189. *Quinquevalent Compounds of Uranium. Part III.*[1] *Uranium Penta-alkoxides.*

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New uranium penta-alkoxides have been prepared from uranium pentaethoxide by alcohol exchange. Volatilities have been measured under reduced pressure, and molecular weights ebullioscopically in benzene. The compounds are compared with penta-alkoxides of niobium and tantalum. Steric effects in binuclear octahedral complexes $M_2(OR)_{10}$ are discussed.

QUINQUEVALENT uranium derivatives from methyl, ethyl, propyl, butyl, and n-pentyl alcohol have been reported previously.[1-5] Some of these compounds were prepared during the present work, and twelve new uranium penta-alkoxides (derivatives of seven isomeric pentyl alcohols, three tertiary C_6 alcohols, and two tertiary C_7 alcohols) have been prepared from uranium pentaethoxide by alcohol exchange. The compounds $U(O{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2)_5$, $U(O{\cdot}CH_2{\cdot}CHMeEt)_5$, and $U(O{\cdot}CHMePr^n)_5$ are brown viscous liquids and the other new alkoxides are brown solids. Hydrolysis occurs in moist air. All except the compounds $U(OCMe_2Pr^i)_5$ and $U(O{\cdot}CMeEtPr^i)_5$ distil or sublime without decomposition under reduced pressure. Uranium penta-alkoxides are soluble in common organic solvents, and molecular weights have been measured ebullioscopically in benzene.

It was claimed[5] that the tan-coloured crystals prepared by addition of t-butyl alcohol to uranium pentaethoxide in ether were uranium penta-t-butoxide, but attempts to repeat this work gave a compound whose analysis corresponded to that of a mixed alkoxide, $U_2(OEt)_5(OBu^t)_5$ which sublimed unchanged at 150°/0·1 mm. From reactions of uranium pentaethoxide with an excess of t-butyl alcohol in boiling benzene, other mixed alkoxides, $U(OEt)_2(OBu^t)_3$ (sublimes at 150°/0·1 mm.; *M*, found 991, calc. 519) and $U(OBu^t)_4{\cdot}OEt$

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[1] Part II, Bradley and Chatterjee, *J. Inorg. Nuclear Chem.*, 1957, **4**, 279.
[2] Bradley, Chakravarti, and Chatterjee, *J. Inorg. Nuclear Chem.*, 1957, **3**, 367.
[3] Taylor, Jorgensen, Mathesen, and Taylor, A. E. C. D. 3144.
[4] Jones, Bindschadler, Karmas, Yoeman, and Gilman, *J. Amer. Chem. Soc.*, 1956, **78**, 4287.
[5] Jones, Bindschadler, Karmas, Martin, Thirtle, Yoeman, and Gilman, *J. Amer. Chem. Soc.*, 1956, **78**, 4289.

were obtained. Reaction of uranium pentaethoxide with a 12·5 molar excess of t-butyl alcohol gave a brown crystalline addition compound, $U(OBu^t)_5,Bu^tOH$, which recrystallised from t-butyl alcohol and was monomeric in benzene. Attempted replacement of this alcohol by ether, trimethylamine, and triethylamine was unsuccessful, but reaction with pyridine gave the addition compound $U(OBu^t)_5,C_5H_5N$. Rust-coloured crystalline uranium penta-t-butoxide was prepared by reaction of uranium pentaethoxide with a 14 molar excess of t-butyl alcohol in boiling benzene for 8 hours under conditions of azeotropic distillation.

Volatilities and degrees of polymerisation, $n = M(\text{obs.})/M(\text{calc.})$, of penta-alkoxides of uranium, niobium, and tantalum are compared in Table 1. Co-ordination polymerisation of alkoxides is caused by donation of electrons on oxygen to vacant orbitals of the metal atom of a neighbouring molecule. The extent of co-ordination depends on the size of the central metal atom and the number, size, and shape of surrounding alkoxide groups. It is of interest that degree of polymerisation appeared to be independent of concentration for dilute solutions containing 0·2—2% of alkoxide in boiling benzene. This situation occurs frequently during ebullioscopic investigations of metal alkoxides even though cryoscopic measurements in the same solvent are dependent on concentration,[6] and no satisfactory explanation can be given.

TABLE 1.

Volatility and degree of polymerisation of penta-alkoxides.

