graphite. The results obtained were compared with the amount of uranium as determined spectrophotometrically after the hydrolysis[4] (*e.g.*, for $C_{6.9}UF_6$ the calculated amount of uranium, based on the weight increase, is 54·7%, according to the analysis it is 55·8% of U). Comparing the results of UF_6 intercalation into the graphites CR-5 and P (Fig. 1) it can be seen that the finer graphite CR-5 intercalates by about 70% more of UF_6 than the graphite P. Increasing the intercalation temperature by 20°C (to 45°C) the same saturation level can be achieved as that achieved at 25°C after a double time (*cf.* Figs 1 and 2). Similarly, increasing the graphite surface area that is exposed to the UF_6 vapors (Experiment No 2) an intercalate of a higher saturation level can be obtained in a shorter time (Fig. 1).

TABLE I

Parameters of the graphites CR-5 and P

	Graphite	
Fraction, µm	CR-5	P
	Fraction content, %	
0–5	56	13
5–10	36	13
10–20	8	29
20–60	—	32
60–100	—	10
over 100	—	3
Bulk density, g/cm^3	190	430

TABLE II

Reaction of graphite with the Ledon 113 solution of UF_6

Experiment No	Graphite	Amount, g		Molality of UF_6 in L-113	Temp. °C	Reaction time h	Graphite weight increase, g
		graphite	UF_6				
1	CR-5	0·4221	1·3602	0·115	23	120	1·6495
2	CR-5	0·1739	0·4555	0·083	23	19	0·5951
3	CR-5	0·1791	0·4666	0·089	23	19	0·5725
4	CR-5	0·6097	1·4983	0·310	23	19	1·8335
5	P	0·6409	1·8503	0·177	20	38	2·0327
6	P	0·8331	3·1537	0·379	20	33	2·9010
7	P	1·0010	4·5572	0·591	20	33	3·4657
8	$(P)_f$	0·3122	1·4398	0·174	20	12	0·9936
9	$(P)_f$	0·4055	1·5995	0·192	20	12	1·2774
10	$(P)_f$	0·5486	1·2230	0·157	20	12	1·5613

After the UF_6 intercalation the greyish-black graphite attained a glossy black color with a bluish tint. X-ray powder diffraction revealed that the main line 002 of pure graphite (d = 335 ppm) disappeared and new lines were observed. In addition to the lines that can be ascribed to the intercalate, also the lines of β-UF_5 appeared. On the basis of hydrolysable fluorine the assumed content of β-UF_5 is about 10–12%.

The formation of uranium pentafluoride can be explained by a reaction of UF_4, formed in the fluorination of graphite by UF_6, with the excess of UF_6. The formation of UF_4 during the UF_6 intercalation of graphite was already described by Ebert[2]. The amount of UF_4 was reported to be 10% of the total uranium content but the presence of β-UF_5 was not observed. However, from the published literature[6] it is known that the formation of β-UF_5 depends on the physico-chemical state of UF_4, on the vapor pressure of UF_6, on the temperature. *etc.*

To confirm the assumption of the partial fluorination of graphite, the original graphites were exposed for 48 hours to the atmosphere of elementary fluorine at the

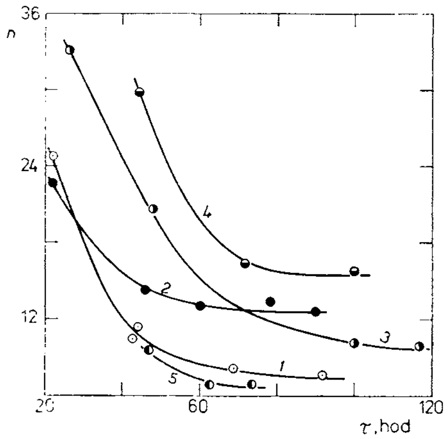

FIG. 1

Time dependence of the amount of intercalated uranium hexafluoride at the constant temperature (25°C) for various types of graphites and for various experimental conditions. The variable n is the stoichiometric coefficient in the formula C_nUF_6; *1* CR-5, experiment No 1; *2* P, experiment No 1; *3* $(\text{CR-5})_f$; experiment No 1; *4* $(\text{P})_f$, experiment No 1; *5* CR-5, experiment No 2

