

### Tertiary Alkoxides of Thorium.

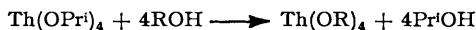
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The thorium alkoxides,  $\text{Th}(\text{OR})_4$  ( $\text{R} = \text{CMe}_3$ ,  $\text{CMe}_2\text{Et}$ ,  $\text{CMeEt}_2$ ,  $\text{CEt}_3$ ,  $\text{CMe}_2\text{Pr}^n$ ,  $\text{CMe}_2\text{Pr}^i$ ,  $\text{CMeEtPr}^n$ , and  $\text{CMeEtPr}^i$ ) were prepared from  $\text{Th}(\text{OPr}^i)_4$  by alcohol interchange. The molecular weights in benzene (ebullioscopic method) and boiling points under reduced pressure were determined. The results are discussed in terms of the stereochemical theory advanced to account for the properties of the alkoxides of other Group IVA elements.

THE new alkoxides of thorium,  $\text{Th}(\text{OR})_4$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{Pr}^i$ ), which we recently (*J.*, 1954, 1091) prepared were complex non-volatile solids whose alkaline reaction suggested the presence of considerable ionic character. In view of the stereochemical theory developed to explain the remarkable physicochemical properties of the alkoxides of titanium, zirconium, and hafnium (Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027, 4204, 5020; 1953, 1634, 2025) it was considered desirable to investigate the tertiary alkoxides of thorium also.

Eight new alkoxides  $\text{Th}(\text{OR})_4$  (see Table 1) were prepared by alcohol interchange involving thorium tetra*isopropoxide* and the appropriate alcohol :



Molecular weights were determined ebullioscopically in benzene and, where possible, boiling points were measured under reduced pressure. The data, including the calculated molecular complexities ( $\alpha = M/\text{formula weight}$ ), are recorded in Table 1.

TABLE 1.

R in $\text{Th}(\text{OR})_4$	B. p./mm.	M	$\alpha$
$\text{CMe}_3$ .....	160°/0.1 (subl.)	1787	3.4
$\text{CMe}_2\text{Et}$ .....	208°/0.3	1601	2.8
$\text{CMeEt}_2$ .....	148°/0.1	1156	1.8
$\text{CMe}_2\text{Pr}^n$ .....	Decomp. >120°/0.1	1653	2.6
$\text{CMe}_2\text{Pr}^i$ .....	"	1444	2.3
$\text{CEt}_3$ .....	148°/0.05	714	1.0
$\text{CMeEtPr}^n$ .....	153°/0.1	1171	1.7
$\text{CMeEtPr}^i$ .....	139°/0.05	709	1.0

The thorium derivative of ethylmethyl*isopropyl*carbinol (1-ethyl-1 : 2-dimethylpropanol) appears to be the most volatile organic compound of thorium yet recorded and several of the other compounds listed in Table 1 are more volatile than the thorium-tetraacetylacetone complex, the only other volatilisable organic thorium compound hitherto reported.

It is evident in Table 1 that the volatility and molecular complexity of thorium alkoxides are determined by the size and shape of the alkyl group. There can be little doubt that this behaviour is predominantly the result of stereochemical effects. Thus there will be only minor variations in electronic effect from one alkyl group to another because they are all tertiary alkyls. Moreover, the molecular complexities decrease with increase in size of the alkyl group and this behaviour is consistent with the stereochemical theory previously advanced to account for the behaviour of the alkoxides of silicon, titanium,

zirconium, and hafnium. This theory suggests that intermolecular bonding  $M \cdots O$  involving the central atom  $M$  ( $= Ti, Zr,$  or  $Hf$ ) and oxygen from a neighbouring alkoxide group gives rise to complex non-volatile alkoxides. In the monomeric alkoxides the central atom is shielded by the rotation of the branched alkoxide groups, intermolecular attraction is minimised, and the compounds are relatively volatile. The theory was supported by a comparison of the behaviour of the alkoxides of silicon, titanium, zirconium, and hafnium. This showed that the size of the central atom controlled the effectiveness of an alkoxide group in shielding. Thus the effect of chain branching on volatility was much greater in the case of zirconium (or hafnium) than in titanium and least for silicon. Thorium, whose atomic radius is the largest of the Group IVA elements, gives alkoxides with properties which accord with these stereochemical requirements. The contrast in the properties of thorium, zirconium, titanium, and silicon alkoxides is demonstrated in Table 2, which contains the boiling points ( $^{\circ}C$  at 0.1 mm.) and molecular complexities (in parentheses) of selected compounds having an increasing degree of chain branching of the alkyl group.

