REACTIONS OF MOLYBDENUM, TUNGSTEN, AND URANIUM HEXAFLUORIDES IN ACETIC AND TRIFLUOROACETIC ACIDS

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It is known that the hexafluorides of molybdenum, tungsten, and uranium are extremely sensitive to moisture and are readily reduced by various organic compounds. In this work we studied the reactions of the hexafluorides of these metals. Acetic acid and its halo derivatives, in particular, trifluoroacetic acid, are of special interest in this respect, since they possess sufficient stability to oxidizing agents.

EXPERIMENTAL

Anhydrous acids were used in the work: CH_3COOH with mp 16.5°, bp 117.5-118.5, CF_3COOH , redistilled twice over P_2O_5 with bp 70.3-71.2° (740 mm). MoF₆ and WF₆ were produced by fluorination of the corresponding metals with elementary fluorine in a quartz reactor. LiF, NaF, KF, RbF, and CsF were high quality.

All the work was conducted in a dry box (dried with P_2O_5) in an atmosphere of nitrogen; the vessels used for the reactions and the supply lines were made of Teflon, polyethylene, and quartz.

Reactions of Hexafluorides in Anhydrous Acetic Acid. The dissolution of molybdenum and tungsten hexafluorides in CH_3COOH was accompanied by a temperature rise of the solution to 40-60°. The solution obtained was colorless, and did not fume in air. The interaction of the components under consideration

Hexafluoride	Sample	Amount of	CH ₃ COF,g	Amount of HF,g		
	weight,g	found	calculated	found	calculated	
MoF6	6,28	1,86	1,85	0,60	0,63	
WF ₆	5,46	2,27	2,26	0,71	0,73	

TABLE 1. Interaction of MF₆ with CH₃COOH

UF₆ Acetyl fluoride detected

TABLE 2.	Results c	of Chemical	Analysis	of the	Isolated Salts
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Compound	Conte	ent of K,%	Content group VI	of metal of ,%	Content of F,%		
	found	calculated	found	calculated	found	calculated	
KM0O2F3 K2WO2F4 K2UO2F4	17,6 19,9 17,3	17,41 21,08 18,35	41,6 48,3 53,2	42,85 49,73 56,2	24,9 21,6 18,6	20,98 20,54 17,9	

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	Found,%					Calculated,%			
		U		F		-	υ	F	
Proposed formula	м	4+ total	from	total	from	total			
			locar	UF ₅			UF ₅	lotur	
$\begin{array}{c} CF_{9}CO_{2}Li\cdot 2UF_{5}\\ CF_{3}CO_{2}Na\cdot 2UF_{5}\\ CF_{3}CO_{2}K\cdot 2UF_{5}\\ CF_{3}CO_{2}Rb\cdot 2UF_{5}\\ CF_{3}CO_{2}Cs\cdot 2UF_{5}\\ \end{array}$	- 7,05 10,0 15,4	29,8 28,6 28,2 25,8 24,7	$\begin{array}{c} 60,6\\ 59,0\\ 58,1\\ 56,0\\ 52,5\end{array}$	23,0 23,0 22,8 22,1 20,8	31,4 30,4 28,6 26,0	0,9 2,9 4,8 9,9 14,6	$\begin{array}{c} 60,5\\ 59,5\\ 58,3\\ 55,1\\ 52,2 \end{array}$	24,2 23,6 23,1 21,9 20,6	31,4 30,8 30,2 28,7 27,0

TABLE 3. Chemical Analysis of the Solid Phases Formed in Reaction (4)



Fig. 1. Kinetics of the reactions of UF_6 with CF_3 · COOH (1) with an addition of KF (2). occurs according to the schemes

 $MoF_6 + CH_3COOH \rightarrow MoOF_4 + CH_3COF + HF$ (1)

$$\begin{array}{l} WF_6 + 2CH_3COOH \rightarrow WO_2F_2 + 2CH_3COF + 2HF \\ UF_6 + 2CH_3COOH \rightarrow UO_2F_2 + 2CH_3COF + 2HF \end{array}$$
(2)

The stoichiometry of the reactions was established by successive distillation of HF and acetyl fluoride from the reaction mixture. HF was trapped at room temperature on tablets of NaF in a Teflon tube and determined according to the weight gain of the tablets, while CH_3COF was condensed in a platinum condenser, cooled with Dry Ice (-70°) and collected in a weighed Teflon receiver. In addition, we conducted the titration of acetyl fluoride with alkali after dissolution in water [1]. The results are cited in Table 1. The acetyl fluoride obtained in all cases was identified according to its boiling point (bp 21°). $MoOF_4$ and WO_3F_2 are appreciably soluble in CH_3COOH ; UO_2F_2 shows negligible solubility.

