Interaction between Uranium Pentafluoride and the Pentafluorides of Vanadium, Arsenic, Niobium, Tantalum, and Bismuth, and the Tetrafluoride of Sulphur

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The interaction of UF_5 with SF_4, SF_4O, and some Lewis-acid pentafluorides of various strengths has been studied. In anhydrous HF solutions, SF_4 was shown to yield an adduct of composition $3UF_5{\cdot}SF_4$ in which both ionic and fluorine-bridged species are present. The pentafluorides of arsenic, tantalum, and niobium combine with UF_5 to give adducts of composition $1.5\ UF_5{\cdot}AsF_5$, $UF_5{\cdot}2TaF_5$, and $UF_5{\cdot}2NbF_5$, respectively. The arsenic derivative is stable at room temperature only under a pressure of AsF_5, whereas the tantalum and niobium adducts decompose at higher temperature forming $UF_5{\cdot}TaF_5$ and $UF_5{\cdot}NbF_5$, respectively. Vibrational spectroscopic study of the pentafluoride adducts of UF_5 has shown that they consist of covalent fluorine-bridged species. Uranium pentafluoride is fluorinated at room temperature by VF_5 and by BiF_5 in anhydrous HF.

Uranium pentafluoride behaves as a Lewis acid with fluoride-ion donors [1] forming ionic derivatives, whereas with the strong Lewis acid SbF_5 it forms fluorine-bridged adducts which have only minor contributions to the bonding from ionic formulations.[2,3] Taking into account recent results obtained on the reaction of UF_4O with a series of pentafluorides [4] and the structural similarity of the UF_5 [2,3] and UF_4O [5] adducts, it seemed worth investigating whether new adducts would be obtained from reaction of UF_5 with Lewis-acid pentafluorides other than SbF_5 or with amphoteric molecules such as SF_4 and SF_4O. This paper reports on the results obtained from a study of the interaction of UF_5 with VF_5, AsF_5, NbF_5, BiF_5, SF_4, and SF_4O.

Experimental

Starting Materials.—β-Uranium pentafluoride was prepared by reduction of UF_6 with sulphur dioxide [6] or by u.v.-photolytic reduction using CO as scavenger.[7] The α form of UF_5 was obtained by heating β-UF_5 at 180 °C in the presence of UF_6.[8] Vanadium, arsenic, niobium, and tantalum pentafluorides were obtained by fluorination of the metals with elemental fluorine.[9] Bismuth pentafluoride (Ozark Mahoning) was purified by vacuum sublimation at 120 °C. Sulphur tetrafluoride (P.C.R.) was used without purification. Sulphur tetrafluoride oxide was prepared by direct fluorination of SF_2O,[10] which had been prepared from SCl_2O and SbF_5 in HF,[11] or by hydrolysis of SF_4. Anhydrous HF was purified by treatment with gaseous F_2 followed by distillation.

Apparatus.—Volatile materials were manipulated in an all-metal vacuum line equipped with Teflon or metal valves. Most reactions were carried out in FEP-Teflon or Monel containers which were checked for leaks, treated with F_2 and/or ClF_3, and pumped to a high vacuum prior to use. Solid products were handled in a glove-box flushed with dry nitrogen.

Characterisation.—Reaction stoicheiometries were monitored by mass balance and/or elemental analysis performed by the Analytical Laboratories, Engelskirchen, West Germany. Infrared spectra were recorded with Perkin-Elmer model 457 or 580 spectrometers. Depending on the wavelength range, the ground solids were sandwiched between AgCl, KBr, or Polythene discs. In order to avoid rapid decomposition of the heat-sensitive reaction products by the i.r. beam, the discs were fixed in a vacuum cryostat cooled with liquid nitrogen. Raman spectra were recorded using a Coderg model T800 spectrometer. Solutions were examined in FEP-Teflon reaction tubes but the solid compounds were mounted in sealed Pyrex capillaries. *X*-Ray patterns were recorded photographically on a Philips camera (diameter 11.46 cm) using Cu-K_α filtered radiation. Thermogravimetric changes were recorded on a Stanton Redcroft TG 750 thermobalance and differential scanning calorimetry was carried out using an Arion MCB microcalorimeter.

