Halogen Exchange Reactions involving Uranium-(V) and -(VI) Halides

By **David Brown,*** Chemistry Division, A.E.R.E., Harwell, Didcot, Oxfordshire OX11 0RA
John A. Berry and **John H. Holloway**, Department of Chemistry, The University, Leicester LE1 7RH

The room temperature halogen exchange reactions of UF_5 with liquid BBr_3 or BCl_3 provide convenient new routes to α-UBr_5 and β-UCl_5, respectively. In both cases the yields are quantitative. Since the uranium pentahalides are the only involatile products of the reactions they are easily isolated. Reactions between BBr_3 and solid UCl_6 or UCl_5 also yield α-UBr_5 but in the presence of CH_2Cl_2, a new crystallographic modification, β-UBr_5, is produced. Interaction of UF_6 and BBr_3 yields either α- or β-UBr_5, depending on the conditions, but the products are usually contaminated with UBr_4. Liquid BCl_3 converts UO_2F_2 to α- or β-UCl_5, depending on the period of contact, whilst exposure of UO_2F_2 to gaseous BCl_3 yields UCl_6. *X*-Ray powder diffraction and vibrational spectroscopic data are reported for α- and β-UBr_5.

THERE are few really satisfactory methods for the preparation of uranium pentachloride and pentabromide in good yield and of high purity.[1-4] Possibly the most attractive published route to gram amounts of UCl_5 involves the room temperature decomposition of UCl_6 in solvents such as methylene dichloride, 1,2-dichloroethane,[5] or carbon tetrachloride,[6] whilst for UBr_5 those involving bromination of the metal or UBr_4 at temperatures up to 55 °C are the most satisfactory.[7,8]

Previous studies in this laboratory [9] have shown that boron tribromide is a valuable reagent for the preparation of actinide(V) bromo-complexes and $PaBr_5$, whilst other workers [10] have employed boron trichloride for the conversion of UF_6 to UCl_6.

We now report new preparative methods for both UCl_5 and UBr_5 which involve halogen exchange between uranium halides such as UF_6, UF_5, UCl_6, or UCl_5 and the appropriate boron trihalide. A new polymorph of UBr_5 is described, and a new route to UCl_6 and a convenient method for converting UCl_6 to UCl_5 are reported.

EXPERIMENTAL

Apparatus and Reagents.—All manipulations were performed either in glass vacuum equipment or in glass apparatus in an inert-atmosphere box (H_2O and O_2 content <20 p.p.m.).

Commercially available UF_6 (B.N.F.L.) and BCl_3 (Matheson) were used directly; the vapour pressure of the former indicated the absence of HF. Boron tribromide (B.D.H.) was distilled *in vacuo* prior to use. The compounds UCl_6,[10] UCl_5,[5,6] and UF_5 [11,12] were prepared by published methods. Finely divided UO_2F_2 was made by controlled hydrolysis of UF_6; reactions were checked using a sample of different origin. Carbon tetrachloride and methylene dichloride were distilled *in vacuo* and stored over molecular sieves under vacuum. Nujol was dried over sodium.

Uranium Hexachloride.—A quantity of UO_2F_2 (0.1—0.2 g; 0.3—0.6 mmol) was exposed to BCl_3 vapour in a sealed, two-compartment vessel for 1—2 weeks. The resulting dark green product, which was extracted into anhydrous CCl_4, was identified as UCl_6 by *X*-ray powder diffraction and chemical analysis (Found: U, 51.8; Cl, 47.25. Calc. for UCl_6: U, 52.75; Cl, 47.25%). The gaseous by-products of this reaction were shown by i.r. spectroscopy to be BF_3, BF_2Cl, $BFCl_2$, and unreacted BCl_3.[13]

α-Uranium Pentachloride.—An excess of BCl_3 was condensed onto UCl_6 (0.1 g; 0.2 mmol) at 77 K and the mixture allowed to warm to room temperature (r.t.). The brown solid product isolated after 1 h was shown by *X*-ray powder diffraction analysis to be α-UCl_5. The same product was obtained from the UO_2F_2–BCl_3 reaction when the reagents were left in contact for *ca.* 1 week. After identification by *X*-ray powder diffraction analysis the product was extracted into anhydrous carbon tetrachloride.