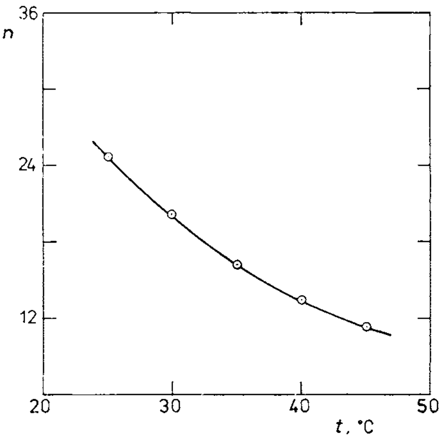

FIG. 2

Temperature dependence of the amount of uranium hexafluoride intercalated into CR-5 graphite at the constant reaction time (22 hours). The variable n is the stoichiometric coefficient in the formula C_nUF_6

pressure corresponding to the vapor pressure of UF_6 at 25°C (16 kPa). In intercalates prepared from such "passivated" graphites no lines of β-UF_5 could be detected by the X-ray diffraction. By "passivation" of graphites by fluorine it can be achieved that the intercalate does not contain any extra-lattice β-UF_5 but at the same time the amount of the intercalated UF_6 decreases for the given period of time (Fig. 1).

Table III presents the X-ray diffraction pattern of the C_8UF_6 intercalate powder (from the CR-5 graphite) with the lines ascribed to β-UF_5 and the X-ray diffraction pattern of $C_{10}UF_6$ intercalate (from the CR-5 graphite passivated by fluorine). The published diffraction lines of the intercalates $C_{9.1}UF_6$ (ref.[1]) and $C_{13.2}UF_6$ (ref.[2]) are quoted for comparison below the table. On the basis of the line assignment in the diffraction pattern it can be assumed that the compound C_8UF_6 is the first-order intercalate with an extra-lattice β-UF_5 and the compound $C_{10}UF_6$ is the first-order, but also partly second-order intercalate. The UF_6 intercalation widened the space

TABLE III

Powder X-ray diffraction pattern of C_8UF_6 with the lines ascribed to β-UF_5 and the powder diffraction pattern of the $C_{10}UF_6$ intercalate in which graphite was passivated by elementary fluorine. The published diffraction lines (pm) for $C_{9.1}UF_6$ (ref.[1]): 545, 440, 415, 387, and for $C_{13.2}UF_6$ (ref.[2]): 1 190, 890, 598, 515, 439, 395, 387, 211, 204, 195, 165.

C_8UF_6		UF_5 (ref.[5])	$C_{10}UF_6$	
d pm	I/I_0	d/I pm/%	d pm	I/I_0
883	m		884·5	s
509	w		505·3	m
472	vw	468/25	450·6	s
431	w		405·8	w
403	vw	403/15	383·4	m
388	w		349·3	vw
363	s	362/100	332	w
244·6	vw	244/40	265·2	vw
235·7	vw	235/40	213·7	w
208·5	vw	208/60	206·7	w
195·6	w	196/80	161·6	vw
191·4	vw	192/20	152·1	vw
189·5	vw	191/15	140·4	vw
185·9	w	186/60		

between the carbon atom layers from 335 ppm (the value for graphite) to I'_c = 884 pm (I'_c – the distance between two parallel carbon atom layers that contain the intercalated substance).

Two exothermic effects with maxima at 185 and 315°C were found by the thermal gravimetric analysis (TGA) for the $C_{6.9}UF_6$ intercalate (from CR-5 graphite), and at 259 and 492°C for the $C_{11.5}UF_6$ intercalate (from P-graphite). It is evident that the intercalate of a lower saturation (in the case of P-graphite) is thermally more stable. The mass decrease during the thermal decomposition is due to the fluorination of graphite accompanied by the release of CF_4 or, eventually, C_2F_6.