Reactions with SF_4 *and* SF_4O.—The reactions with SF_4 were carried out using *ca.* 2 mmol samples of UF_5. When SF_4 was condensed on to either α-UF_5 or β-UF_5 neither dissolved in the liquid SF_4 at temperatures up to its boiling point. The only change observed was a slow transformation of α-UF_5 into β-UF_5 suggesting that an intermediate soluble uranium species may exist which precipitates immediately as β-UF_5. When an SF_4–HF solution was used, all of the pentafluoride dissolved in a four-fold excess of SF_4 yielding a blue solution, Raman spectroscopy of which indicated the presence of the $[UF_6]^-$ ion. On removing all volatile material at room temperature by pumping, β-UF_5 precipitated readily but minute amounts of a blue compound were also formed. The weight uptake was of the order of 1%. If fresh samples of the uranium-containing solutions were cooled to −78 °C a finely divided light blue crystalline solid precipitated and, in some experiments, after standing for 2 d at this temperature, dark blue crystals were also formed which dissolved readily, along with the light blue material, on slight warming. Pumping at −78 °C yielded a blue powder with a weight increase corresponding to $\frac{1}{3}$ mol SF_4 per mol UF_5. This result was confirmed by elemental analysis [Found: F, 32.7; S, 2.75; U, 64.3. Calc. for $SF_4(UF_5)_3$: F, 32.6; S, 2.90; U, 64.5%].

It is worth mentioning that the formation of an $[SF_3]^+$-containing uranium fluoride derivative was also encountered during attempts to prepare the still unknown UF_4S. In these experiments the conditions described by Wilson [12] for the preparation of UF_4O (*i.e.* a large excess of UF_6 in HF solution) were used but H_2S replaced H_2O. The main products of the reaction were found to be SF_4 and UF_4, the latter reacting with UF_6 to give UF_5 and U_2F_9, in such a way that the products are the same as those obtained from the reaction in the gaseous phase.[13] When UF_5 and SF_4O were mixed in the presence of HF neither dissolution nor reaction occurred up to room temperature or up to 120 °C without HF.

The UF_5–VF_5 *System*.—When VF_5 (3.5 mmol) was condensed onto β-UF_5 (0.2 mmol) an immediate reaction took place as the VF_5 melted at room temperature yielding a deep brown colour. The volatile part of the solution was found to consist of VF_5 and UF_6 by Raman spectroscopy and the solid residue was identified as VF_4 by its *X*-ray powder pattern.

The AsF_5–UF_5 *System*.—Experimental observations were similar to those on the SF_4–UF_5 system. Complete solubilisation of UF_5 in HF was only attained when a *ca.* four-fold excess of AsF_5 was employed. The blue crystalline product obtained could only be isolated at low temperature and was characterised while permanently cooled with solid CO_2. At room temperature, AsF_5 evolution and formation of β-UF_5 takes place whereas, in a sealed capillary, probably due to the pressure of AsF_5 generated by partial dissociation, the product can be kept for weeks at room temperature. Nevertheless, due to the high dissociation pressure at this temperature, determination of the composition of the adduct was only possible by measurement of the weight uptake of the initial β-UF_5. Based on four preparations, the UF_5–AsF_5 ratio was found to range from 1.51 to 1.59 : 1 with a mean value of 1.55 : 1. Contrary to the results previously reported by others,[14] under the conditions described above, no adduct of definite composition such as $UF_5 \cdot AsF_5$ was obtained.