β-Uranium Pentachloride.—An excess of BCl_3 was condensed onto α- or β-UF_5 (0.1—0.2 g; 0.3—0.6 mmol) at 77 K and the mixture allowed to warm to r.t. Unreacted BCl_3 and gaseous by-products were removed from the brown product by vacuum distillation after 2—3 d. *X*-Ray powder diffraction analysis showed the presence of only β-UCl_5 (Found: U, 57.8. Calc. for UCl_5: U, 57.3%). β-UCl_5 was also obtained from the reaction between UO_2F_2 and liquid BCl_3 when the reagents were left in contact for several weeks. The product was extracted into anhydrous CCl_4 after removal of excess BCl_3 and gaseous by-products as before.

α-Uranium Pentabromide.—An excess of liquid boron tribromide (1 cm^3; 10.6 mmol) was added to solid UCl_6, β-UCl_5, or α-UF_5 (0.2—0.5 g; 0.4—1.5 mmol) at r.t. The mixture was allowed to stand in a stoppered or sealed vessel for 3 or 4 d and then heated for a few minutes (*ca.* 40 °C) for the chloride reactions, whilst continuous stirring was applied to the UF_5–BBr_3 mixture for *ca.* 1 week. The resulting black solid was isolated by centrifugation and decantation, and vacuum dried at r.t. (10^{-4} Torr †) or, alternatively, by removal of the boron trihalides by vacuum evaporation. Yields were quantitative. The product of the UF_5–BBr_3 reaction was characterised by elemental analysis (Found: U, 37.65; Br, 61.6. Calc. for UBr_5: U, 37.35;

---

† Throughout this Note: 1 Torr = (101 325)/760 Pa.

Br, 62.65%). Products from other preparations were identified by *X*-ray powder diffraction analysis.

β-*Uranium Pentabromide*.—An excess of BBr_3 (0.5 cm^3; 5.3 mmol) was added to UCl_6 (0.1 g; 0.2 mmol) dissolved in anhydrous, oxygen-free CH_2Cl_2 (*ca.* 6 cm^3) at r.t. The red solution initially turned dark blue-green but this colour faded within a few minutes as a black solid deposited. After a few hours the product was isolated by centrifugation and decantation, washed with CH_2Cl_2, and vacuum dried at r.t. (10^{-4} Torr) (Found: U, 37.4; Br, 62.5. Calc. for UBr_5: U, 37.35; Br, 62.65%). UCl_5 may also be employed as a starting material.

Analysis and Physical Measurements.—Uranium was determined by addition of aqueous ammonia to halide samples cooled to 77 K. The resulting hydrous oxide was isolated by filtration and ignited to U_3O_8. Halide in the supernatant was precipitated after acidification with HNO_3 and weighed as the silver salt.

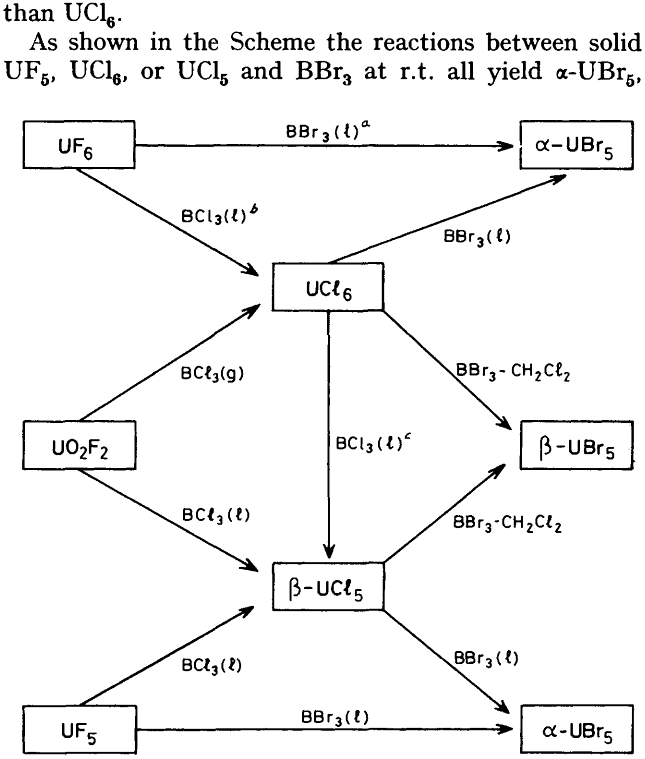
X-Ray powder photographs were recorded as described previously.[14] Infrared spectra (4 000—100 cm^{-1}) were recorded for samples mounted in Nujol between AgCl or Si plates. Raman spectra were recorded as described previously.[15]