Metal:	U		Nb [e, f]		Ta [e, g]	
Cov. rad. (Å): [a]	1·421		1·342		1·343	
R in $M(OR)_5$	B. p./mm.	*n*	B. p./mm.	*n*	B. p./mm.	*n*
Me	140—150°/0·01 * [b, d]	3·01 [b]	153°/0·1	2·11	130°/0·2	1·98
Et	161°/0·05 [b, c]	1·90 [b]	156°/0·05	2·02	146°/0·15	1·98
Pr^n	181°/0·07 [b, d]	1·95 [b]	166°/0·05	2·02	184°/0·15	1·95
Pr^i	150°/0·05 * [d]	1·93	80°/0·1 *	—	122°/0·1	0·99
Bu^n	206°/0·15 [b, d]	1·94 [b]	197°/0·15	2·01	217°/0·15	2·02
Bu^i	192°/0·01 [d]	1·97	160°/0·1	1·83	185°/0·1	2·04
Bu^s	175°/0·05 * [d]	1·85	112·5°/0·1	1·14	137·5°/0·1	1·06
Bu^t	120°/0·05 * [d]	1·35	90°/0·1 *	—	96°/0·1 *	1·00
$Me{\cdot}[CH_2]_4$	246°/0·05 [b]	1·94 [b]	228°/0·1	2·00	233°/0·1	2·01
$Pr^i{\cdot}CH_2{\cdot}CH_2$	225°/0·05	1·76	199°/0·1	1·81	210°/0·1	1·98
$MeEtCH{\cdot}CH_2$	220°/0·05	1·82	183°/0·1	1·81	204°/0·1	1·97
$Bu^t{\cdot}CH_2$	160—170°/0·1 *	1·61	126°/0·1	1·52	130°/0·1	1·35
Et_2CH	180°/0·1	1·66	138°/0·1	1·16	153°/0·1	1·02
$MePr^nCH$	175°/0·1	1·70	137·5°/0·1	1·03	148°/0·1	0·99
$MePr^iCH$	160°/0·1 *	1·58	139°/0·1	1·05	137°/0·1	1·02
Me_2EtC	130°/0·05 *	1·26	—	—	139°/0·1	1·00
Me_2Pr^nC	200°/0·1	1·28	—	—	—	—
Me_2Pr^iC	Decomp.	—	—	—	—	—
$MeEt_2C$	200°/0·1 *	1·09	—	—	—	—
$MeEtPr^iC$	Decomp.	1·01	—	—	—	—
Et_3C	210°/0·1 *	1·00	—	—	—	—

* Sublimation. [a] Moeller, " Inorganic Chemistry," John Wiley and Sons, Inc., New York, 1952, pp. 150, 893. [b] Ref. 1. [c] Cf. refs. 3, 4. [d] Cf. ref. 5. [e] Bradley *et al.*, *J.*, 1956, 2381, 4439; 1958, 99. [f] Ref. 7. [g] Ref. 8.

The degree of polymerisation ($n = 3$) of uranium pentamethoxide suggested the presence of eight co-ordinated uranium.[2] Other primary alkoxides of uranium, niobium, and tantalum are predominantly dimeric, and in these compounds it is probable that the metals are six-co-ordinated. The most volatile uranium primary pentyloxide, uranium pentaneopentyloxide, $U(O{\cdot}CH_2Bu^t)_5$, has the lowest degree of polymerisation, $n = 1{\cdot}61$; and since there is little change in the positive inductive effects of primary alkyl groups,

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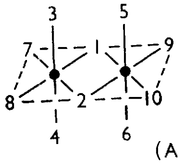
[6] Bradley, " Progress in Inorganic Chemistry," ed. Cotton, Interscience Publishers, Inc., New York, 1960, Vol. II, p. 340.

the abrupt change of volatility and degree of polymerisation must be caused by the shape of the neopentyl group.

Secondary alkoxides of niobium and tantalum are predominantly monomeric (n = 0·99—1·16). The larger uranium atom is shielded less effectively, and the boiling points of uranium secondary alkoxides are some 30° higher than those of analogous niobium and tantalum compounds. The variation of degrees of polymerisation of uranium secondary alkoxides (n = 1·58—1·93) illustrates the influence of chain-branching.

Niobium penta-t-butoxide was prepared recently by Thomas.[7] The molecular weight was not reported but the compound is almost certainly monomeric, like tertiary alkoxides of tantalum.[8] Degrees of polymerisation of the penta-t-butoxide (n = 1·35), penta-t-pentyloxide (n = 1·26), the tertiary pentahexyloxides (n = 1·09, 1·28), and tertiary pentaheptyloxides (n = 1·00, 1·01) of uranium show how co-ordination polymerisation in uranium penta-alkoxides is prevented by the steric effects of bulky alkyl groups.