The UF_5–NbF_5 *and* UF_5–TaF_5 *Systems*.—For these experiments, measured quantities of β-UF_5 (typically *ca.* 1 mmol) were mixed with a five-fold excess of MF_5 (M = Ta or Nb), onto which HF was condensed. After the mixture had been left at room temperature for 2 h, a pale blue solid above which was a flocculent white solid was obtained. After removal of the HF by distillation the excess of MF_5 was removed from the warmed reaction tube by vacuum sublimation. This procedure allowed monitoring of the initial UF_5 weight uptake. For both NbF_5 and TaF_5, the stoicheiometry of the final adduct was found to be $UF_5 \cdot 2MF_5$. This formulation was cross-checked through elemental analysis of the Ta adduct (Found: F, 32.1; Ta, 40.7; U, 26.65. Calc. for $UF_5 \cdot 2TaF_5$: F, 32.2; Ta, 40.9; U, 26.9%). Adducts with identical composition were also obtained in glass sublimation vessels by reaction of UF_5 with either NbF_5 or TaF_5 in the melt under 200 mmHg (*ca.* 26 800 Pa) pressure of dry argon.

The UF_5–BiF_5 *System*.—Bismuth pentafluoride (4 mmol) was mixed with β-UF_5 (*ca.* 1.6 mmol). The mixture, onto which HF was condensed, was warmed and left at room temperature for 2 h. A blue-green solution over an insoluble residue was observed. The Raman spectrum of the solution showed the presence of UF_6 and BiF_5. After pumping off the volatile material at room temperature, the weight of the solid residue together with the identification of UF_6 in the volatile part indicated that 77% of the initial UF_5 had been converted into UF_6. Treatment of the solid with a BiF_5–HF mixture followed by filtration and pumping yielded a white solid which did not contain uranium, and the *X*-ray powder diffraction pattern of which was not identified. The vibrational spectrum of this solid residue corresponded to that of BiF_5 with only minor changes. For instance, the Raman band at 242 cm^{-1} was found to be broader than the one corresponding to BiF_5 alone. These features are explained by the formation of an adduct[15] between BiF_5 and BiF_3. A thermal decomposition study of this adduct indicated a composition with at least 2 mol of BiF_3 per mol of BiF_5. No attempts were made to characterise a possible intermediate step in the fluorination of UF_5 by BiF_5 since the hypothetical adduct would have to be isolated at low temperature.

Results and Discussion

No adduct was obtained with VF_5, BiF_5, or SF_4O. With the pentafluorides, fluorination of UF_5 took place while SF_4O is probably too weak a base to react. Formation of new adducts only resulted from the interaction of SF_4, AsF_5, NbF_5, and TaF_5 with UF_5.

The *X*-ray powder patterns of the adducts are too complex to be indexed. Nevertheless they clearly demonstrate that the new adducts are well defined crystalline compounds which do not contain UF_5 and, in the cases of $UF_5 \cdot 2NbF_5$ and $UF_5 \cdot 2TaF_5$, the other component pentafluorides, as impurities.

The $3UF_5 \cdot SF_4$ adduct dissociates rapidly at 30 °C into SF_4 and β-UF_5. Warming further in a sealed tube produces SF_6 and a brown uranium compound which can be identified by its *X*-ray diffraction powder pattern as U_2F_9. Features arising from both $[SF_3]^+$ [16,17] and $[UF_6]^-$ [18] ions are apparent from the vibrational spectra of $SF_4 \cdot 3UF_5$ given in the Table. A comparison with the spectra of UF_5[19] and $[UF_6]^-$ salts[18] shows that the Raman bands at 623 and 610 cm^{-1} and the i.r. bands at 566 and 509 cm^{-1} are identical to bands associated with β-UF_5. However, the band at 509 cm^{-1} in the i.r. and that at 623 cm^{-1} in the Raman could also be assigned to the ν_3 and ν_1 vibrations of the $[UF_6]^-$ ion, and if this is the case the very weak Raman lines at 470 and at 216 cm^{-1} could be attributed to the ν_2 (e_g) and ν_5 (f_{2g}) modes of $[UF_6]^-$ respectively. Taking into account the absence of UF_5 (α or β form) lines in the *X*-ray powder pattern of the adduct, the i.r. bands at 629, 592, and 542 cm^{-1} and the Raman bands at 556 and 523 cm^{-1} are assigned to a dimeric or polymeric form of UF_5. On this basis it is tempting to formulate the adduct as $[SF_3]^+[UF_6]^- \cdot 2UF_5$. Definitive characterisation, however, is not possible without a single-crystal structure determination.

