THE REACTION OF IODINE OXIDE PENTAFLUORIDE AND RHENIUM OXIDE PENTAFLUORIDE
WITH GRAPHITE

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SUMMARY

IOF_5 intercalates into graphite accompanied by partial oxygenation of
the graphite host. The intercalated species was identified by ^{19}F nmr spect-
roscopy. Oxygenation of the graphite was established by analyses of the
gaseous reaction products. Intercalation of $ReOF_5$ into graphite is accom-
panied by liberation of large amounts of ReF_6 and traces of CO_2 and COF_2.
The oxygenation of the graphite was established by weight increase. The stoi-
chiometry of the reactions and physical measurements indicated that the inter-
calated species is ReF_4 together with varying amounts of ReF_6. The formation
of these fluorides from $ReOF_5$ can be explained in terms of an intermediate
formation of ReF_5 followed by its disproportionation.

INTRODUCTION

The ability of graphite to form intercalation compounds with volatile
inorganic fluorides in high valency states has been amply demonstrated in
recent years [1][2]. In a previous study [3] the behavior of halogen

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fluorides towards graphite has been investigated. It was shown that IF_7 intercalated into graphite with partial fluorination of the host and reduction to IF_5, which is partially retained in the lattice.

Iodine [4][5], rhenium [5][7] and osmium [8][9] are the only elements forming heptavalent fluorides and oxide pentafluorides. The heptafluorides and oxide pentafluorides belong to the symmetry groups D_{5h} [8][10][11] and C_{4v}, respectively [12]. The identical structures for each series of compounds suggest similar chemical behavior vis-a-vis graphite.

To decide whether oxide pentafluorides react as fluorinating and/or oxygenating agents, we investigated the reactions of IOF_5 and $ReOF_5$ with graphite in comparison with the known reaction of IF_7 [3].

EXPERIMENTAL

The intercalation compounds were prepared by direct exposure of GTA Grafoil or SP-1 graphite powder from Union Carbide Co., or Ceylon graphite powder to IOF_5 or $ReOF_5$ at room temperature. Procedure and apparatus have been given elsewhere [13]. Fluorine (Matheson) was used as supplied. IF_5 and IOF_5 were prepared after methods described [14]. IOF_5 was conveniently freed from HF and SiF_4 by condensing the gases onto NaF. The purity of IOF_5 was checked by IR spectroscopy [15], molecular weight and vapor pressure measurements [14]. The gaseous reaction products were separated by fractional vacuum sublimation out of the reaction vessel: $- 126^{o}C$, CO_2. COF_2; $-78^{o}C$, IOF_5; room temperature, IF_5. The amount of oxygen produced was estimated from its pressure at $- 196^{o}C$ in the known gas volume. IF_5 and CO_2 were identified by IR spectroscopy and comparison with original samples, COF_2 by comparison with its reported spectrum [16]. In addition, CO_2 and COF_2 were analyzed by mass spectrometry (Varian Mat 311, 70eV). Details of ^{19}F nmr measurements of solids have been given [3].

$ReOF_5$ was synthesized by heating ReO_2 in a static fluorine atmosphere to $250^{o}C$ as described in [12]. The purity was established by IR spectroscopy [12] and vapor pressure measurements [17]. The gaseous reaction product ReF_6 was identified by IR spectroscopy [18] and by its vapor pressure [19].

The air and moisture sensitive intercalation compounds were handled in a drybox (HE-43 DRI LAB, Vacuum Atmosphere Corp.) and their composition established by weight increase, quantitative analysis of gaseous reaction products and check of the weight balances of all products present.

TABLE 1.

Mass Balances of the Graphite IOF_5 Reactions

Starting Materials		Products				Conversion of	Weight increase	Intercalated species		Formula
		Composition of the gas phase								
IOF_5	Graphite	$CO_2 + COF_2$	O_2	IOF_5	IF_5	IOF_5		O_2	IF_5	
(mmol)	(mmol)	(mmol)	(mmol)	(mmol)	(mmol)	(mmol)	(g)	(mmol)	(mmol)	
10.4	55[P]	0.1	2		1.6	8.4	1.64	4.2	6.8	$(C_{6.5}O)_{1.2} \cdot IF_5$
10.3	36[P]	0.1	2.2		2.8	8.1	1.31	4.05	5.3	$(C_{4.5}O)_{1.5} \cdot IF_5$
8.27	40[G]	0.1	0.35		3.1	8.27	1.21	3.93	5.17	$(C_{5.10}O)_{1.5} \cdot IF_5$

P: SP-1 Graphite powder, G: Grafoil.

X-ray spectra (Cu, Kα radiation) were taken on powdered samples. The magnetic susceptibility was measured by the Faraday method (Alpha Subsidiary, Systron Donner, Model 1403). Thermogravimetric analyses were conducted on a Mettler Thermo-balance.