Intercalation in the Ledon-113 *solution of* UF_6. The reaction conditions for the UF_6 intercalation of graphite in the Ledon-113 solution are reviewed in Table II. The overall formulas of individual products were calculated from the initial amount of graphite, from the increase of the product weight, and from the determined content of uranium (Table IV). The products obtained have a higher volume and attained a blue-black metallic color. Their stoichiometric compositions are under the given conditions (type of graphite, reaction time, temperature) comparable.

The most intense line observed by the powder X-ray diffraction corresponded always to the first-order intercalate, *i.e.*, to the compound in which all the space between the layers of carbon atoms is saturated with the intercalated substance. The residual, very weak lines in the diffraction patterns of products can be ascribed to the intercalates of higher orders (second or third). During the intercalation the distance between the carbon atom layers increased from 335 pm to 848 – 875 pm in the intercalates under study. Table V presents the data of the intercalation degree, the I_c (I_c – the identity period) and I'_c values for the prepared intercalates. Some measured powder diffraction patterns with the ascribed *hkl* lines and the intercalation degrees are also given in the Table VI. The formation of non-intercalated β-UF_5 (along with the intercalate) was not observed in any of the products.

TABLE IV
The overall formulas of the prepared ternary intercalates

Experiment No	Overall formula of the intercalate	Experiment No	Overall formula of the intercalate
1	$C_{9.88 \pm 0.34}UF_6(Ledon)_{0.59 \pm 0.02}$	2	$C_{17.16 \pm 0.19}UF_6(Ledon)_{1.88 \pm 0.02}$
3	$C_{18.41 \pm 0.43}UF_6(Ledon)_{1.89 \pm 0.08}$	4	$C_{17.89 \pm 0.67}UF_6(Ledon)_{1.87 \pm 0.05}$
5	$C_{16.75 \pm 0.30}UF_6(Ledon)_{1.52 \pm 0.03}$	6	$C_{16.66 \pm 0.26}UF_6(Ledon)_{1.83 \pm 0.03}$
7	$C_{16.14 \pm 0.34}UF_6(Ledon)_{1.70 \pm 0.04}$	8	$C_{21.45 \pm 0.60}UF_6(Ledon)_{2.49 \pm 0.07}$
9	$C_{21.49 \pm 1.54}UF_6(Ledon)_{2.45 \pm 0.17}$	10	$C_{23.66 \pm 0.68}UF_6(Ledon)_{2.43 \pm 0.07}$

It was observed by TGA that the thermal decomposition of the chosen samples of UF_6 intercalates with Ledon proceeds in four steps (in the presence of air). In the first three steps, that are analogous to the decomposition of binary UF_6 intercalates with graphites, the products of the fluorination of the graphitic carbon intercalated by uranium hexafluoride are released. At the same time a part of the intercepted

TABLE V

Intercalation degree, the identity period I_c (pm), distance between the parallel layers of carbon atoms with the intercalated substance, I'_c (pm) for the ternary intercalates

Experiment No	Intercalation degree 1		2		3	
	I_c	I'_c	I_c	I'_c	I_c	I'_c
1	874	874	1 173	838	1 585	915
2	875	875	1 176	841		
4	868	868	1 146	811	1 512	842
5	860	860			1 514	844
6	865	865	1 204	869		
7	859	859				
9	848	848	1 160	826		
10	865	865	1 167	832	1 502	832

TABLE VI

Powder X-ray diffraction patterns of some ternary intercalates with the ascribed *hkl* lines for individual intercalation steps (*n*)

$C_{16.66}UF_6$(Ledon 113)$_{1.83}$				$C_{17.89}UF_6$(Ledon 113)$_{1.57}$				$C_{23.66}UF_6$(Ledon 113)$_{2.43}$			
d, pm	I/I_0	*hkl*	*n*	*d*, pm	I/I_0	*hkl*	*n*	*d*, pm	I/I_0	*hkl*	*n*
865	s	001	1	868	m	001	1	865	s	001	1
433	s	002	1	431	m	002	1	508	w	003	3
301	vw	004	3	382	w	003	2	433	s	002	1
								389	m	003	2
								370	vw	004	3
								213	w	004 100	1
								178	vw	005	1

Ledon is released, too. Uranium is not released from the intercalate. In the fourth, strongly exothermic step, the remaining, rather substantial part of the intercalated Ledon is released and this release is accompanied by a loss of carbon in an amount proportional to the content of uranium. Results of the thermogravimetric analysis of selected UF_6 intercalates with Ledon recalculated with respect to the virtual relative molecular weights of products are given in Table VII.