Besides SF_4 bands[20] the Raman spectrum of a solution of UF_5 in SF_4–HF shows the ν_1 (a_{1g}) vibration of the $[UF_6]^-$ ion and the features of the $[SF_3]^+$ stretching vibration are broadened.

Vibrational spectra of solid 1.5 $UF_5 \cdot AsF_5$ are tentatively assigned in terms of a covalent compound containing bridged $F \cdots AsF_5$ entities with C_{4v} symmetry. In the Raman spectrum only ν_1 (a_1)[21] (677 cm^{-1}) is observed. This is also found as the strongest band in other fluorine-bridged AsF_5 adducts.[22] The corresponding i.r. absorption at 663 cm^{-1} is also observed together with other i.r. modes, $\nu_5(b_1)$ (540 cm^{-1}), $\nu_2(a_1)$ (642 cm^{-1}), and the degenerate asymmetric stretching mode $\nu_8(e)$ (768 and 710 cm^{-1}), attributable to the AsF_5 group. For the interpretation of the remaining bands it is useful to compare the known spectra of the UF_5–SbF_5 adducts[2] with those reported here for the UF_5–AsF_5 compound. This shows clearly that absorptions in the U–F stretching region (Raman 647, 601, 595, and 577; i.r. 628, 620, 610, and 576 cm^{-1}) are similar, although at somewhat lower frequency for the highest band (647 *vs.* 657 cm^{-1}). This shift can be explained by the weaker Lewis acidity of AsF_5 compared with that of SbF_5, leading to a smaller positive charge on the uranium atom. The relative intensities of the appropriate U–F stretching modes in the AsF_5 adduct are identical to those of the SbF_5 adduct. In AsF_5–HF solution the U–F stretching bands are at 638, 599, and 578 cm^{-1} and no evidence of AsF_5 entities of C_{4v} symmetry is observed. On the contrary, the spectrum is more

Table. Vibrational data (1 000—200 cm^{-1}) for the adducts of UF_5 with SF_4, AsF_5, TaF_5, and NbF_5

SF_4–UF_5 System					AsF_5–UF_5 System					
Solid [a]		HF(soln.)	Assignment [b]		Solid [a]		HF(soln.)	$UF_5\cdot 2TaF_5$		$UF_5\cdot 2NbF_5$
I.r.	Raman	Raman [c]	$[SF_3]^+$ [d]	$[UF_6]^-$	I.r.	Raman	Raman [e]	I.r.	Raman	I.r.
962m	962w		$\nu_1(a_1)$							
		952								
		947								
		940 w,br								
		934	$\nu_3(e)$							
907m	906m									
	894m	892s *								
885m										
					768m			750s	754s	761s
					710m		705s(ν_1)	709 (sh)		757 (sh)
						677m		695 (sh)		732s
					663s			678vs		688vs
					642s	647s	638m	662 (sh)	664m	661 (sh)
					628s					
629m	623s	627m		$\nu_1(a_{1g})$	620s					
	610w				610s					
						601w	599w	600 (sh)		602 (sh)
592s						595w				583vs
566s	556vw				576m (sh)	577m	578w	576vs	566m	577 (sh)
542 (sh)		540s *	$\nu_2(a_1)$		540s		573w(ν_2)			
	535vw	533								
	523vw	530 s *								511 (sh)
509s		525		$\nu_3(f_{1u})$				488s		472s
	470w			$\nu_2(e_g)$						
		455vw *						373m		
							355w(ν_5)			
	216w			$\nu_5(f_{2g})$				317m		321m

[a] Recorded at −196 °C. [b] From refs. 16—18. [c] Bands arising from SF_4 are marked with an asterisk. [d] $\nu_4(e)$ was not observed. [e] Assignment given for the $[AsF_6]^-$ ion in O_h symmetry from ref. 22.

