Notes

The structures involving methyl bridges are intuitively less satisfying than the halide-bridged structures. The ion pair structures are in accord with the Raman spectra, (i.e. symmetry for II' C_{zr} ; T_{d} , the numbers and polarizations of lines predicted agreeing with experiment quite as well as for the methyl-bridged structures but without the rather strange assumption that only the cis isomer (I) is found.⁽⁴⁾ The time of observation for the Raman spectra, essentially the time for a vibration, is sufficiently short so that the structures observed correspond to the "ion-pair" structures, while the observation time for the NMR experiments is sufficiently longer so that the chloride exchange could cause but one line for the methyls. A mechanism for exchange of methyls in the mixture of I' and II'would be simple metathesis. Methyl exchange in hexamethyl could proceed through the equivocable ethane-like structure that was concluded from electron diffraction⁽⁶⁾ on this substance. This "no electron bond" intermediate will be described further elsewhere.⁽⁷⁾

The chemistry of the alkyl aluminium compounds lends credence to the halide-bridged structures.⁽⁸⁾ As the electron-donating character of the alkyl group decreases, the stabilities of the compounds decrease and conversely. A rather critical observation is that compounds $Al_{a}R_{n}Cl_{6-n}$ are reported only for n = 0, 2, 4, 6; even in the hydrides polymerization occurs to the extent necessary for formation of AlR₂⁺ units.⁽⁸⁾

The lack of compounds of n = 1, 3 and 5 can be reasonably ascribed to the processes

$$2Al_{2}MeCl_{5} = Al_{2}Me_{2}Cl_{4} + Al_{2}Cl_{6}$$
$$2Al_{2}Me_{3}Cl_{3} = Al_{2}Me_{4}Cl_{3} + Al_{2}Me_{3}Cl_{4}$$
$$2Al_{2}Me_{5}Cl = Al_{2}Me_{4}Cl_{3} + Al_{3}Me_{6}$$

with the driving force for these reactions possibly derived from the stability of the AlMe_a⁺ unit, and the stability conferred by double chloride bridges, except, of course, for the hexamethyl.

The only gas phase dipole moment measurement for the compounds $Al_2Me_nCl_{6-n}$ is for the tetrachloride: a dipole moment of 1.9 D was found, an impossible situation on the basis of the methylbridged structures but quite reasonable with halide bridges. Unfortunately, as the authors have indicated, the clarity of the result is not conducive to the drawing of firm inferences.⁽⁹⁾

The electron-diffraction results of BROCKWAY and DAVIDSON⁽⁶⁾ favour the halide-bridged structures, although here too, equivocation is possible. The totality of the evidence seems more compatible with the halide-bridged structures than with the methyl bridged structures.

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Some studies in the inorganic chemistry of the reaction between uranyl fluoride and chlorine trifluoride

(Received 25 May 1960)

THE fluorination of uranium tetrafluoride with chlorine trifluoride to yield uranium hexafluoride has been discussed by LABATON⁽¹⁾. Another process by which uranium hexafluoride may be made involves the treatment of uranyl fluoride with chlorine trifluoride, and an attempt has been made to define the inorganic chemistry of the reaction by establishing the nature of the gaseous products.

⁽¹⁾ V. Y. LABATON, J. Inorg. Nucl. Chem. 10, 86 (1959).

Notes

Experimental

Chemicals

Uranyl fluoride used in all experiments was prepared by the interaction of uranium hexafluoride with steam. The water content of the material as prepared was approximately 0.6 wt.%, corresponding with an approximate formula $UO_{2}F_{2}.0.1H_{2}O$. Determination of surface area by the B.E.T. method⁽³⁾ using nitrogen as adsorbate gave a value of $12.2 \text{ m}^{3}/\text{g}$.

Commercial chlorine trifluoride was freed from impurities by redistillation, and its purity checked by gas chromatography.

Apparatus

The apparatus was a modification of that of ELLIS *et al.*⁽³⁾, adapted to include a reaction vessel adjoining the sample volume (see Fig. 1). The reaction vessel was a 5 in. length of 1 in. i.d. nickel pipe.



mounted horizontally, into which a nickel boat containing uranyl fluoride could be loaded. The reaction vessel was fitted into the apparatus with flanged couplings sealed with copper joint rings of diamond cross-section. Heat was supplied to the apparatus using tape heaters controlled by a variable-voltage transformer.