The experimentally determined total weight losses are higher than the assumed sum of weights of Ledon and of the products of internal fluorination. The difference is equal to the value corresponding to one carbon atom. It can be deduced from the balance of the composition of the intermediate in the third step $(n_{\mathrm{III}}/m_{\mathrm{III}})$ that the carbon loss mentioned above occurs during the fourth step of decomposition, probably due to the oxidation by air. Solid intermediates from the third step exhibit a rather high stability on the TGA curves. In spite of the different content of uranium, about 12 carbon atoms correspond to one molecule of Ledon.

On the basis of the chemical analysis, X-ray diffraction, and DTA we assume the formation of ternary intercalates graphite–UF_6–Ledon 113 in the reaction of graphite with the Ledon 113 solution of UF_6. The ternary intercalate, in which an organic substance is the second component, was described by Amiell and coworkers[7], namely the intercalates of the type $C_{24}K(THF)_1$ and $C_{24}K(THF)_2$ that were prepared by the action of the mixture of tetrahydrofurane with aromatic hydrocarbons on the previously prepared potassium intercalate, $C_{24}K$. A similar intercalate, $C_{24}M(C_6H_6)_{2.25-3.1}$ (M = K, Rb, Cs) was prepared by the action of benzene on the alkali metal intercalates[8].

TABLE VII

Thermal gravimetric analysis of the intercalates $C_nUF_6(\text{Ledon } 113)_m$

Sample No (*cf.* Table IV)	4	6	7	9
Type of graphite	CR-5	P	P	$(P)_f$
Composition: *n*	17·89	16·66	16·44	21·49
m	1·87	1·83	1·70	2·45
Gaseous products				
I. step 40—200°C	18·4	30·4	9·4	14·0
II. step 175—250°C	40·1	51·2	42·9	88·4
III. step 210—450°C	46·8	51·2	53·6	72·1
IV. step 430—715°C	300·9	256·5	286·8	331·6
Total decrease (calc.)	394·4	386·9	362·5	503·1
Total decrease (exp.)	406·2	398·3	375·5	506·1
$n_{\mathrm{III}}/m_{\mathrm{III}}$	11·28	11·94	11·42	11·97

The reason for the simultaneous intercalation of Ledon 113 and UF_6 into graphite remains open. In the absence of UF_6, graphite absorbs (or, eventually, adsorbs) only negligible amounts of Ledon 113 (C_{60-85} Ledon 113) as proved by a parallel "blind" experiment with graphite and Ledon that were treated by the same procedure as the intercalate. The fact that perfluoroalkanes and freons (Ledons) form stable solutions with volatile fluorides[9,10] can be taken for a possible explanation for the simultaneous intercalation of UF_6 and Ledon 113. However, these solutions need not be ideal as proved by the system WF_6 and $n\text{-}C_5F_{12}$ (ref.[11]). It is well known that alkanes, cycloalkanes, and their halogen derivatives are weak Lewis bases, *i.e.* donors of the σ-type[12]. In the contact of a σ-donor with an acceptor (like UF_6) a complex may be formed that need not be observed as a solid complex. This fact could enable the simultaneous intercalation of UF_6 and Ledon 113 into the graphite lattice. On the basis of the composition of ternary intercalates it can be concluded that the amount of Ledon 113, the intercalation of which depends on the simultaneous intercalation of UF_6, is intercalated with such a supplementary amount of UF_6 that the ratio C_s: intercalated components ranges from 5·8 to 6·8. During a prolonged intercalation, the amount of Ledon 113 decreases and the content of UF_6 in the intercalate increases.

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