J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 71 to 78. Pergamon Press Ltd. Printed in Great Britain.

# SEXAVALENT COMPOUNDS OF URANIUM-I

## URANYL ALKOXIDES AND URANIUM HEXA-ALKOXIDES.

# D. C. BRADLEY, AMAR K. CHATTERJEE and AMIYA K. CHATTERJEE Birkbeck College, Malet Street, London, W.C.1

(Received 23 February 1959)

Abstract-The preparation of uranyl alkoxides was complicated by either the insoluble nature of these compounds or their tendency to disproportionate. Insoluble uranyl methoxide, UO<sub>2</sub>(OMe)<sub>2</sub>, MeOH was obtained from the reaction involving uranyl chloride and methanolic lithium methoxide. Uranyl ethoxide UOg(OEt)2, 2EtOH was obtained similarly. Uranyl iso-amyloxide was obtained by the action of iso-amyl alcohol and ammonia on either uranyl chloride or dipyridinium uranyl chloride. The action of various alcohols on uranyl methoxide was studied and in some cases (mainly secondary and tertiary alcohols) a remarkable disproportionation occurred with the ultimate formation of uranium hexa-alkoxide  $U(OR)_6$ . Some properties of the hexa-alkoxides are described. The hexa-t-butoxide is remarkably resistant to hydrolysis.

A STRIKING feature of the chemistry of sexavalent uranium is the existence of many compounds containing the  $UO_2$  group. However, a survey of the literature<sup>(1)</sup> reveals few cases in which structures of uranyl compounds have been determined and there is still doubt as to the structure of the UO<sub>2</sub> group itself.<sup>(2)</sup> In view of recent structural work on the metal alkoxides<sup>(3)</sup> it seemed worthwhile to prepare and study uranyl alkoxides. Only two references to uranyl alkoxides could be found in the literature. ALBERS et al.<sup>(4)</sup> obtained uranyl iso-amyloxide as a red solid soluble in hydrocarbon solvents by the reaction between uranyl chloride and sodium iso-amyloxide in isoamyl alcohol. Recently, JONES et al.<sup>(5)</sup> described two interesting uranyl alkoxides. One was a brown crystalline solvated ethoxide  $UO_2(OEt)_2$ , 3EtOH, obtained from the reaction involving uranyl chloride and sodium ethoxide, in which the three molecules of co-ordinated alcohol resisted the action of heat at 200°C under 0.004 mm pressure. This is very surprising and we have not succeeded in repeating this work. Their second compound, provisionally assigned the formula  $UO_2(OBu^t)_2$ , 4Bu<sup>t</sup>OH, was obtained as red crystals from uranium (IV) tetra-t-butoxide, either by the action of heat *in vacuo* or by treatment with oxygen in petroleum ether solution.

In a preliminary communication<sup>(6)</sup> we reported that the preparation of uranyl alkoxides by reactions involving alcoholic solutions of uranyl chloride with either ammonia or the appropriate sodium alkoxide was complicated by the insoluble nature

- (4) H. ALBERS, M. DEUTSCH, W. KRASTINAT and H. VON OSTEN, Ber. Disch. Chem. Ges. 85, 267 (1952). (5) R. G. JONES, E. BINDSCHADLER, G. A. MARTIN, J. R. THIRTLE and H. GILMAN, J. Amer. Chem. Soc. 79, 4921 (1957).

A. E. COMYNS, AERE/C/R 2320 (1957).
L. SACCONI, G. CAROTI and P. PAOLETTI, J. Chem. Soc. 4257 (1958).
D. C. BRADLEY, Nature, Lond. 182, 1211 (1958).

<sup>(6)</sup> D. C. BRADLEY, AMAR K. CHATTERJEE and AMIYA K. CHATTERJEE, Proc. Chem. Soc. 260 (1957).

of some of the uranyl alkoxides or their tendency to disproportionate. Nevertheless, due to the high solubility of lithium chloride in methanol we prepared the very sparingly soluble uranyl methoxide by means of the following reaction:

 $UO_2Cl_2 + 2LiOMe + MeOH \longrightarrow UO_2(OMe)_2$ ,  $MeOH \downarrow + 2LiCl$ 

The disproportionation of uranyl alkoxides in alcoholic solution with the ultimate formation of some hexa-alkoxide must involve the splitting of the  $UO_2$  group under very mild conditions. To our knowledge this process was without precedent in uranium chemistry and required further investigation. We now report the results of the action of various alcohols on uranyl methoxide and of the preparation of some new uranyl alkoxides and uranium hexa-alkoxides.