The gas chromatographic unit was identical with that described by ELLIS *et al.*⁽³⁾ using the 11 ft 6 in. column packed with a 50 wt. % loading of Kel-F grade '10' oil (Kellogg Corp., Jersey City, U.S.A.) on ground polytetrafluoroethylene powder sieved to 30–60 B.S. mesh; argon was used as carrier gas and a Martin gas density balance acted as detector. Calibration curves were recorded for oxygen (retention time referred to peak maximum-2·0 min at carrier flow rate 27.5 cm³/min), chlorine mono-fluoride (2·7 min), hydrogen fluoride (3·4 min), perchloryl fluoride (ClO₃F) (4·7 min), chlorine (5·7 min), chlorine trifluoride (R·3 min) and uranium hexafluoride (37·5 min). Perchloryl fluoride and chloryl fluoride were prepared by reaction of potassium chlorate with fluorine and chlorine trifluoride, respectively, as described by ENGLEBRECHT and ATZWANGER⁽⁴⁾, and purified by redistillation.

⁽³⁾ S. BRUNAUER, P. H. EMMETT and E. TELLER, J. Amer. Chem. Soc. 60, 309 (1938).

(3) J. F. ELLIS, C. W. FORREST and P. L. ALLEN, Analyt. Chim. Acta 22, 27 (1960).

(4) A. ENGLEBRECHT and H. ATZWANGER, J. Inorg. Nucl. Chem. 2, 348 (1956).

Procedure

In each run 1.0 g of uranyl fluoride was spread evenly over the base of the nickel boat, the couplings of the reaction tube were remade and the tube was evacuated. After degassing for 2 hr at 100°C to remove any free water, the reaction vessel was allowed to attain a desired temperature, and batches (about 0.25 g) of chlorine trifluoride at 300 mm Hg pressure were introduced. After allowing time for complete reaction, the resultant gases were allowed to expand into the evacuated sample volume, which was isolated. After the pressure had been measured, and surplus gas pumped away, the sample containing product gases was immediately passed to the gas chromatographic unit and analysed.

Results

The reaction was investigated at three temperatures: 150, 100 and 50°C. At 150 and 100°C, with reaction times of 10 min, the whole of each batch of chlorine trifluoride reacted, with the exception of the final two or three batches in each case, when only a small amount of unreacted chlorine trifluoride was recovered. At 50°C only about half the chlorine trifluoride was profitably used after 30 min reaction time, and the final batches in each run needed some hours to react completely. In run 5 the average reaction time was 30 min, increasing to 60 min in run 6 and 90 min in run 7.

A summary of the reaction products from interaction of uranyl fluoride with chlorine trifluoride at various temperatures is given in Table 1. Results have been converted to molar equivalents.

Run	Temp. (°C)	Total contact time (hr)	Reactants, molar equivalents		Gaseous products, molar equivalents						
			UO2F2	CIF ₈	UF.	0,	Cl.	CIF	ClO ₂ F	C10,	
1	150	13	1.0	1.87	1.0	0.49	0.49	0.46	0.40	_	
2	150	11	1.0	1.97	1.0	0.37	0.43	0.47	0.47	-	
3	100	2	1.0	1.94	1.0	0.12	0.16	1.02	0.59	-	
4	100	2	1.0	2·01	1.0	0.11	0.17	1.00	0.57	-	
5	50	25	1.0	2·16	1.0	0.04	0.04	1.56	0.51	0.20	
6	50	27	1.0	2.22	1.0	0.01	0.03	1.61	0.60	0.04	
7	50	32	1.0	2.70	1.0	0.03	0.04	1.78	0.55	-	

TABLE 1.-PRODUCTS OF CIF₃-UO₂F₂ REACTION

All the compounds quoted in Table 1 were positively identified, with the exception of chlorine dioxide: this substance is the most probable cause of a distorted peak at 8.0 min retention time (cf. above) overlapping the ClF₃ peak in elution traces. A specimen of chlorine dioxide was prepared and shown to elute at 8.0 min, but tended to decompose somewhat on the column. The figures quoted for this material in Table 1 are very approximate. The figure given for chlorine trifluoride was obtained by subtracting the amount recovered from the total admitted to the reaction vessel. On balancing the elements admitted and recovered, there is an over-all deficiency in recovery of all elements except uranium. This is shown in Table 2, in which the mean stoicheiometry of the ClF₃-UO₃F₃ reaction is summarized.