RESULTS AND DISCUSSION

The halogen exchange reactions between UF_5 and the liquid boron trihalides which occur at r.t. in the absence of a solvent provide excellent routes to quantitative yields of β-UCl_5 and α-UBr_5. The results for the UF_5–BCl_3 reaction differ from those of O'Donnell and Wilson[16] who reported that the products are UCl_6, UF_4, and BF_3. The formation of UF_4 and UCl_6 was surprisingly attributed to an initial disproportionation of the pentafluoride ($2UF_5 \rightarrow UF_4 + UF_6$), the hexafluoride so produced being converted to the hexachloride. The only apparent major difference between the experimental conditions employed in the two studies is the method of preparation of the UF_5. In the present work, the pentafluoride was isolated and characterised by *X*-ray powder diffraction analysis, whereas in the earlier investigation[16] it was made *in situ* by reacting the correct proportions of UF_6 and UF_4. One possible explanation for the different observations is that the UF_6–UF_4 mixture had not reacted to form UF_5 as intended and thus the reaction studied was that of UF_6, with the UF_4 playing no part. The temperature at which UF_6 will fluorinate UF_4 is very variable, being extremely dependent on the form of UF_4, in particular its surface area.[17] The absence of tetrafluoride from the present products was confirmed by the fact that they were completely soluble in anhydrous methyl cyanide.

When UO_2F_2 is exposed to BCl_3 vapour the product (after a period of 1—2 weeks) is UCl_6. In contrast to this, liquid BCl_3 converts UO_2F_2 virtually quantitatively to UCl_5 at r.t.; the α-phase being formed during reaction periods of *ca.* 1 week, whilst β-UCl_5 is the product after several weeks. This difference in behaviour was further studied by the addition of an excess of liquid BCl_3 to solid UCl_6. By the time the reaction mixture had warmed to r.t. (*ca.* 0.5 h) conversion to α-UCl_5 was complete. The presence of chlorine in the supernatant BCl_3 was confirmed spectroscopically. Prolonged contact of the α-phase with liquid BCl_3 resulted in a phase change to β-UCl_5. This rapid conversion of UCl_6 to UCl_5 on contact with liquid BCl_3 indicates that the previously reported[10] UF_6–BCl_3 reaction may be extended to yield UCl_5 rather than UCl_6.

As shown in the Scheme the reactions between solid UF_5, UCl_6, or UCl_5 and BBr_3 at r.t. all yield α-UBr_5, which is the phase prepared previously[7,8] by bromination of uranium metal or UBr_4, and shown recently[18] to be isostructural with β-UCl_5. The reactions involving the chlorides are complete within 2—3 d at r.t., or more quickly on application of heat (*ca.* 40 °C), but it is necessary to stir the UF_5–BBr_3 mixture for several days at r.t.



[a] This reaction can also yield β-UBr_5; the products are generally contaminated with UBr_4. [b] Ref. 10. [c] β-UCl_5 is the ultimate product; short reaction periods yield α-UCl_5.

SCHEME Halogen exchange reactions of uranium-(VI) and -(V) fluorides and chlorides

Addition of BBr_3 to a solution of UCl_6 in methylene dichloride initially yields a dark blue-green solution which turns reddish brown after a few minutes as a black solid is deposited. This product is a new polymorph of uranium pentabromide which we have designated β-UBr_5. The same phase is obtained from UCl_5 in methylene dichloride and, mixed with UBr_4, from the low temperature reaction between UF_6 and BBr_3. The latter observation is again at variance with results reported by O'Donnell *et al.*[10] who state that UF_6 is reduced to the tetrafluoride by BBr_3. In contrast to this we find that, depending on the rate at which the reactants are allowed to warm from 77 K to r.t., the product is either a mixture of β-UBr_5 and UBr_4 (slow warm up), or α-UBr$_5$ and UBr$_4$ (fast warm up). The reaction appears to proceed slowly even at *ca.* 77 K as indicated by the development of a dark colour on condensation of BBr$_3$ onto UF$_6$ at this temperature. Although pure α- and β-UBr$_5$ have on occasions been obtained from such reactions, exact conditions for reproducible formation of pure pentabromide have proved elusive and some tetrabromide contamination is usually encountered. However, the extent of tetrafluoride formation in several different reactions ranged from zero to *ca.* 1%.