## Reactions involving uranyl methoxide and primary alcohols

When uranyl methoxide was treated with either ethyl, n-propyl or isobutyl alcohols, methyl alcohol was liberated and the sparingly soluble crystalline uranyl alkoxide was formed. The amount of disproportionation accompanying these alcohol interchanges was very small. Similarly, iso-amyl alcohol caused interchange to a soluble uranyl iso-amyloxide. This is important because it rules out the possibility that straightforward interchange is confined to alcohols which produce insoluble uranyl alkoxides.

## Reactions involving uranyl methoxide and secondary or tertiary alcohols

When uranyl methoxide was treated with either isopropyl, s-butyl or t-butyl alcohols the interchange was accompanied by disproportionation. In each case the solution assumed a deep blood-red colour and an insoluble residue was formed. From the solution a deep red crystalline solid was obtained with the composition close to that of UO(OR)<sub>4</sub>, ROH and which gave, when heated in vacuo, the volatile hexa-alkoxide and an insoluble non-volatile residue. These reactions were repeated several times in order to establish this unique disproportionation reaction beyond doubt and, although the precise compositions of the intermediate products varied slightly from one preparation to another, the general pattern of the reaction was constant and some hexa-alkoxide was always formed. It must be emphasised that even a small amount of hydrolysis would have a very marked effect on the composition and proportions of the intermediate products of the disproportionation. Nevertheless, we were able to establish, by means of a careful uranium and alkoxide balance between starting material and products, that the reaction involved was a true disproportionation. For example, in one of the reactions involving isopropyl alcohol the products agreed reasonably with the requirements of the following equations:

(a) Solvolytic disproportionation:

 $3UO_2(OPr^i)_2$ ,  $Pr^iOH \longrightarrow U_2O_5(OPr^i)_2$ ,  $2Pr^iOH \downarrow + UO(OPr^i)_4$ ,  $Pr^iOH$ 

(b) Thermal disproportionation:

5UO(OPr<sup>i</sup>)<sub>4</sub>, Pr<sup>i</sup>OH  $\longrightarrow$  U<sub>2</sub>O<sub>5</sub>(OPr<sup>i</sup>)<sub>2</sub>, 2Pr<sup>i</sup>OH + 3U(OPr<sup>i</sup>)<sub>6</sub>  $\uparrow$  + 3Pr<sup>i</sup>OH  $\uparrow$ 

On the other hand, when uranyl methoxide was treated with t-amyl alcohol, no disproportionation occurred, and uranyl t-amyloxide  $UO_2(OAm^t)_2$  was isolated as a solid which was soluble in t-amyl alcohol but insoluble in benzene. This was most interesting because it might have been suggested that the presence of secondary or tertiary-alkyl groups was essential for the disproportionation process to occur. This may yet be true because it is possible that steric factors may prevent the disproportionation when tertiary amyloxide groups are involved.

## Uranium hexa-alkoxides

Uranium hexa-isopropoxide was first described by JONES et al.<sup>(7)</sup> who also prepared the hexa-ethoxide, -methoxide and -n-propoxide. Their molecular weight determination on the hexa-ethoxide in benzene (cryoscopic method) indicated a degree of polymerization (i.e. ratio of observed mol. wt. : mol. wt. of monomer) of ca. 1.2 which suggests a significant proportion of dimer species. The hexa-s-butoxide and hexa-t-butoxide obtained in this work are now reported for the first time although the latter was first obtained independently by one of us<sup>(8)</sup> in an attempted preparation of uranium (V) penta-t-butoxide by alcoholysis of the penta-ethoxide. We have determined the volatilities and molecular weights of the hexa-alkoxides: U(OR)6 where  $R = Pr^{i}$ ,  $Bu^{s}$  and  $Bu^{t}$ , and the results are given in Table 1.