Salts of oxofluorometallates were isolated from solutions of the hexafluorides in CH_3COOH (which were actually solutions of the oxyfluorides) when solutions of Na, K, Rb, and Cs fluorides in CH_3COOH were added. In all cases except for NaF, precipitates were formed. The precipitates obtained were centrifuged and washed with CH_3COOH . From Table 2 it follows that in the case of MoF_6 , the reaction with CH_3COOH in the presence of KF does not stop at the step corresponding to the formation of a salt derivative of MoO_2F_4 ; hydrolysis goes farther, since the complex compound $KMoO_2F_4$, a derivative of MoO_2F_2 , is formed. For tungsten and uranium, salts based on oxofluorides of the same type are obtained. These salts were mentioned earlier in the literature [2-5].

Reactions of Uranium Hexafluoride in Anhydrous Trifluoroacetic Acid. Uranium hexafluoride is readily soluble in CF_3COOH [6]. When the solution is allowed to stand, green crystals with the composition HUF_6 are isolated as a result of the reaction

$$2UF_{6} + 2CH_{3}COOH \rightarrow 2HUF_{6} + CF_{3}COF + COF_{2} + CO_{2}$$
(3)

The isolated phase was subjected to chemical and thermogravimetric analyses, as well as stepwise pyrohydrolysis at temperatures corresponding to the hydrolytic effects on the thermograms. Volatile reaction products were identified according to the boiling points and chemical analyses. The results obtained confirmed the proposed scheme. Such a compound in the hydrated form $HUF_6 \cdot 2.5H_2O$ was isolated from a solution of 48% HF at -10° [7]; at -80° the compound $HUF_6 \cdot 1.25H_2O$ crystallized from a solution of 80-90% HF.

In the opinion of the authors of [7], hydrated water does not displace fluorine from the inner sphere of these coordination compounds, widely represented by the corresponding salts of the alkali elements. Unsuccessful attempts to obtain an anhydrous compound corresponding to HUF_6 from liquid HF gave a basis for assuming that compounds of this type are capable of existing only in the hydrated form. This hypothesis was advanced by analogy with the hypothesis of the existence of $HNbF_6 \cdot 1.3H_2O$ and $HTaF_6 \cdot 1.5H_2O$ [8, 9], the anhydrous forms of which also have not been isolated.

Such hypotheses are based on the idea of the existence of a hydrated proton in a coordination compound of the type of $\text{HM}^{V}F_{6}$ a, which includes the UF_{6}^{-} ion, which possesses octahedral symmetry. The stability of the anhydrous compound HUF_{6} , isolated in this work, is low: even at 40° an HF molecule is eliminated [6].



Fig. 2. Thermogram (a) and thermogravigram (b) of the salt $CF_3CO_2Na \cdot 2UF_5$, taken in a stream of moist air: 1) simple recording; 2) differential recording. Sample weight 145 mg.

Fig. 3. Thermogram (a) and thermogravigram (b) of the salt $CF_3CO_2Cs \cdot 2UF_5$; taken in a stream of moist air: 1) simple recording; 2) differential recording. Sample weight 300 mg.

Reaction of Uranium Hexafluoride and Fluoride of the Alkali Elements in Anhydrous Trifluoroacetic Acid. The fluorides of the alkali elements dissolve in CF_3COOH , liberating the corresponding trifluoro-acetates and hydrogen fluoride according to the reaction [10, 11]

$$\begin{split} \mathrm{MF} + \mathrm{CF_3COOH} &\to \mathrm{CF_3COOM} + \mathrm{HF} \\ \mathrm{M} = \mathrm{Li}, \ \mathrm{Na}, \ \mathrm{K}, \ \mathrm{Rb}, \ \mathrm{Cs}. \end{split}$$

In this case, the following dissolve in 100 g of anhydrous acid at 20°: LiF - 0.09 g; NaF - 2.61 g; KF - 2.98 g; RbF - 7.46 g; CsF - 9.85 g.

The reactions of uranium hexafluoride and fluorides of the alkali elements in CF_3COOH were conducted by mixing the solutions, taking a freshly prepared solution of uranium hexafluoride. When the solutions were poured together, the reaction mixture immediately acquired a yellow color, which later turned green. The reaction proceeded with an evolution of gas and precipitation of lightly colored blue deposits.