TABLE 2.

	Si	Ti	Zr	Th
Atomic radius, Å .....	1.17	1.36	1.48	1.65
Alkoxide				
$O \cdot CH_2Me$ .....	$-15^{\circ} * (1.0)$	$102^{\circ} (2.4)$	$180^{\circ} (3.4)$	Non-volatile
$O \cdot CHMe_2$ .....	$15 (1.0)$	$49 (1.4)$	$160 (3.0)$	$210^{\circ} (3.8)$
$O \cdot CMe_3$ .....	—	$52 (1.0)$	$50 (1.0)$	$160 (3.4)$
$O \cdot CMeEt_2$ .....	—	$128 (1.0)$	$128 (1.0)$	$148 (1.8)$
$O \cdot CEt_3$ .....	—	$166 (1.0)$	$166 (1.0)$	$154 (1.0)$

\* Calculated.

An interesting feature of Table 2 is the behaviour of the monomeric tertiary  $C_7$ -alkoxides of titanium, zirconium, and thorium. Their boiling points are close together, suggesting that they have similar molar heats of vaporisation because the effect of the central atom has been obviated by the screen of organic groups. This emphasises the powerful effect of highly branched alkoxide groups in shielding a central atom. Thus, in addition to suppressing the intermolecular attraction involving the central atom and oxygen, it appears that the contribution due to the marked ionic character in the thorium alkoxide is also nullified.

## EXPERIMENTAL

The special precautions to avoid hydrolysis reported earlier (*J.*, 1954, 1091) were observed and, owing to the sensitivity of thorium tertiary alkoxides to oxygen, experiments were con-

TABLE 3.

R	Th(OPr) <sub>4</sub> taken (g.)	ROH taken (g.)	C <sub>6</sub> H <sub>6</sub> (ml.)	Yield of Th(OR) <sub>4</sub> (g.)	Th (%)	
					Found	Reqd.
$CMe_3$ .....	5.22	ca. 150 *	ca. 350 *	5.6 <sup>a</sup>	45.15	44.25
$CMe_2Et$ .....	8.4	10.8	70	10.3 <sup>b</sup>	40.85	40.0
$CMeEt_2$ .....	7.6	8.44	57.4	10.4 <sup>a</sup>	36.7	36.4
$CMe_2Pr^a$ .....	6.7	10.22	56	8.14 <sup>c</sup>	36.95	„
$CMe_2Pr^i$ .....	4.07	6.12	55	5.04 <sup>c</sup>	37.15	„
$CEt_3$ .....	4.0	8.29	60	5.63 <sup>d</sup>	33.7	33.5
$CMeEtPr^a$ .....	4.7	6.5	60	7.0 <sup>c</sup>	34.1	„
$CMeEtPr^i$ .....	6.9	8.0	60	10.4 <sup>c</sup>	33.0	„

\* Added in 3 stages.

<sup>a</sup> White solid. <sup>b</sup> Viscous liquid. <sup>c</sup> Very viscous liquid. <sup>d</sup> Mobile liquid.

TABLE 4.

R in Th(OR) <sub>4</sub>	Solute, range of wts. (g.)	Benzene (g.)	R in Th(OR) <sub>4</sub>	Solute, range of wts. (g.)	Benzene (g.)
$CMe_3$ .....	0.120—1.159	15.72	$CMe_2Pr^i$ .....	0.168—1.135	17.28
$CMe_2Et$ .....	0.170—1.942	16.30	$CEt_3$ .....	0.219—1.324	16.21
$CMeEt_2$ .....	0.112—0.993	16.71	$CMeEtPr^a$ .....	0.219—0.795	14.82
$CMe_2Pr^a$ .....	0.282—1.201	17.84	$CMeEtPr^i$ .....	0.138—0.922	14.20

ducted in the presence of oxygen-free nitrogen. Otherwise the apparatus and experimental technique used were similar to those described by Bradley, Mehrotra, and Wardlaw (*loc. cit.*);

accordingly the experimental details are presented only in Table 3. The molecular-weight determinations are given in Tables 1 and 4. No evidence of variation of molecular complexity with concentration of solute was observed within the ranges of concentration reported.

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