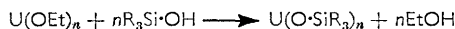


30. Organosiloxy-derivatives of Metals. Part II.¹ Trialkylsilyloxides of Quinquevalent and Sexivalent Uranium.

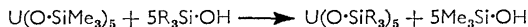
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Reaction of trialkylsilanols with uranium pentaethoxide or uranium hexaethoxide gives uranium pentakis- or hexakis-trialkylsilyloxides. The pentakis-trialkylsilyloxides have been prepared also from uranium pentakis-trimethylsilyloxide by silanol exchange. The physicochemical properties of these compounds are compared with those of the corresponding uranium t-alkoxides and tantalum pentakis-trialkylsilyloxides. The preparation of uranium hexakis-t-pentyloxide is reported.

TRIALKYL-SILYLOXIDES of titanium, zirconium, niobium, and tantalum were described by Bradley and Thomas:¹ the preparation and properties of uranium pentakis- and hexakis-trialkylsilyloxides are now reported. Almost quantitative yields of uranium trialkylsilyloxides were obtained from reactions of trimethyl-, ethyldimethyl-, diethylmethyl-, and triethyl-silanol with uranium pentaethoxide or hexaethoxide, the silanols being added slowly to solutions of uranium ethoxide in boiling benzene to avoid condensation. Ethanol was removed as an azeotrope with benzene, and water did not appear in the distillate.



An alternative preparation of the compounds $\text{U(O}\cdot\text{SiMeEt}_2)_5$ and $\text{U(O}\cdot\text{SiEt}_3)_5$ from uranium pentakis-trimethylsilyloxide involved reaction with the appropriate silanol in hexamethyldisiloxane. Trimethylsilanol, which forms an azeotrope with the solvent, was removed by distillation:



Uranium hexa-t-pentoxide was prepared from uranium hexaethoxide by reaction with t-pentyl alcohol in boiling benzene. Ethanol was removed by distillation as the benzene azeotrope.

Uranium trialkylsilyloxides are solids with interesting differences from uranium alkoxides. Colours, sublimation temperatures, and degrees of polymerization in boiling benzene are reported in Table I. Colours give no clear indication of valency, although as a rule uranium tetra-alkoxides are green, penta-alkoxides brown, and hexa-alkoxides red. Uranium trialkylsilyloxides are hydrolysed less readily than the corresponding alkoxides, probably because of the water-repelling property of trialkylsilyloxy-groups. Stability to water increases with increasing size of the alkyl groups.

TABLE I.

Uranium trialkylsilyloxides.

Compound	Colour	Sublimation (°/mm.)	<i>n</i> *	Compound	Colour	Sublimation (°/mm.)	<i>n</i> *
$\text{U(O}\cdot\text{SiMe}_3)_5$...	Yellow-brown	140—150°/0.1	1.77	$\text{U(O}\cdot\text{SiMe}_3)_6$...	Orange	145—150°/0.1	1.05
$\text{U(O}\cdot\text{SiMe}_2\text{Et})_5$	Yellow-brown	155°/0.1	1.31	$\text{U(O}\cdot\text{SiMe}_2\text{Et})_6$	Orange	160—165°/0.1	0.98
$\text{U(O}\cdot\text{SiMeEt}_2)_5$	Orange	160°/0.1	1.13	$\text{U(O}\cdot\text{SiMeEt}_2)_6$	Red	175°/0.1	1.00
$\text{U(O}\cdot\text{SiEt}_3)_5$...	Green-brown	170—180°/0.1	1.00	$\text{U(O}\cdot\text{SiEt}_3)_6$...	Red	195°/0.05	0.97

* *n* = degree of polymerization.

Replacement of carbon by silicon has a noticeable effect on the volatility and degree of polymerization. Trialkylsilanols are more acidic than alcohols because of π -bonding between oxygen and silicon, and metal derivatives are more salt-like than corresponding derivatives of tertiary alcohols. The degree of polymerization depends on the size of the central metal atom and the size and shape of surrounding groups. Silicon is larger than

¹ Part I, Bradley and Thomas, *J.*, 1959, 3404.

carbon, but trialkylsilyl groups in trialkylsilyloxides are further from the central metal atom and provide less shielding than do alkyl groups in tertiary alkoxides.

Degrees of polymerization of uranium pentakistrialkylsilyloxides decrease as expected on steric grounds with increasing size of the alkyl groups. Uranium pentakistriethylsilyloxide and pentakistriethylmethoxide are monomeric in boiling benzene, but other pentakistrialkylsilyloxides are more polymeric than the corresponding penta-t-alkoxides. Sublimation temperatures of uranium trialkylsilyloxides increase with increasing molecular size, but a comparison of pentakis with hexakis derivatives reveals the effect of polymerization on volatility. Thus, for monomeric compounds the pentakis should be more volatile than the hexakis derivative, and this is so for the triethylsilyloxy-compounds. In the trimethylsilyloxy-compounds the polymerization in the pentakis derivative causes that compound to be comparable in volatility with the monomeric hexakis derivative.