The addition of a solution of the fluoride of the alkali element in CF_3COOH to a solution of the hexa-fluoride was conducted until the uranium was completely precipitated. As a result, phases with the composition: $CF_3COOM \cdot 2UF_5$, M = Li, Na, K, Rb, and Cs were obtained according to the scheme

$$2UF_{s} + MF + 3CF_{3}COOH \rightarrow CF_{3}CO_{2}M \cdot 2UF_{5} + CF_{3}COF + COF_{2} + CO_{2} + 3HF$$
(4)

The kinetics of the process is depicted graphically in Fig.1. The salts obtained were identified by methods of chemical analysis (Table 3), stepwise pyrohydrolysis, thermogravimetric analysis in a moist atmossphere on a derivatograph, and IR absorption spectra. The thermograms (Figs.2 and 3) of the compounds obtained were taken in air. Considering this, we can assume a superposition of hydrolysis under the action of atmospheric moisture onto all the thermal effects described. To establish the temperatures of the

	CF₃C	CF3COOK					
Assignment	according to [12]	according our to [12] data		CF ₃ COONa •2UF5	CF3COOK +2UF5	CF3COORD •2UF5	
^V as COO	1675	1670	1800	1735 (1615) ?	1790 1695	1 79 0 1670	
^v s COO	1445	1443	3	?	5	3	
^V as GF	1200 1140	1220 1155	1230 1180	1235 1180 ~1155	1230 1195 1130	1208 ~1175 1093	
$v_{U} = 0 *$		—	-		~965 922 903	968 945 920 900	
v _U -0		_		-	750	~740	
v _{C-C}	835	842	?	826	815	810 ?	
v _{s CF}	806 802	809	805	798 786	792	?	
δ _{CCO} ,	725	725	?	740 ? 715	715	?	
δ _{s CFs}	592	597	?	?	5	3	
δ _{as CFs}	510	517	?	?	?	?	
v _{UF}	-		518	555 533	~530	~550	
5 5	_	483 	_		487 462	455	
ρ _{CCF3}	431	437	5	460 ? 437	?	3	
δ _{CCO₂} Nonplanar	405	405 ?	3	3	?	406 ?	

TABLE 4. Wave Numbers (cm⁻¹) of the Maxima of the Bands Found in the IR Absorption Spectra

*Bands of impurities of hydrolysis products.

hydrolytic effects, the thermograms were taken in a stream of moist air. The effects obtained in this case were interpreted by the method of stepwise pyrohydrolysis: the sample was maintained at the temperature of the effect in a stream of vapor for 40-60 min until complete liberation of HF.

The first effect for the compound (~200°) corresponds to hydrodisproportionation of uranium pentafluoride, which agrees with the literature data. Then a stepwise hydrolysis of UO_2F_2 is observed on the thermogram, with the liberation of two molecules of HF (each at its own temperature), then hydrolysis of UF_4 with subsequent liberation of four moles of HF, and finally, the last effect on the thermogram corresponds to the destruction of the $CF_3CO_2^-$ group. The data of thermal analysis were confirmed by the results of stepwise pyrohydrolysis of the corresponding compounds. This enabled us to propose the following scheme of hydrolysis:

$$2[CF_{3}CO_{2}M \cdot 2UF_{5}] \xrightarrow{4H_{2}O} 2CF_{3}CO_{2}M + 2UO_{2}F_{2} + 2UF_{4} + 8HF$$

$$\xrightarrow{2H_{2}O} 2CF_{3}CO_{2}M + 2UO_{3} + 2UF_{4} + 12HF$$

$$\xrightarrow{4H_{4}O} 2CF_{3}CO_{2}M + 2UO_{3} + 2UO_{2} + 20HF$$

$$\xrightarrow{4H_{4}O} 2CF_{3}CO_{2}M + 2UO_{3} + 2UO_{2} + 20HF$$

$$\xrightarrow{3H_{4}O} 2CF_{3}CO_{2}M + 2UO_{3} + 2UO_{2} + 20HF$$

$$\xrightarrow{2(CF_{3}CO_{2}M \cdot 2UF_{4}) + 13H_{2}O} \{4UO_{2} + M_{2}O\} + 4CO_{2} + 26HF$$

$$(5)$$

Then thermal stability of the decomposition products of these compounds with respect to the last effect decreases in the series

$$CF_3CO_2Na \cdot 2UF_5 > CF_3CO_2K \cdot 2UF_5 > CF_3CO_2Rb \cdot 2UF_5 > CF_3CO_2Cs \cdot 2UF_5$$

The IR absorption spectra ($400-4000 \text{ cm}^{-1}$) of all the isolated phases were studied. The spectra were recorded on a UR-10 spectrophotometer, using the method of trituration with liquid petrolatum. To avoid



Fig. 4. IR absorption spectra (in liquid petrolatum): a) CF_3CO_2K ; b) $CF_3CO_2K \cdot 2UF_5$. Absorption bands of liquid petrolatum are marked by asterisks.