ATR-infrared measurements of $C/O/IF_5$ compounds failed because of reaction with the KRS-5 windows.

RESULTS AND DISCUSSION

The reaction of IOF_5 with graphite

The mass balances of the reactions carried out are summarized in Table 1.

IOF_5 in direct contact with graphite (ratio $C/IOF_5 \sim 5$) reacted after several days with formation of deep black intercalation compounds with the general formula $(C_nO)_mIF_5$. The reaction can be expressed by equation 1.

$$C_n + IOF_5 = C_nO(IF_5)_{1-x} + x \; IF_5 \tag{1}$$
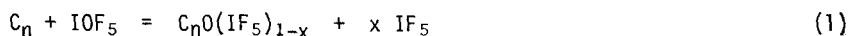
Using an excess of graphite (ratio $C/IOF_5 \sim 18$ to 20) the reaction only started after heating to $75^\circ C$. The partial oxygenation can be deduced from Table 1. In all cases nearly all of the starting IOF_5 had been converted to IF_5 which was partially intercalated. Only small amounts of oxygen containing compounds were liberated. The difference between liberated oxygen (O_2, CO_2, COF_2) and the total amount of oxygen from IOF_5 which was converted to IF_5 thus must have been introduced into the graphite. The identity of the inter-calated iodine species was determined by ^{19}F nmr spectroscopy. A broad line nmr spectrum exhibited two signals: $S_1 = -74$ ppm and $S_2 = -134$ ppm (CF_3COOH, external standard) with an intensity ratio of $S_1/S_2 \approx 3,4$. These are very close to those observed for IF_5 intercalated in partially fluorinated graphite ($S_1 = -86$ ppm, $S_2 = -128$ ppm)[3] and neat IF_5 [20].

Thermogravimetric analyses of the brittle, still diamagnetic com-pounds showed that they started to decompose at $100^\circ C$. In two cases the decomposition was violent and the materials were blown out of the TGA crucibles. Upon heating, traces of CO_2, COF_2 and IF_5 accompanied by large amounts of I_2 were liberated. Weight loss was complete at about $450^\circ C$. The TGA curves indi-cated no evidence of formation of compounds of higher stages and more diluted samples with compositions of $C_{18}O.IF_5$ to $C_{20}OIF_5$ decomposed at the same tem-

perature. X-ray powder photography showed the absence of the strong graphite line at d = 33.5 pm and the appearance of new very broad lines centered at d = 37 pm $((C_{20}O)IF_5)$ and d = 40.4 pm $((C_{6.5}O)_{1.2}IF_5)$. Powder diffraction diagrams of the TGA residues indicated an expanded graphite lattice with d = 338.8 to 341.4 pm.

The reaction of $ReOF_5$ with graphite

$ReOF_5$ reacted rapidly and exothermically with graphite to produce unstable blue compounds which turned black after a short time. The formation of true intercalation compounds was established by the disappearance of the strong graphite line at d = 335 pm and the appearance of a new, very broad line centered at d = 378 pm in the X-ray spectra. Besides ReF_6, very small amounts of CO_2 and COF_2 were liberated. Formation of the latter could be suppressed by conducting the reaction at 0°C.

Table 2 summarizes the mass balances of the reactions. The fluorine products 1,2,3 (Table 2) released ReF_6 continuously upon standing. Product 4 (Table 2) was pumped under vacuo until no more ReF_6 was collected (10 days!).

TABLE 2.

Mass Balances of the Graphite/$ReOF_5$ Reaction.

No.	STARTING MATERIALS		PRODUCTS		
			GAS PHASE	BLACK SOLIDS	
	$ReOF_5$	Graphite	ReF_6	Composition	Weight Increase (g)
	(mmol)	(mmol)	(mmol)		calc. found
1	6.5	67.3[G]	0.3	$C_{20.7}O_2(ReF_4)(ReF_6)_{0.9}$	1.729 1.843
2	9.19	101[C]	1.1	$C_{21.2}O_2(ReF_4)(ReF_6)_{0.7}$	2.404 2.428
3	3.7	75.6	0.33	$C_{40.3}O_2(ReF_4)(ReF_6)_{0.8}$	1.087 1.040
4	9.25	84.7	3.7	$C_{18.3}O_2(ReF_4)(ReF_6)_{0.2}$	2.431 2.506

G: Grafoil, C: Ceylon graphite powder

Thus about 40% of the initial rhenium was recovered as ReF_6 and the ratio of F/Re (intercalated) approached 4. This strongly suggested that 2 mol $ReOF_5$ had been converted to 1 mol ReF_6, which was partially retained in the host and 1 mol of a less volatile rhenium fluoride, oxide fluoride or oxide with graphite being either unreacted, fluorinated or oxygenated. Possible inter-calated species are $ReO_2F_4^-$ (diamagnetic) [21], $ReOF_4$ μ = 1.21 to 1.33 BM $\ominus$ = +34°) [22], ReF_4 (no values given) [22] and ReO_2 (μ = $\sim$ 0.5 BM). The magnetic moment of the intercalation compound, μ_{eff} = 1.53 BM (300K), μ = 2.2 BM (77 to 200K), $\ominus$ = -45°, makes the presence of ReF_4 in the lattice most pro-bable, although the magnetic moment is lower than would be expected for Re +IV.