The formation of the mixed ethoxide t-butoxides, $U_2(OEt)_5(OBu^t)_5$, $U_2(OEt)_4(OBu^t)_6$, and $U(OBu^t)_4{\cdot}OEt$ calls to mind the similar behaviour on t-butanolysis of aluminium tri-isopropoxide[9] (replacement of third isopropoxide group is slow) and zirconium alkoxides.[10] In a dimeric penta-alkoxide $M_2(OR)_{10}$ involving a 6-co-ordinated metal (cf. A) the alkoxide groups at the bridging positions 1 and 2 will experience the most steric interaction, followed by groups at positions 3—6, while least interaction ocurs at positions 7—10. Thus in the progressive replacement of ethoxide groups in $U_2(OEt)_{10}$ by t-butoxides the ease of formation of mixed alkoxides should be in the order $U_2(OEt)_6(OBu^t)_4 \gg U_2(OEt)_4(OBu^t)_6 > U_2(OEt)_2(OBu^t)_8$. The uranium ethoxide t-butoxides isolated in this work are qualitatively in agreement with this scheme. Steric factors obviously oppose dimerisation of uranium penta-t-butoxide (n = 1·35) but steric hindrance to the formation of $U(OBu^t)_5,Bu^tOH$ should be less, in agreement with the ready formation of the solvate. Similarly the failure of diethyl ether or triethylamine to co-ordinate to the penta-t-butoxide and the formation of the solvate $U(OBu^t)_5,C_5H_5N$ are readily explained in terms of steric factors.



(A)

EXPERIMENTAL

Starting Materials.—Anhydrous uranium tetrachloride was prepared from uranium trioxide and hexachloropropene.[11] Organic solvents were dried carefully by conventional methods before passage through molecular-sieve columns. The following alcohols were synthesised from Grignard reagents: pentan-3-ol, pentan-2-ol, 3-methylbutan-2-ol, 3-methylpentan-3-ol, 2,3-dimethylbutan-2-ol, 2,3-dimethylpentan-3-ol, and 3-ethylpentan-3-ol. The products were purified by fractional distillation, and middle fractions boiling within a range of less than 0·5° were collected.

Analysis.—Uranium was determined gravimetrically as U_3O_8. The valency of uranium was established by double oxidation with ceric sulphate solution.[2] Alkoxide groups were estimated volumetrically with chromic acid.[12]

Molecular Weights.—Molecular weights were measured ebullioscopically in benzene, by methods described previously.[13] For each compound the apparatus was calibrated internally with fluorene.

Uranium Pentaethoxide.—Uranium pentaethoxide, b. p. 180°/0·1 mm., was prepared as a mobile brown liquid (88% yield) from uranium tetrachloride and sodium ethoxide by the bromine method described by Jones *et al.*[5] (Found: U, 51·3; OEt, 48·7%; valency, 5·0. Calc. for $C_{10}H_{25}O_5U$: U, 51·4; OEt, 48·6%).

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[7] Thomas, *Canad. J. Chem.*, 1961, **39**, 1386.

[8] Bradley, Wardlaw, and Whitley, *J.*, 1955, 726; 1956, 1139.

[9] Bains and Bradley, *Chem. and Ind.*, 1961, 1032; *Canad. J. Chem.*, 1962, **40**, 381.

[10] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4202.

[11] Hermann and Suttle, *Inorg. Synth.*, 1957, **5**, 143.

[12] Bradley, Abd-El Halim, and Wardlaw, *J.*, 1950, 3450.

[13] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977; Bradley, Wardlaw, and Whitley, *J.*, 1956, 5.

Uranium Penta-t-butoxide.—Addition of t-butyl alcohol (6·5 g.) to a solution of the pentaethoxide (7·0 g.) in dry ether (20 ml.) gave a tan precipitate which sublimed as *pentaethoxypenta-t-butoxydiuranium*, $U_2(OEt)_5(OBu^t)_5$ (8·0 g.). Analytical data are in Table 2. A mixture of t-butyl alcohol (7·2 g.), uranium pentaethoxide (5·6 g.), and benzene (100 ml.) was boiled under reflux for 2 hr. The ethanol–butyl alcohol–benzene azeotropes and excess of benzene were removed by distillation, and *tetraethoxyhexa-t-butoxydiuranium*, $U_2(OEt)_4(OBu^t)_6$, was obtained as a tan crystalline solid. *Ethoxytetra-t-butoxyuranium*, $UOEt(OBu^t)_4$, was obtained similarly from reaction of t-butyl alcohol (10·7 g.) with uranium pentaethoxide (6·8 g.) in benzene (120 ml.). Reaction of t-butyl alcohol (16·0 g.) with uranium pentaethoxide (8·0 g.) in benzene (120 ml.) gave brown crystals of *uranium penta-t-butoxide–t-butyl alcohol.* Complete reaction (8 hr.) of t-butyl alcohol (11·0 g.) with uranium pentaethoxide (4·9 g.) in benzene (100 ml.) gave *uranium penta-t-butoxide* after azeotropic removal of t-butyl alcohol.

TABLE 2.

Derivatives of t-butyl alcohol.