hydrolysis, the samples were prepared for the recording of the spectra in a dry box. Figure 4 presents as an example the spectrum of the potassium salt $CF_3CO_2K \cdot 2UF_5$ (b). The spectrum of CF_3CO_2K (a) is given there for comparison. Table 4 presents the vibrational frequencies found and their assignment. A comparison of the spectra of the compounds $CF_3CO_2M \cdot 2UF_5$ (M = Li, Na, K, or Rb) and CF_3CO_2K shows that the basic absorption bands corresponding to the trifluoroacetate group are present in the spectra of the compound $CF_3CO_2M \cdot 2UF_5$ (see Table 4), although they are not sufficiently clearly expressed in all cases. Consequently, it may be concluded that the compounds studied actually contain trifluoroacetate groups. In the region of the frequencies primarily of the antisymmetrical stretching vibrations of the COO groups in the spectra, two bands were detected: high-frequency band (around 1730-1790 cm⁻¹) and a low-frequency band (around 1700 cm⁻¹). In the spectrum of CF_3CO_2K the band ν_{asCOO} lies around 1670 cm⁻¹.

A substantial increase in the frequency ν_{asCOO} in comparison with the frequency of the ionized carboxyl group is usually characteristic of complexes of metals containing monodentate coordinated groups of the type of R-C-O-M, where M is an atom of the metal complex-former. It is usually assumed that the larger ν_{asCOO} or the difference $\Delta = \nu_{asCOO} - \nu_{sCOO}$, the more covalent the O-M bond (since in salts of the alkali metals Δ and ν_{asCOO} are minimal, while in esters they are a maximum). In the spectra of the investigated compounds we were unable to unambiguously identify the bands ν_{sCOO} ; nonetheless, the presence of a high-frequency band around ~1730-1790 cm⁻¹ permits us to hypothesize the presence of monodentate trifluoroacetate groups bonded to uranium atoms in the investigated compounds. In this case the O-U bond is apprently essentially covalent. Moreover, there are intense bands around ~530 cm⁻¹, which undoubtedly belong to the stretching vibrations of the U-F bonds.

All this gives a basis for proposing the following structural formula for the complex anion

$$\begin{bmatrix} F & F & F \\ F & -U - F & -U - 0 - C - CF_3 \\ F & F & F & F \end{bmatrix}$$

The structure cited presupposes the presence of the bridge fluorine, which contradicts the analysis of the IR spectra. At the same time, the simultaneous presence in the spectra of low-frequency components v_{asCOO} around ~1700 cm⁻¹ indicates the possibility of the existence of bidentate (or bridge) trifluoroacetate groups as well.

Despite all the precautions taken to avoid contact of the investigated compounds with moisture, some of them still underwent hydrolysis, which is evidenced by the appearance of bands around \sim 750 and 930 cm⁻¹ (belonging to the stretching vibrations of the U-O bonds and hydrolysis products) in the spectra of certain compounds.

We should note that in this work only the steps of the reaction of UF_6 with CF_3COOH are presented. The general picture of the process is depicted by the scheme

 $UF_6 \rightarrow UF_5 \rightarrow HUF_6 \rightarrow CF_3COOH \cdot 2UF_5$ (in the absence of M⁺ ions)

 $UF_6 \rightarrow MUF_6 \rightarrow CF_3CO_2M \cdot 2UF_5$ (in the presence of M⁺ ions).

The similarity of the reaction of UF_6 with CF_3COOH in the absence and in the presence of an alkali metal is evident from the scheme cited, and the step of formation of the complex dipentafluorouranotri-fluoroacetic acid and its salts is shown.

CONCLUSIONS

1. Molybdenum, tungsten, and uranium hexafluorides react with anhydrous acetic acid, with the formation of oxyfluorides: $MoOF_4$, WO_2F_2 , and UO_2F_2 . In the presence of fluorides of the alkali metals, complex compounds of the type of $KM^{VI}O_2F_3$ (M = Mo) and $K_2M^{VI}O_2F_4$ (M = W and U) were isolated from solution.

2. Uranium hexafluoride reacts with anhydrous trifluoroacetic acid, with the formation of HUF_6 . In the presence of fluorides of the alkali metals, complex compounds of the type of $CF_3CO_2M^{I} \cdot 2UF_5$ (M = Li, Na, K, Rb, Cs).

3. The decrease in the strength of trifluoroacetic acid in comparison with acetic acid with respect to uranium hexafluoride (CF₃COOH undergoes destruction, while CH₃COOH is dehydrated) is explained by the presence of a large number of fluorine atoms at the carbon atom next to the carboxyl.

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