R in U(OR)6	Volatility at 0 <sup>.</sup> 01 mm	Mol. wt.	Degree of polymerization	
Isopropyl	65°	656	1.1	
s-Butyl	. 75°	680	1.0	
t-Butyl	85°	680	1.0	

TABLE 1

Isopropyl	65°	656	1.1
s-Butyl	. 75°	680	1.0
t-Butyl	85°	680	1.0

The molecular weights were determined ebullioscopically in benzene and it is interesting to note that although the s-butoxide and t-butoxide are monomeric the isopropoxide contains a small proportion of dimer (cf. ethoxide). From the structural viewpoint it has been predicted<sup>(3)</sup> that uranium in a hexa-alkoxide can achieve the eight-co-ordinated state in the dimer  $U_2(OR)_{12}$  but it is clear that such a structure would be very sensitive to steric factors. We hope to obtain more conclusive evidence on this matter in future studies on uranium hexa-methoxide. It was surprising to find the hexa-t-butoxide less volatile than the s-butoxide but it must be remembered that the temperatures recorded above are not equilibrium boiling points but sublimation points.

## Uranyl ethoxide

The uranyl ethoxide obtained by ethanolysis of uranyl methoxide was a light brown powder with a composition near to UO<sub>2</sub>(OEt)<sub>2</sub>, 2EtOH. It lost the addended alcohol at 80°/0.05 mm in contrast to the compound described by JONES et al. (loc cit.) which retained its ethanol even at 200° in vacuo. We repeated the reaction described by JONES et al. but obtained no uranyl ethoxide. On the other hand, treatment of ethanolic uranyl chloride with lithium ethoxide followed by exhaustive

<sup>(7)</sup> R. G. JONES, E. BINDSCHADLER, D. BLUME, G. KARMAS, G. A. MARTIN, J. R. THIRTLE, F. A. YEOMAN and H. GILMAN, J. Amer. Chem. Soc. 78, 6030 (1956). (8) D. C. BRADLEY. Unpublished work.

extraction of the precipitate with ethanol to remove lithium chloride left uranyl ethoxide similar in composition to that obtained by ethanolysis of uranyl methoxide. Moreover, aerial oxidation of ethanolic uranium (V) penta-ethoxide caused the deposition of crystalline  $UO_2(OEt)_2$ , 2EtOH and we are convinced that this is the proper composition of uranyl ethoxide. Unfortunately the very low solubility of the compound in either ethanol or benzene precluded a molecular weight determination. It is noteworthy that uranyl chloride also formed a di-ethylalcoholate  $UO_2Cl_2$ , 2EtOH. This compound was sparingly soluble in benzene while in boiling ethanol it was practically monomeric.

### Uranyl isoamlyoxide

When uranyl methoxide was treated with a boiling iso-amyl alcohol-benzene mixture the uranium compound slowly dissolved and from the red solution the uranyl isoamyloxide was isolated as a brown solid with a composition near to  $UO_2(OAm^4)_2$ , Am<sup>4</sup>OH. The anhydrous compound, obtained by heating the solvate at 78°/0.05 mm, was insoluble in benzene. The solvate was also isolated from reactions involving either uranyl chloride or pyridinium uranyl chloride with iso-amyl alcohol and ammonia:

$$\begin{array}{r} (C_5H_6N)_2UO_2Cl_4 + 3Am^iOH + 4NH_3 & \longrightarrow & UO_2(OAm^i)_2, \\ Am^iOH + 4NH_4Cl + 2C_5H_5N \end{array}$$

 $UO_2Cl_2 + 3Am^iOH + 2NH_3 \longrightarrow UO_2(OAm^i)_2, Am^iOH + 2NH_4Cl.$ 

## Structural aspects of uranyl alkoxides

It is unfortunate that all of the uranyl alkoxides obtained in this work were too insoluble to permit molecular weight determinations. However, it is noteworthy that the solvated uranyl ethoxide  $UO_2(OEt)_2$ , 2EtOH, in which each uranium atom is presumably linked to at least six oxygens, should be insoluble. We should expect a monomeric unit containing six-co-ordinated uranium to be soluble and it therefore seems probable that the uranium is here exhibiting a higher co-ordination number (e.g. eight). In the latter case the *smallest* possible polymer should be a trimer (assuming the -OEt and HOEt groups to be disposed roughly octahedrally around the UO<sub>2</sub> groups), although infinite linear polymers could not be ruled out. With uranyl methoxide  $UO_2(OMe)_2$ , MeOH similar arguments would predict an octamer as the *smallest* possible polymer for eight-co-ordinated uranium whilst an alternative configuration involving a two-dimensional infinite sheet polymer is feasible. Therefore, it is reasonable to suppose that the low solubility of uranyl alkoxides is due to the polymeric nature of these compounds which results from the eight-co-ordination of the uranium by oxygen.