Compound	Sublimes at temp./mm.	Found				Required		
		U (%)	OEt (%)	Valency	*M*	U (%)	OEt (%)	*M*
$U_2(OEt)_5(OBu^t)_5$	150°/0·1	44·8	20·6	—	—	44·6	21·1	—
$U_2(OEt)_4(OBu^t)_6$	150°/0·1	44·0	16·0	5·0	991	43·5	16·4	1038
$U(OEt)(OBu^t)_4$	—	41·8	7·6	5·0	—	41·4	7·8	—
$U(OBu^t)_5$	120°/0·05	39·2	0	5·0	817	39·4	0	604
$U(OBu^t)_5,Bu^tOH$	130°/0·1	35·4	0	5·0	631	35·2	0	678
$U(OBu^t)_5,C_5H_5N$	—	35·1	(2·0 *)	5·0	—	34·9	(2·05 *)	—

* Nitrogen.

TABLE 3.

Preparation of uranium penta-alkoxides.

	$U(OEt)_5$ (g.)	Alcohol (g.)	Product		Found			Required	
			(g.)	(%)	U (%)	Valency	*M*	U (%)	*M*
$U(OPr^i)_5$ *	12·8	20·0	13·8	94	44·5 ‡	5·0	1029	44·6	533
$U(OBu^i)_5$ †	5·2	11·2	5·7	85	39·9	5·0	1189	39·4	604
$U(OBu^s)_5$ †	4·8	9·6	5·4	86	39·9	5·0	1116	39·4	604
$U(O{\cdot}CH_2{\cdot}CH_2Pr^i)_5$	7·6	11·1	10·4	94	35·2	5·0	1187	35·4	674
$U(O{\cdot}CH_2{\cdot}CHMeEt)_5$	5·9	10·0	8·2	95	35·2	5·0	1226	35·4	674
$U(O{\cdot}CH_2Bu^t)_5$	5·0	6·0	5·8	80	35·3	5·1	1086	35·4	674
$U(O{\cdot}CHEt_2)_5$	8·2	11·3	10·8	90	35·6	5·0	1122	35·4	674
$U(O{\cdot}CHMePr^n)_5$	8·5	11·5	11·8	96	35·2	5·0	1149	35·4	674
$U(O{\cdot}CHMePr^i)_5$	6·5	10·0	7·5	80	35·9	5·1	1063	35·4	674
$U(O{\cdot}CMe_2Et)_5$	5·5	12·0	7·2	90	35·6	5·0	849	35·4	674
$U(O{\cdot}CMe_2Pr^n)_5$	3·5	10·2	5·4	96	31·9	5·0	956	32·0	744
$U(O{\cdot}CMe_2Pr^i)_5$	4·0	8·0	6·3	98	31·9	5·0	—	32·0	744
$U(O{\cdot}CMeEt_2)_5$	6·5	12·0	9·0	86	32·7	5·1	817	32·0	744
$U(O{\cdot}CMeEtPr^i)_5$	4·4	10·0	6·9	89	28·9	5·1	825	29·2	814
$U(O{\cdot}CEt_3)_5$	9·2	16·0	14·8	90	30·3	5·1	820	29·2	814

* Ref. 1. † Ref. 5. ‡ Found: OPr^i, 54·8. Calc. for $C_{15}H_{35}O_5U$: OPr^i, 55·4%.

Reaction of uranium penta-t-butoxide–t-butyl alcohol (4·0 g.) with pyridine (6 ml.) in boiling benzene gave brown crystals of *uranium penta-t-butoxide–pyridine* (3·9 g.). The presence of pyridine was proved by gas–liquid chromatography on the products of hydrolysis and by infrared absorption measurements (we are indebted to Dr. C. Barraclough for these). The pyridine complex showed bands at 1600 and 700 cm.$^{-1}$ which are absent from the spectrum of $U(OBu^t)_5,Bu^tOH$, whilst the OH band at 3500 cm.$^{-1}$ in the latter was absent from the spectrum of the pyridine complex. Uranium penta-t-butoxoide–t-butyl alcohol was recovered unchanged after being boiled under reflux for 2 hr. with dry ether.

Uranium Penta-alkoxides.—Other *uranium penta-alkoxides* were prepared by reaction of uranium pentaethoxide with an excess of the appropriate alcohol in boiling benzene. The benzene–ethanol azeotrope, b. p. 68—69°, was removed by distillation, and complete reaction was indicated by the temperature reaching the b. p. of pure benzene. The excess of benzene was removed under reduced pressure, and uranium penta-alkoxides were purified by distillation or sublimation *in vacuo*. Analytical data are recorded in Table 3. The absence of residual ethoxy-groups was established by gas–liquid chromatographic examination of the alcohols produced on hydrolysis.

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