Crystallographic Data.—Although there are similarities between the *X*-ray powder patterns of α- and β-UBr$_5$ it is apparent from the sin^{2}θ values and intensities listed in Tables 1 and 2 that they are not identical. Furthermore, the relative intensities of the reflections on films of β-UBr$_5$ were the same for all preparations regardless of the method employed, indicating that the products were single phase. Attempts to obtain single crystals of β-UBr$_5$ have so far been unsuccessful and it has not been possible to index the observed reflections. Comparison with reflection positions and intensities calculated for the β-PaBr$_5$ structure has shown that the two phases are not isostructural. However, *X*-ray powder data for several different samples of PaBr$_5$ prepared over a period of years in this laboratory are virtually identical with those now reported for β-UBr$_5$. It is hoped that structural work currently in progress will establish whether these powder patterns correspond to α-PaBr$_5$ or whether another crystal modification of this compound exists, in addition to the α-,[19] β-,[19] and γ-phases[14] previously reported.

TABLE 1

Partial *X*-ray powder diffraction results for β-UBr$_5$

sin^{2}θ$_{obs.}$	$I_{est.}$	sin^{2}θ$_{obs.}$	$I_{est.}$
0.0154	s−	0.1362	m
0.0242	m	0.1515	s−
0.0271	m−	0.1588	s−
0.0310	m−	0.1827	m−
0.0543	vw−	0.1941	w
0.0585	w−	0.2090	vw−
0.0658	s	0.2193	m
0.0685	m+	0.2300	w−
0.0735	m−	0.2345	w−
0.0781	m−	0.2389	w−
0.0826	w+	0.2435	w−
0.0854	w	0.2484	vw−
0.1097	s−	0.2575	vw−
0.1124	m+	0.2629	w+
0.1226	w	0.2686	vw−

s = Strong, m = medium, w = weak, vw = very weak.

Only very limited *X*-ray powder data have been reported for α-UBr$_5$.[7] Comparison of observed with calculated sin^{2}θ values and reflection intensities (Table 2) confirms that this is the phase formed in reactions involving solid UF$_5$, UCl$_6$, or UCl$_5$ and BBr$_3$.

TABLE 2

Partial *X*-ray powder pattern for α-UBr$_5$

sin^{2}θ$_{obs.}$	sin^{2}θ$_{calc.}$ [a]	*h, k, l*	$I_{calc.}$ [b]	$I_{obs.}$ [c]
0.0153	0.0150	$\bar{1}$ 1 0	28	w+
0.0175	0.0171	$\bar{1}$ 0 1	25	w−
	0.0174	0 0 1	16	
0.0203	0.0199	$\bar{1}$ 1 1	15	w
	0.0206	0 $\bar{1}$ 1	11	
0.0270	0.0266	0 2 0	15	vw−
	0.0275	1 1 $\bar{1}$	4	
	0.0276	0 1 1	4	
0.0300	0.0296	1 1 0	7	vw−
0.0541	0.0537	$\bar{1}$ 3 0	7	vw−
	0.0541	1 $\bar{2}$ 1	6	
0.0602	0.0596	$\bar{1}$ 1 2	6	w−
	0.0599	0 3 0	1	
	0.0600	$\bar{2}$ 2 0	5	
0.0634	0.0627	2 0 0	2	vw−
0.0660	0.0656	$\bar{1}$ 3 1	99	s
	0.0658	2 1 $\bar{1}$	100	
0.0695	0.0693	0 $\bar{1}$ 2	46	m
	0.0696	0 0 2	1	
0.1104	0.1101	$\bar{2}$ 4 1	40	m
	0.1101	2 2 $\bar{2}$	1	
	0.1103	0 2 2	2	
	0.1103	$\bar{3}$ 0 1	35	
	0.1107	$\bar{2}$ 4 0	5	
0.1123	0.1120	2 0 1	35	m
	0.1123	$\bar{1}$ 3 2	7	
	0.1123	1 $\bar{4}$ 1	14	
0.1152	0.1146	$\bar{3}$ 0 2	13	m
	0.1149	$\bar{3}$ 3 1	7	
	0.1153	1 $\bar{2}$ 2	45	
0.1376	0.1379	0 4 1	7	w
0.1417	0.1413	2 3 $\bar{1}$	10	w
	0.1414	1 3 1	4	
	0.1417	$\bar{2}$ 2 3	3	
0.1517	0.1514	1 4 0	27	m−
0.1577	0.1574	$\bar{1}$ 2 3	63	m+
	0.1574	$\bar{3}$ 2 3	7	
	0.1581	2 2 $\bar{3}$	27	
0.1669	0.1664	2 3 0	2	w−
	0.1665	0 5 0	4	
	0.1665	1 $\bar{4}$ 2	9	
0.1740	0.1738	0 1 3	5	w−
	0.1738	3 2 $\bar{1}$	10	
	0.1743	$\bar{4}$ 2 2	0.4	
0.1849	0.1846	$\bar{3}$ 5 1	1	w
	0.1848	$\bar{4}$ 1 1	1	
	0.1850	0 $\bar{3}$ 3	1	
	0.1854	$\bar{4}$ 3 2	44	
0.1881	0.1876	3 $\bar{1}$ 1	48	m+
	0.1879	2 $\bar{5}$ 1	47	
0.2202	0.2201	1 3 2	34	m−
	0.2203	1 0 3	2	
	0.2204	2 1 $\bar{4}$	1	
0.2258	0.2261	$\bar{3}$ 1 4	37	m−
0.2399	0.2395	$\bar{3}$ 6 1	1	m−
	0.2397	0 6 0	0.5	
	0.2400	$\bar{4}$ 4 0	22	
0.3355	0.3363	$\bar{3}$ 7 2	19	w