suggestive of the presence of ionic species, since the Raman bands of the ion $[AsF_6]^-$ are observed. Consequently, partial loss of F^- from the uranium fluoride species to yield fluoronium ions such as $[H_2F]^+$ or $[H_3F_2]^+$ may be involved. This assumption is compatible with the solubilisation of UF_5 in these acidic media and the 15 cm^{-1} increase of the highest U–F Raman frequency as compared to that of UF_5. An identical spectrum was obtained when UF_6 was reduced slowly in AsF_5–HF solution by FEP-Teflon material. This enhanced reactivity of UF_6 in acidic media has been observed previously in SbF_5 solution.[2,23]

When the adducts $UF_5\cdot 2MF_5$ (M = Nb or Ta) are heated in a dynamic vacuum they lose MF_5. Weight-loss measurements during the decomposition at 100 °C show that each mol of $UF_5\cdot 2MF_5$ loses 1 mol of MF_5. Thermogravimetric analysis (t.g.a.) of the adducts yielded no sharply defined plateaux indicating the presence of 1 : 1 species, but points of inflection in the t.g.a. curve were found in the region expected for 1 : 1 adducts.

A differential scanning calorimetric study showed that when $UF_5\cdot 2TaF_5$ is heated two phenomena take place. The first is the formation of $UF_5\cdot TaF_5$ with the evolution of TaF_5, the maximum thermal effect being observed at 144 °C (135 °C from t.g.a.). The second is the decomposition of $UF_5\cdot TaF_5$, the maximum thermal effect being detected at 189 °C (186 °C from t.g.a.), and is accompanied by the evolution of a volatile material. It is assumed that this decomposition can be accounted for by equation (1) since the solid residue after heating was shown by *X*-ray powder diffraction to be UF_4.

$$2UF_5\cdot TaF_5 \longrightarrow UF_4 + UF_6 + 2TaF_5 \tag{1}$$

Similar results were obtained with $UF_5\cdot 2NbF_5$. The maximum thermal effect for the 1 : 2 to 1 : 1 conversion being observed at 130 °C (135 °C from t.g.a.). The second step, *i.e.* decomposition of the 1 : 1 adduct into UF_4, UF_6, and NbF_5, has a maximum thermal effect at 187 °C (175 °C from t.g.a.). The residue, after heating, was again shown to consist of UF_4.

The thermal behaviour of the adducts of both Ta and Nb is quite comparable to that reported for the antimony adducts.[3] The vibrational data for the $UF_5\cdot 2MF_5$ adducts are given in the Table. However, the niobium derivative decomposed in the laser beam even at low temperature so that no Raman spectrum was obtained. The vibrational spectra of both $UF_5\cdot 2NbF_5$ and $UF_5\cdot 2TaF_5$ are related to that of $UF_5\cdot 2SbF_5$.[2] Bands in the region 760—600 cm^{-1} may be attributed to terminal Nb–F and Ta–F stretching modes, whilst those in the region 600—500 cm^{-1} are associated with M–F and U–F stretching. Bands in the region below 500 cm^{-1} may be assigned to U–F–U, M–F–U, and M–F–M bridging (M = Nb or Ta). On the basis of these results and those reported [2,3] for $UF_5\cdot 2SbF_5$ it is postulated that the adducts consist of interlinked lattices of UF_5 and MF_5 (M = Nb or Ta) molecules linked by fluorine bridges. The i.r. spectra of the intermediate adducts $UF_5\cdot NbF_5$ and $UF_5\cdot TaF_5$ were found to be closely related to those of their parent adducts in the same way as the i.r. spectrum of $UF_5\cdot SbF_5$ is almost identical [2] to that of $UF_5\cdot 2SbF_5$. Both $UF_5\cdot NbF_5$ and $UF_5\cdot TaF_5$ decompose rapidly in laser beams even at low temperature. The diffraction patterns for the 1 : 1 adducts also resemble those of the 1 : 2 adducts, the only differences being small changes in the position of the low-angle lines. This means that the only definitive data on the 1 : 1 adducts come from the thermal decomposition studies. However, an elemental analysis of $UF_5 \cdot NbF_5$ has given additional support to the existence of the 1 : 1 adduct (Found: F, 36.3; Nb, 18.05; U, 45.0. Calc. for $UF_5 \cdot NbF_5$: F, 36.45; Nb, 17.85; U, 45.7%).