### EXPERIMENTAL

Uranyl alkoxides are very readily hydrolysed and special precautions were taken throughout this work to exclude moisture by means of the techniques already described in our earlier work.<sup>(9,10)</sup>

 <sup>(9)</sup> D. C. BRADLEY, B. N. CHAKRAVARTI and A. K. CHATTERJEE, J. Inorg. Nucl. Chem. 3, 367 (1957).
(10) D. C. BRADLEY and A. K. CHATTERJEE, J. Inorg. Nucl. Chem. 4, 279 (1957).

#### Sexavalent compounds of uranium

#### Analytical methods

(i) Uranium. When chloride was present, the uranium in nitric acid solution was precipitated in carbonate-free conditions as ammonium diuranate. The precipitate was filtered off, washed with ammoniacal 2 per cent ammonium nitrate solution and carefully ignited and the uranium determined as  $U_8O_8$ . The filtrate was acidified with nitric acid and the chloride determined gravimetrically as AgCl. When no chloride was present the sample was weighed into a platinum crucible and hydrolysed with water. The residue, left after evaporating off the volatile products under an infra-red lamp, was dissolved in a few drops of nitric acid (d. 1.42), the solution was then evaporated to dryness and the uranyl nitrate was ignited to  $U_8O_8$ .

(ii) Alkoxide. The ethoxide and isopropoxide determinations were carried out volumetrically by the chromic acid method already described.<sup>(9)</sup> Methoxide was determined similarly but with the following modification to ensure complete oxidation to carbon dioxide: the mixture of sample and chromic acid was kept in a closed vessel for 2 hr at room temperature and then boiled under reflux for about 10 min. The excess chromic acid in the cooled solution was then determined iodometrically in the usual way.

#### Pyridinium uranyl chloride

Uranyl chloride hydrate (20 g) was dissolved in ethanol (325 ml) and the solution was saturated with hydrogen chloride. Pyridine (17 g) was added and, on treatment with more hydrogen chloride, the pale yellow-green complex chloride (28.5 g) crystallized out. (Found: U, 41.5; Cl, 24.8. Calc. for  $(C_{6}H_{6}N)_{2}UO_{2}Cl_{4}$ ; U, 41.6; Cl, 24.8%.)

#### Anhydrous uranyl chloride

Although various methods are available for preparing anhydrous uranyl chloride, we found difficulty in obtaining the pure material. Following a considerable amount of research we found that the pure compound could be obtained from the hydrated chloride as follows: the powdered hydrate in a silica boat was heated in a stream of anhydrous hydrogen chloride for several hours at 300°. The solid was next ground up under dry nitrogen and then heated at 400° in a mixture of hydrogen chloride and chlorine for a further 2–3 hr. (Found: U, 69.8; Cl, 20.6. Calc. for UO<sub>2</sub>Cl<sub>2</sub>; U, 69.8; Cl, 20.8%.)

#### Uranyl chloride ethyl alcoholate

Uranyl chloride hydrate (23.1 g) was dissolved in a mixture of ethanol (300 ml) and benzene (130 ml) and the solution was carefully fractionated to remove the water as the ternary azeotrope water-ethanol-benzene. When the solution had become concentrated to 250 ml more benzene (50 ml) was added and the fractionation continued. When all of the benzene had been removed, the alcoholic solution was concentrated under reduced pressure but the product would not crystallize. Finally, the solution was taken to dryness at room temperature under low pressure (0.1 mm) and gave a pale yellow solid (25.4 g). (Found: U, 54.7; Cl, 16.0; EtO, 20.4. Calc. for UO<sub>2</sub>Cl<sub>2</sub>, 2EtOH: U, 54.9; Cl, 16.4; EtO, 20.8%.) In boiling ethanol the *alcoholate* has a molecular weight of 421 (Calc. for UO<sub>2</sub>Cl<sub>2</sub>, 2EtOH: 433). It was practically insoluble in benzene.