TABLE 2.

Uranium penta-t-alkoxides and tantalum pentakistrialkylsilyloxides.

Uranium cpds.*	B. p./mm.	<i>n</i>	Tantalum *	B. p./mm.	<i>n</i>
U(O·CMe ₃) ₅	120—130°/0·1	1·35	Ta(O·SiMe ₃) ₅	84°/0·05	1·08
U(O·CMe ₂ Et) ₅	130—140°/0·1	1·26	Ta(O·SiMe ₂ Et) ₅	135°/0·1 †	0·98
U(O·CMeEt ₂) ₅	200°/0·1	1·09	Ta(O·SiMeEt ₂) ₅	170°/0·1 †	1·00
U(O·CEt ₃) ₅	210°/0·1	1·00	Ta(O·SiEt ₃) ₅	210°/0·1 †	0·98

* Note: r (U) = 1·421 Å; r (Ta) = 1·343 Å (Moeller, "Inorganic Chemistry," John Wiley, New York, 1952, pp. 150, 893). † Sublimes.

Data for uranium penta-t-alkoxides and tantalum pentakistrialkylsilyloxides are shown in Table 2. Tantalum, being smaller than uranium, is better shielded by a given trialkylsilyloxy group and all the tantalum compounds are monomeric. Nevertheless, a comparison of the volatilities of tantalum and uranium pentakistrialkylsilyloxides shows some interesting effects. In the monomeric compounds intermolecular forces are predominantly due to the peripheral methyl groups, and the identity of the metal atom is obscured. This should result in similar volatilities for tantalum and uranium compounds with the possibility that the mass-entropy effect will cause the heavier molecule to be more volatile.² Polymerization will lower the volatility and this is clearly the reason why the trimethylsilyloxy- and dimethylethylsilyloxy-derivatives of uranium are less volatile than the corresponding tantalum compounds. The diethylmethylsilyloxy-derivative of uranium, although slightly polymeric, appears to be more volatile than the monomeric tantalum compound, suggesting that the mass-entropy effect is decisive. Both triethylsilyloxy-derivatives are monomeric, and the higher volatility of the uranium compound must be due to the mass-entropy effect. Further evidence of the latter is revealed by a comparison of uranium penta-t-alkoxides with uranium pentakistrialkylsilyloxides: in the monomeric compounds U(O·CEt₃)₅ and U(O·SiEt₃)₅ the triethylsilyloxy, having the larger mass, is more volatile. Similarly with the slightly polymeric compounds U(O·CMe₂Et)₅ and U(O·SiMe₂Et)₅ the heavier species is the more volatile. However, as the degree of polymerization becomes greater, the mass-entropy effect is obscured by the greater effects of intermolecular bonding, and hence the compound U(O·SiMe₃)₅ with a higher degree of polymerization than U(O·CMe₃)₅ is the less volatile.

The uranium hexakistrialkylsilyloxides, the first sexicovalent siloxy-derivatives, are monomeric, and volatility decreases, as expected, with increase in molecular size. The compound U(O·SiMe₃)₆ is less volatile than the monomeric U(O·CMe₃)₆ (sublimes at 85°/0·01 mm.³ or 100°/0·1 mm.⁴), and U(O·SiMe₂Et)₆ is less volatile than U(O·CMe₂Et)₆

² Bradley, *Nature*, 1954, **174**, 323.

³ Bradley, Amar K. Chatterjee, and Amiyar K. Chatterjee, *J. Inorg. Nuclear Chem.*, 1959, **12**, 71.

⁴ Bradley, Kapoor, and Smith, *J. Inorg. Nuclear Chem.*, in the press.

(sublimes at 120°/0.1 mm.), and it is surprising that the mass-entropy effect is not apparent in these systems.

EXPERIMENTAL

Uranium Alkoxides.—Uranium pentaethoxide,^{4,5} a mobile brown liquid, b. p. 180°/0.1 mm., was prepared from uranium tetrachloride and sodium ethoxide by oxidation with bromine. Uranium hexaethoxide⁶ was obtained as a deep red mobile liquid, b. p. 140°/0.1 mm., from uranium pentaethoxide, sodium ethoxide, and benzoyl peroxide (Found: U, 46.1; OEt, 52.2. Calc. for C₁₂H₃₀O₆U: U, 46.8; OEt, 53.2%).

Uranium hexaethoxide reacted with t-pentyl alcohol in boiling benzene (4 hr.), and the ethanol-benzene azeotrope and the excess of benzene were removed by distillation. Sublimation at 120°/0.1 mm. gave red crystals of *uranium hexakis-t-pentylsiloxide* (Found: U, 31.9. C₃₀H₆₆O₆U requires U, 31.1%).