Discussion and Conclusions

Most of the over-all fluorine loss is undoubtedly caused by reaction of the initial chlorine trifluoride batches with the unfluorinated walls of the reaction vessel, to produce nickel fluoride. This has been identified by X-ray crystallographic examination of scrapings from the reaction vessel walls. A further loss is caused by reaction of chlorine trifluoride with residual water in the uranyl fluoride; this yields hydrogen fluoride which is mostly adsorbed on the vessel walls, though traces have been recorded in the first batch analysis of some runs. The relatively high amount of unaccountable fluorine at the lowest temperature may well be a result of the increased contact times involved.

The discrepancy in the chlorine balance is not particularly serious in any case, and is negligible at the lower temperatures. The 5 per cent loss at 150°C is probably caused by the formation of metal chloride as well as fluoride in wall reactions.

Notes

Temp. (°C)	Reactants, molar equivalents		Products, molar equivalents							Unaccountable, equivalents		
	UO ₂ F ₂	CIF ₃	UF ₆	0,	Cl ₂	ClF	ClO ₃ F	C10,	0,	F	Cl	
150 100 50	1·0 1·0 1·0	1·92 1·98 2·36	1·0 1·0 1·0	0·43 0·12 0·03	0·46 0·17 0·04	0·46 1·01 1·65	0-44 0-58 0-55	- 0·08	0·13 0·30 0·36	0.86 0.35 0.88	0·10 0·05 -	

TABLE 2.—MEAN STOICHEIOMETRY OF THE CIF3-UO3F3 REACTION

The over-all deficiency in oxygen is more difficult to account for. At 50°C the balance is worst in run 7 when the longest reaction times were permitted and no chlorine dioxide was recorded. Further, the nearest approach to a balance is in run 5 where reaction times were shorter and a relatively large amount of chlorine dioxide appeared to be present. As the reaction temperature increased, no chlorine dioxide was noted, and the oxygen balance improved. It seems possible, therefore, that chlorine dioxide may form in the early stages of the reaction and subsequently dissociate, most rapidly at higher temperatures. Whilst it exists it is possible that oxidation of the apparatus occurs, resulting in a deficiency of volatile oxygen compounds recovered (cf. the strong oxidizing power of chlorine dioxide mentioned by MELLOR⁽³⁾).

This study shows that uranyl fluoride may be completely converted to uranium hexafluoride by treatment with chlorine trifluoride at temperatures from 50 to 150°C. The other gaseous reaction products are oxygen, chlorine, chlorine monofluoride and chloryl fluoride, with the possibility of chlorine dioxide as a reaction intermediate. The relative amounts of these products vary with the reaction temperature. At 150°C the stoicheiometry of the reaction may be reasonably expressed by:

$$2UO_2F_2 + 4ClF_3 \rightarrow 2UF_6 + Cl_2 + ClF + ClO_2F + O_2 + (F_2)$$
Lost to
reaction

Molecular oxygen and chlorine in appreciable quantities only result at the higher temperatures in the range considered. There is an increasing tendency for chlorine monofluoride to be produced at the lower reaction temperatures, with a corresponding fall in chlorine production. This is probably caused by secondary reaction of chlorine monofluoride with uranyl fluoride at the higher temperatures. Amounts of chloryl fluoride vary little with reaction temperature. A kinetic study of the reaction is being pursued by Kennedy *et al.*⁽⁶⁾ These authors have shown that the initial reaction of residual water of hydration in uranyl fluoride with chlorine trifluoride is very rapid compared with the subsequent process producing uranium hexafluoride. The strongly exothermic reaction with residual water creates local high temperatures which enhance the rate of the chlorine trifluoride–uranyl fluoride reaction at its outset.

Though it is generally seen that a temperature in excess of 100° C is required to complete the reaction relatively rapidly, it is evident that the interpretation of results and the assignation of stoicheiometrical equations is complicated by side reactions of the reactive halogen gases both with residual water in the uranyl fluoride (which is most difficult to dehydrate beyond UO₂F₂.0·1H₂O) and with the walls of the reaction vessel.

Acknowledgements—This note is published by permission of Sir WILLIAM COOK, Managing Director, and Dr. H. KRONBERGER, Director of Research and Development, of the U.K.A.E.A. (Development and Engineering Group).

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