#### Uranyl methoxide

Uranyl chloride (anhydrous, 16.6 g) was dissolved in methanol (200 ml) in the boiler flask of a Soxhlet extractor. Lithium (0.67 g) was placed in a sintered glass (porosity No. 2) extraction thimble in the Soxhlet and allowed to react with methanol condensing from the boiling solution of uranyl chloride. The lithium methoxide solution was then siphoned over automatically into the uranyl chloride solution. This was continued until all of the lithium had dissolved. The suspension of uranyl methoxide was heated for a further 27 hr and then allowed to cool and settle. The methanolic lithium chloride solution was then decanted off and the uranyl methoxide was washed several times by decantation with anhydrous methanol (50 ml portions). After drying at room temperature under low pressure (0.1 mm), the uranyl methoxide was left as a bright yellow microcrystalline solid. (Found: U, 65.0; MeO, 24.0. Calc. for UO<sub>2</sub>(OMe)<sub>2</sub>, MeOH: U, 65.4; MeO, 25.5%.) A sample of the foregoing product heated at  $100^{\circ}/0.05$  mm for 3 hr slowly changed colour to brown and lost the majority of its addended alcohol. (Found: U, 68.3; MeO, 18.6. Calc. for UO<sub>2</sub>(OMe)<sub>2</sub>: U, 71.7; MeO, 18.7%.)

#### Uranyl ethoxide

(i) From uranyl methoxide. Ethanol (179 g) and benzene (88 g) were added to uranyl methoxide (10 g) and the mixture was subjected to fractional distillation to remove the methanol-benzene azeotrope. The colour of the solution became wine-red but little solid appeared to dissolve. When the interchange was judged complete, the mother liquor was decanted off and the buff-coloured uranyl ethoxide (11.9 g) was dried at room temperature under 0.1 mm pressure. (Found: U, 53.5; EtO, 37.5. Calc. for  $UO(_{2}OEt)_{2}$ , 2EtOH: U, 52.7; EtO, 39.8%.) The mother liquor was evaporated to dryness and left only a trace of red liquid which from its volatility was doubtless uranium hexaethoxide. A sample or uranyl ethoxide heated at  $80^{\circ}/0.05$  mm for 4 hr lost its addended ethanol. (Found: U, 66.7; EtO, 23.1. Calc. for  $UO_{2}(OEt)_{2}$ : U, 66.1; EtO, 25.0%.)

(ii) From uranyl chloride. Anhydrous uranyl chloride (6.8 g) in boiling ethanol (200 ml) was caused to react with lithium ethoxide obtained from lithium (0.28 g) in the Soxhlet extractor. The sparingly soluble uranyl ethoxide was obtained as a buff-coloured solid (6.3 g) after being washed several times with ethanol by decantation and dried at room temperature under 0.1 mm pressure. (Found: U, 52.1; EtO, 36.1; Cl, 1.0%.) A sample heated at  $100^{\circ}/0.05$  mm for 5 hr changed to a brick-red colour and had obviously decomposed. (Found: U, 68.5; EtO, 20.5; ratio EtO: U, 1.58.) In view of the fact that uranyl ethoxide obtained in this work lost its addended ethanol at 80° *in vacuo* and began decomposing at  $100^{\circ}$ , we were surprised by the behaviour reported by JONES *et al.*<sup>(5)</sup> for a compound UO<sub>8</sub>(OEt)<sub>2</sub>, 3EtOH. They claimed that this compound was obtained by allowing sodium ethoxide to react with ethanolic uranyl chloride (10.2 g) and sodium ethoxide (from Na, 1.30 g), carried out under closely similar conditions, we obtained a black residue which was completely insoluble in ether and which had an analysis near to that of the expected mixture of uranium trioxide and sodium chloride. (Found: U, 59.2. Calc. for mixture of UO<sub>3</sub> + 2NaCl: U, 59.1%.)