Silanols.—Trimethylsilanol was prepared from trimethylfluorosilane by the method of Sommer, Pietrusza, and Whitmore;⁷ the other trialkylsilanols were prepared by alkaline hydrolysis of trialkylchlorosilanes.¹

Uranium Trialkylsilyloxides.—Trialkylsilanols (10% excess) in benzene (20 ml.) were added during 3 hr. to uranium pentaethoxide or hexaethoxide in boiling benzene (150 ml.). The ethanol-benzene azeotrope was removed continuously until the temperature of condensing solvent reached the b. p. of benzene. The excess of solvent was removed, and *uranium trialkylsilyloxides* were sublimed *in vacuo*. Preparative and analytical data are reported in Table 3. No trace of ethoxide was found in the products.

TABLE 3.

Preparation of uranium trialkylsilyloxides.

	U(OEt) ₅ (g.)	Silanol (g.)	Product		Found				Required		
			(g.)	(%)	U (%)	Si (%)	Valency	M	U (%)	Si (%)	M
U(O·SiMe ₃) ₅	10.4	12.2	15.4	100	34.4	20.0	5.0	1211	34.8	20.4	684
U(O·SiMe ₂ Et) ₅ ...	9.8	12.8	14.1	90	31.6	18.6	5.0	988	31.6	18.3	753
U(O·SiMeEt ₂) ₅ ...	8.0	12.5	13.2	93	28.4	17.25	5.0	933	28.9	17.0	824
U(O·SiEt ₃) ₅	7.65	12.0	14.2	98	26.4	15.8	5.0	896	26.6	15.7	894
	U(OEt) ₆ (g.)										
U(O·SiMe ₃) ₆	3.0	3.5	3.8	85	31.2	21.7		812	30.8	21.8	773
U(O·SiMe ₂ Et) ₆ ...	2.6	3.8	4.3	98	28.0	19.6		840	28.9	19.7	857
U(O·SiMeEt ₂) ₆ ...	3.8	6.0	6.8	95	25.3	17.6		947	25.3	17.9	941
U(O·SiEt ₃) ₆	2.9	5.2	5.3	92	23.5	16.3		991	23.2	16.4	1025

Triethylsilanol (4.0 g.) in hexamethyldisiloxane (15 ml.) was added during 2 hr. to uranium pentakis-trimethylsilyloxide (3.2 g.) in boiling hexamethyldisiloxane (60 ml.). The trimethylsilanol-hexamethyldisiloxane azeotrope was removed continuously until the temperature reached the b. p. of hexamethyldisiloxane. A brown solid crystallized on cooling. Sublimation at 170—180°/0.1 mm. gave greenish-brown crystals of *uranium pentakis-triethylsilyloxide* (4.0 g., 95%) which recrystallized from hexamethyldisiloxane (Found: Si, 15.8; U, 26.7%; Valency, 5.0. C₃₀H₇₅O₅Si₅U requires Si, 15.7; U, 26.6%).

Uranium pentakisdieethylmethylsilyloxide was obtained similarly as orange crystals which sublimed at 160°/0.1 mm. (Found: Si, 17.0; U, 28.8%; Valency, 5.0. C₂₅H₆₅O₅Si₅U requires Si, 17.0; U, 28.9%).

Analyses.—*Uranium.* Uranium silyloxides were dissolved in ethanol in a platinum crucible. Ammonia was added, and volatile silanols were removed by heating with an infrared lamp. The residue was ignited to U₃O₈. The valency of uranium was established by double oxidation with ceric sulphate solution.⁸

⁵ Jones, Bindschadler, Karmas, Yoeman, and Gilman, *J. Amer. Chem. Soc.*, 1956, **78**, 4287.

⁶ Jones, Bindschadler, Blume, Karmas, Martin, Thirtle, and Gilman, *J. Amer. Chem. Soc.*, 1956, **78**, 6030.

⁷ Sommer, Pietrusza, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 2282.

⁸ Bradley, Chakravarti, and Chatterjee, *J. Inorg. Nuclear Chem.*, 1957, **3**, 367.

Silicon. Ammonium nitrate and ammonium sulphate were added to uranium siloxides dissolved in concentrated sulphuric acid. The mixture was evaporated to dryness, poured into water, and filtered through a Whatman No. 41 filter paper which was transferred with its contents to a platinum crucible and ignited by a Meker burner. Silicon was weighed as SiO_2 .

Alkoxy-groups. Alkoxy-groups were estimated volumetrically with chromic acid.⁹

Molecular weights. Molecular weights were measured ebullioscopically in benzene. The apparatus was calibrated internally with fluorene.¹⁰

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⁹ Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

¹⁰ Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977; Bradley, Wardlaw, and Whitley, *J.*, 1956, 5.