Substantial contribution of ReF_6 could be ruled out on the basis of its low magnetic moment (μ = 0.25 BM, $\ominus$ = 0°) [24] and ReF_5 on the basis of the mass balance (Table 2) and its magnetic moment (μ_{eff} = 0.95 to 1.41, $\ominus$ = 580) [22].

This interpretation was supported by thermogravimetric measurements. ReF_6 rich products 2,3 (Table 2) started to decompose at room temperature with rapid decomposition occurring at 80°C. A plateau was reached at 200°C followed by other rapid decomposition steps at 350°C and 450°C. Weight loss was complete at 500°C. The weight loss versus temperature curve of the ReF_6 poor product 4 (Table 2) was almost identical (fast decomposition steps at 300-350°C and 450°C), except for the step at 200°C which was no longer pro-minent. The latter could thus be attributed to extercalating ReF_6, whereas the other steps were in accordance with the evaporation of ReF_4 (300-350°C, sublimation point) 300°C [22] and the dissociation of C-O bonds in oxygenated graphite ($\sim$450°C). X-ray powder diffraction diagrams of the graphite residues indicated a slightly expanded graphite lattice with d = 342.6 pm.

Comparison of the reactions of IF_7, IOF_5 and $ReOF_5$ with graphite

IF_7 reacts with graphite with formation of intercalation compounds of IF_5 in partially fluorinated graphite with a ratio of IF_5/C = 1/21 to 33. IOF_5, however, acts as oxygen donor and forms IF_5 intercalates in partially oxygenated graphite with ratios of IF_5/C as high as 1/6.75. This ratio is even higher than those achieved by direct intercalation of IF_5 [13]. IOF_5 decomposes upon heating (eq.2) [25].
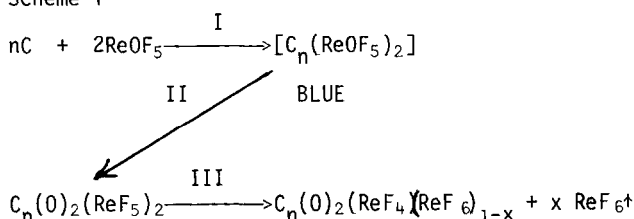
$$IOF_5 = IF_5 + \tfrac{1}{2}O_2 \tag{2}$$

The driving force of this reaction is the high tendency to formation of mole-cular oxygen (ΔH_{diss} = 494 kJ/mol) and the formation of IF_5, the most stable

iodine fluoride (ΔH_f° = -837.3 kJ/mol) [26]. In addition IF_5 readily intercalates into graphite [13]. This might explain the readiness with which this reaction (eq.2) occurs in the presence of graphite at room temperature and the oxygenation of the host itself.

The reaction of $ReOF_5$ with graphite might be explained in similar terms (Scheme 1).

Scheme 1

$$nC \ + \ 2ReOF_5 \xrightarrow{\quad I \quad} [C_n(ReOF_5)_2]$$

BLUE

$$C_n(O)_2(ReF_5)_2 \xrightarrow{\quad III \quad} C_n(O)_2(ReF_4)(ReF_6)_{1-x} + x\ ReF_6\uparrow$$

(with II indicated on the diagonal arrow from the blue compound)

The first fast step lead to a blue unstable $ReOF_5$ intercalate, which by analogy to the IOF_5/graphite reaction decomposes rapidly to ReF_5 intercalated in partially oxygenated graphite. ReF_5 is known to disproportionate into ReF_6 and ReF_4 at 140°C [22]. This might explain the stoichiometry of the $ReOF_5$/graphite reaction. Graphite might promote this disproportionation at much lower temperature. ReF_6 itself has been reported not to intercalate except in the presence of fluorine [27]. This may account for the removal of ReF_6 from the host. The exothermic formation of a stable intercalation compound may have shifted the equilibrium towards ReF_4 intercalated in oxygenated graphite.

The possibility that both products are intercalation compounds of graphite oxide analogous to graphite fluoride intercalated with SbF_5 [28] is intriguing.

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