According to the results obtained by this study several types of interaction have been observed between uranium pentafluoride and the fluoride investigated. As far as the sulphur compounds are concerned, whereas SF_4O is found to be too weak a base or acid to interact, SF_4 acts as a base to yield an adduct in which both true ionic and polymeric, fluorine-bridged entities are present. For the pentafluorides of the Group 5 elements, studied here in a manner similar to that reported for SbF_5, the pentafluorides of arsenic, niobium, and tantalum yield fluorine-bridged adducts whereas those of vanadium and bismuth are reduced to lower fluorides.

References

1 R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.*, 1964, **3**, 126.
2 R. Bougon and P. Charpin, *J. Fluorine Chem.*, 1979, **14**, 235.
3 W. Sawodny, K. Rediess, and U. Thewalt, *Z. Anorg. Allg. Chem.*, 1980, **469**, 81.
4 J. H. Holloway, D. Laycock, and R. Bougon, *J. Chem. Soc., Dalton Trans.*, 1983, 2303.
5 R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1979, 1881.
6 B. Moncelon, J. Lucas, and T. Kikindai, *C.R. Acad. Sci., Ser. C*, 1965, **261**, 1855.
7 G. W. Halshead, P. G. Heller, L. B. Asprey, and K. V. Salazar, *Inorg. Chem.*, 1978, **17**, 2967.
8 A. S. Wolf, W. E. Hobbs, and K. E. Rapp, *Inorg. Chem.*, 1965, **4**, 755.
9 A. D. Beveridge and H. C. Clark, in 'Halogen Chemistry,' ed. V. Gutmann, Academic Press, London, 1967, vol. 3, p. 191; F. Fairbrother, *ibid.*, vol. 3, p. 123; L. Kolditz, *ibid.*, vol. 2, p. 116.
10 J. K. Ruff, *Inorg. Synth.*, 1968, **11**, 131.
11 K. Rediess, unpublished work.
12 P. W. Wilson, *J. Inorg. Nucl. Chem.*, 1974, **36**, 303.
13 L. E. Trevorrow, J. Fischer, and W. H. Gunther, *Inorg. Chem.*, 1963, **2**, 1281.
14 B. Frlec and D. Gantar, *J. Fluorine Chem.*, 1980, **16**, 633.
15 K. O. Christe, W. W. Wilson, and E. C. Curtis, *Inorg. Chem.*, 1979, **18**, 2578.
16 M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, 1967, **47**, 4159.
17 M. Brownstein and J. Shamir, *Appl. Spectrosc.*, 1972, **26**, 77.
18 J. P. Masson, J. P. Desmoulin, P. Charpin, and R. Bougon, *Inorg. Chem.*, 1976, **15**, 2529 and refs. therein.
19 L. B. Asprey and R. T. Paine, *J. Chem. Soc., Chem. Commun.*, 1973, 920.
20 K. O. Christe, E. C. Curtis, C. J. Schack, S. J. Cyvin, J. Brunvoll, and W. Sawodny, *Spectrochim. Acta, Part A*, 1976, **32**, 1141.
21 A. K. L. Aljibury and R. L. Redington, *J. Chem. Phys.*, 1970, **52**, 453.
22 B. Frlec, D. Gantar, and J. H. Holloway, *J. Fluorine Chem.*, 1982, **19**, 485.
23 A. D. Turissimi and R. F. Stahl, *Ind. Eng. Chem.*, 1958, **50**, 1771.

Received 26th October 1983; *Paper* 3/1906