[a] Calculated from the published unit cell.[18] [b] Calculated from the published positional parameters[18] and corrected for absorption. [c] Visually estimated; s = strong, m = medium, w = weak, vw = very weak.

Vibrational Spectra.—The i.r. and Raman spectra we have recorded for β-UCl$_5$ are in close agreement with those published by Kolitsch and Müller[20] apart from the absence of a shoulder at 308 and weak bands at 263 and 64 cm^{-1}. The two phases α- and β-UBr$_5$ give almost identical i.r. spectra with bands at 244s (U–Br$_{ax.}$), 230s (U–Br$_{eq.}$), 200m (U–Br$_{ax.}$), 148m (ring mode), and 120w, br cm^{-1} (deformation mode).

One of us (J. A. B.) thanks the S.R.C. for the award of a research associateship.

[1/1546 *Received, 6th October*, 1981]

REFERENCES

[1] K. W. Bagnall, ' The Halogen Chemistry of The Actinides,' Chapter 7 in ' Halogen Chemistry,' ed. V. Gutmann, Academic Press, London, 1967, vol. 3.

[2] D. Brown, ' Halides of the Lanthanides and Actinides,' Wiley and Son, London, 1968.

[3] D. Brown in ' Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1973, vol. 5.

[4] D. Brown in ' Gmelin Handbuch der Anorganischen Chemie,' ed. C. Keller, System No. 51, Uranium, ' Compounds with Chlorine, Bromine, and Iodine,' 1979, vol. C. 9.

[5] U. Müller and W. Kolitsch, *Z. Anorg. Allg. Chem.*, 1974, **410**, 32.

[6] D. Brown, G. De Paoli, and B. Whittaker, A.E.R.E. Report R8260, 1976.

[7] F. Lux, G. Wirth, and K. W. Bagnall, *Chem. Ber.*, 1970, **103**, 2807.

[8] F. Lux and G. Wirth, *Proc. 13th Int. Conf. Co-ord. Chem., Cracaw*, 1970, p. 207.

[9] D. Brown, J. Hill, and C. E. F. Rickard, *J. Chem. Soc. A*, 1970, 476.

[10] T. A. O'Donnell, D. F. Stewart, and P. Wilson, *Inorg. Chem.*, 1966, **5**, 1438; *Inorg. Synth.*, 1976, **16**, 143.

[11] W. Bacher and E. Jacob, in ' Gmelin Handbuch der Anorganischen Chemie,' ed. C. Keller, System No. 51, Uranium, ' Compounds with Fluorine,' 1980, vol. C. 8.

[12] J. A. Berry, A. Prescott, D. W. A. Sharp, and J. M. Winfield, *J. Fluorine Chem.*, 1977, **10**, 247.

[13] D. F. Wolfe and G. L. Humphrey, *J. Mol. Struct.*, 1969, **3**, 293.

[14] D. Brown, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 219.

[15] D. Brown, B. Whittaker, and P. E. Lidster, A.E.R.E. Report R8035, 1975.

[16] T. A. O'Donnell and P. Wilson, *Aust. J. Chem.*, 1968, **21**, 1421.

[17] J. S. Broadley and P. B. Longton, U.K.A.E.A. Report DDC/P-68, 1958.

[18] J. H. Levy, J. C. Taylor, and P. W. Wilson, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1055.

[19] D. Brown, T. J. Petcher, and A. J. Smith, *Acta Crystallogr., Sect. B*, 1969, **25**, 178.

[20] W. Kolitsch and U. Müller, *Z. Anorg. Allg. Chem.*, 1975, **418**, 235.