#### Uranyl isopropoxide

(i) Reaction involving pyridinium uranyl chloride. The complex chloride (13 g) suspended in a mixture of isopropanol (119 g) and benzene (129 g) was treated with excess ammonia and an exothermic reaction occurred. After filtration, evaporation of the filtrate left a red-brown substance (0.84 g). (Found: U, 45.6; Pr<sup>4</sup>O, 11.4; Cl, 15.5%; Ratio Pr<sup>4</sup>O: U, 1.01; Cl: U, 2.27.) The precipitate of impure ammonium chloride (15.2 g) evidently contained the major proportion of the uranium. (Found U, 37.4; Pr<sup>4</sup>O, 18.2; Cl, 22.3; NH<sub>2</sub>, 13.5%.)

(ii) Reaction involving sodium isopropoxide and uranyl chloride. Uranyl chloride hydrate (8.2 g) was azeotropically dehydrated in benzene-isopropanol solution, the benzene removed by fractionation and the isopropanolic solution treated with sodium isopropoxide formed from sodium (0.90 g) in a Soxhlet apparatus. The precipitate was filtered off and the filtrate evaporated to dryness under 0.1 mm pressure left a red-brown solid (3 g). (Found: U, 43.1; Pr4O, 52.1; Cl, 2.1%. Ratio Pr4O: U, 4.75; Cl: U, 0.33.) A sample (2 g) of the foregoing product was refluxed with isopropanol (93 g) and on cooling some crystals (0.52 g) were formed. (Found: U, 51.5; Pr4O, 38.7. Calc. for  $UO_2(OPr4)_8$ , Pr4OH: U, 53.1; Pr4O, 39.5%.) This experiment is typical of several carried out with these reactants.

(iii) Isopropanolysis of uranyl iso-amyloxide. Uranyl iso-amyloxide (2.6g) was treated with increasing quantities of boiling isopropanol until 110 ml had been added. However, some insoluble material still remained and the cooled wine-red solution was filtered and the filtrate taken to dryness under 0.1 mm pressure leaving a deep red solid (0.5 g). (Found: U, 45.7; Pr<sup>4</sup>O, 56.5. Calc. for UO(OPr<sup>4</sup>)<sub>4</sub>, Pr<sup>4</sup>OH: U, 43.3; Pr<sup>4</sup>O, 53.6%.) The insoluble fraction appeared to be a hydrolysis product. (Found: U, 67.9; Pr<sup>4</sup>O, 23.2%. Ratio Pr<sup>4</sup>O: U, 1.37). In the light of subsequent work it is clear that disproportionation of the uranyl isopropoxide must have occurred in this reaction.

(iv) Isopropanolysis of uranyl methoxide. When uranyl methoxide UO<sub>2</sub>(OMe)<sub>2</sub>, MeOH was treated with isopropanol, methanol was fractionated off but the solution became red and the insoluble uranium compound became brown. From the filtrate a red solid (near to UO(OPr<sup>4</sup>)<sub>4</sub>, Pr<sup>4</sup>OH in composition) was isolated and this gave uranium hexa-isopropoxide when heated *in vacuo*. Some typical results are given in Table 2 for the solvolytic disproportionation.

In Table 3 some results are presented for the thermal disproportionation at  $110^{\circ}/0.05$  mm of the soluble fractions (B).

To establish the presence of "active hydrogen" (i.e. isopropanol) in the soluble fraction (B), a sample (0.421 g) from experiment (iv) (Table 2) was treated with methyl magnesium iodide in di-n-butyl ether and the methane (20.61 ml at s.t.p.) collected in a gas burette. (Found: Active H, 0.225. Calc. for UO(OPr<sup>4</sup>)<sub>4</sub>, Pr<sup>4</sup>OH: Active H, 0.184%.) This determination does not necessarily distinguish between UO(OPr<sup>4</sup>)<sub>4</sub>, Pr<sup>4</sup>OH and U(OH)(OPr<sup>4</sup>)<sub>5</sub>. A portion of the sublimed uranium hexa-isopropoxide obtained in experiment (iii) (Table 3) was heated in a molecular still at 0.01 mm and it began to sublime at  $65^{\circ}$ . Sublimation was rapid at  $85^{\circ}$  and no residue remained.

Wt. of UO <sub>2</sub> (OMe) <sub>2</sub> , MeOH taken (g) Wt. of Pr <sup>4</sup> OH (g)		Ins	Insoluble residue A			Soluble product B		
	$\begin{array}{c c} \mathbf{h} \mathbf{h} \mathbf{h} \mathbf{h} \mathbf{h} \mathbf{h} \mathbf{h} h$	Wt.	Composition (%)		Wt. (g)	Composition (%)		
	(g)	U	PriO	U		Pr <sup>4</sup> O		
(i) 6·72	301.5	3.66	63·4	22.8	4.07	49.5	43.3	
(ii) 7·01	193.8	4.79	60·1	27.5	2.01	42·4	53.9	
(iii) 12·08	261.4	9.04			3.24	43·2	51.5	
(iv) 11·76	236.0	10 02	63·3	27.9	3.64	41·7	55.8	

I ABLE .	2
----------	---

#### Uranyl n-propoxide

Uranyl methoxide (11·1 g) was treated with boiling n-propanol (400 ml) until no more methanol could be collected by fractionation. Not all of the solid dissolved and the solution became red and, on cooling, deposited crystals. Some of the crystals were separated from the main solid residue by flotation in the mother liquor from which they were finally separated by filtration. The crystalline n-propoxide (0.5 g) was cream-coloured. (Found: U, 61·3. Calc. for  $UO_2(OPr^4)_2$ : U, 61·3%.) The mother liquor was evaporated to dryness leaving a small amount of viscous red product which, at 120–125°/0.05 mm, gave a drop of red condensate. There was insufficient of the latter for analysis but from its appearance and volatility it was undoubtedly uranium hexa-n-propoxide. The main solid product (13·6 g) was extracted with boiling n-propanol and gave a second crop of crystalline uranyl n-propoxide which was separated from undissolved product by flotation. (Found: U, 62·0%.)

Wt. of (B) taken (g) Wt (g)	Non	Non-volatile residue		Sublimate			U(OPr <sup>4</sup> ) <sub>6</sub> requires	
	Wt.	Wt. Composition (		(%) Wt.	Composition (%)		U	Pr <sup>4</sup> O
	(g)	U	Pr <sup>4</sup> O	(g)	U	Pr <sup>4</sup> O	(%)	(%)
(i) 3·0	2.2	63.3	29.1	0.402	<b>40</b> ·1	60.1	40.2	59.8
(ii) 1·85			_	1.04	40.1	60.1	40.2	59.8
(iii) 2·70		-		1.30	40.2	60-0	<b>40</b> ∙2	59.8

#### TABLE 3

#### Uranyl isobutoxide

The reaction involving isobutanol and uranyl methoxide resembled that involving n-propanol. A sparingly soluble crystalline solvated uranyl isobutoxide was obtained. (Found: U, 48.5. Calc. for  $UO_2(OBu')_2$ , Bu'OH: U, 48.6%.)

#### Uranyl iso-amyloxide

(i) From pyridinium uranyl chloride. The complex chloride  $(11 \cdot 1 \text{ g})$  suspended in isoamyl alcoholbenzene azeotrope (200 ml) was treated with ammonia until the exothermic reaction was complete. After the removal of ammonium chloride the wine-red filtrate was evaporated under 0.1 mm pressure and left a brown solid (6.8 g). (Found: U, 44.8. Calc. for UO<sub>2</sub>(OAm<sup>4</sup>)<sub>2</sub>, Am<sup>4</sup>OH: U, 44.7%.)

(ii) From uranyl chloride hydrate. The hydrate (5.0 g) was azeotropically dehydrated using isoamyl alcohol (25 ml), benzene (75 ml) and isopropanol (5 ml). The latter served to effect the removal of water as the ternary azeotrope of benzene-isopropanol-water. Then the remainder of the isopropanol was removed as the binary azeotrope with benzene leaving a benzene-iso-amyl alcohol solution of uranyl chloride iso-amyl alcoholate. The latter was treated with excess ammonia and, after filtering off the ammonium chloride, uranyl isoamyloxide alcoholate (2.6 g) was obtained by evaporation of the filtrate. (Found: U, 44.1%.) The co-ordinated isoamyl alcohol was removed by heating at 75°/0.05 mm. (Found: U, 53.6%. Calc. for UO<sub>2</sub>(OAm<sup>4</sup>)<sub>2</sub>: U, 53.6%.)

(iii) From uranyl methoxide. Uranyl methoxide (9.5 g) slowly dissolved when treated with boiling iso-amyl alcohol-benzene azeotrope (275 ml) and gave a clear red solution. Evaporation of the solvent under 0 1 mm pressure left uranyl iso-amyloxide solvate (12.8 g). (Found: U, 46.2%.)

	Banga of with of	Wt of C H	Signa $(4T^{\circ}/2)$	Mol. wt.	
	solute (g)		510pe (21 /g)	Found	Calc.
lsopropyl	0.0288-0.2098	15.93	0.280	656	592
s-Butyl	0.0110-0.0406	15.63	<b>0</b> ·276	680	676
t-Butyl	0.0321-0.1581	14.77	0.296	680	676

TABLE 4	4
---------	---

#### Uranyl t-amyloxide

Uranyl methoxide (8.09 g) was interchanged with t-amyl alcohol (300 ml) giving a brown solution and a small amount (1.2 g) of insoluble residue. (Found: U, 62.0%.) From the mother liquor, evaporated to dryness, a deep maroon crystalline product (8.36 g) was obtained. (Found: U, 54.2; C, 23.3; H, 4.51. Calc. for UO<sub>2</sub>(OAm<sup>4</sup>)<sub>2</sub>: U, 53.6; C, 27.2; H, 4.95%.) The product gave no volatile fraction when heated to  $120^{\circ}/0.05$  mm and at  $135^{\circ}$  it turned black due to decomposition. (Found: U, 72.9%.)

#### Disproportionation of uranyl t-butoxide

When uranyl methoxide was treated with t-butanol-benzene azeotrope, alcohol interchange was accompanied by disproportionation. One experiment using uranyl methoxide (10.34 g) and t-butanol-benzene azeotrope (250 ml) gave an insoluble residue (8.09 g) and a soluble red crystalline solid (3.74 g). (Found: U, 38.6; C, 38.7; H, 7.48. Calc. for UO(OBu<sup>t</sup>)<sub>4</sub>, Bu<sup>t</sup>OH: U, 38.4; C, 38.7; H, 7.40%.) The latter (2.3 g) heated at  $110^{\circ}/0.05$  mm in a molecular still gave a deep red sublimate of uranium hexa-t-butoxide (0.267 g, Found: U, 34.7; C, 42.2; H, 8.05. Calc. for U(OBu<sup>t</sup>)<sub>6</sub>: U, 35.2; C, 42.6; H, 7.90%.) The hexa-t-butoxide, in a molecular still, began to sublime at  $85^{\circ}/0.04$  mm and sublimed rapidly at  $110^{\circ}$  leaving no residue. Compared with metal alkoxides in general, uranium hexa-t-butoxide is remarkably resistant to hydrolysis, apparently remaining unaffected by exposure to the air. A benzene solution of the hexa-t-butoxide could be shaken with water for some time before hydrolysis occurred. In aqueous acetone solution the compound was slowly hydrolysed to uranium trioxide. The resistance to hydrolysis is undoubtedly due to the strong shielding of the uranium by six t-butoxide groups preventing nucleophilic attack by water molecules.

#### Disproportionation of uranyl s-butoxide

The reaction involving uranyl methoxide and s-butanol closely paralleled that involving t-butanol. From the methoxide (11.4 g) and s-butanol-benzene azeotrope (350 ml) an insoluble brown fraction (7.98 g, Found: U, 62.5%) and a soluble red compound (5.82 g, Found: U, 40.3%) were obtained. A sample (4.83 g) of the latter heated in a molecular still gave at 110-125°/0.05 mm a deep red sublimate (0.84 g, Found: U, 35.1. Calc. for U(OBu<sup>t</sup>)<sub>6</sub>: U, 35.2%) of the hexa-s-butoxide and a non-volatile residue (Found: U, 53.0%). The hexa-s-butoxide began to sublime at 75°/0.01 mm in a molecular still and sublimed rapidly and completely at 110°.

#### Molecular weights of uranium hexa-alkoxides

The molecular weights were determined ebullioscopically in benzene using the previously described<sup>(10)</sup> all-glass ebulliometer. The compounds showed no variation of molecular weight with concentration over the range studied. The results are given in Table 4.