330. *Hafnium Alkoxides.*

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The alkoxides of hafnium, $Hf(OR)_4$, where R = Me, Et, Pr^i, Bu^t, and *tert.*-amyl, have been prepared; their boiling points are lower than those of the corresponding zirconium compounds. Hafnium *tert.*-amyloxide has a slightly higher latent heat and entropy of vaporisation and a greater molecular volume than the zirconium analogue. The relative volatilities of zirconium and hafnium alkoxides are discussed.

THE need for hafnium-free zirconium has given a fresh impetus to the study of the chemistry of hafnium. Previous investigation of the comparative chemistry of these elements has been handicapped by the complex nature of their compounds in aqueous solution (cf. Lister and McDonald, *J.*, 1952, 4315). However, by operating in non-aqueous solutions, alkoxides of zirconium and hafnium have been isolated, and their properties suggest a promising means of separation of zirconium and hafnium. In addition, it appeared from the results of fractional distillation (Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204) that hafnium *tert.*-amyloxide must be more volatile than its zirconium analogue and this unexpected order of volatilities clearly required further investigation in view of its theoretical importance.

The following alkoxides of hafnium were prepared: $Hf(OR)_4$ where R = Me, Et, Pr^i, Bu^t, and *tert.*-amyl. The tetraethoxide and the tetra*iso*propoxide, $Hf(OPr^i)_4,Pr^iOH$, were obtained by the action of ammonia on pyridinium hafnium hexachloride in benzene in the presence of the appropriate alcohol:

$$(C_5H_6N)_2HfCl_6 + 4ROH + 6NH_3 \longrightarrow Hf(OR)_4 + 6NH_4Cl + 2C_5H_5N$$

The tetramethoxide and the tetra-*tert.*-amyloxide were obtained by interchange of alkoxy-groups with the *iso*propoxide. The action of *tert.*-butyl alcohol on the tetramethoxide gave a solid hafnium methoxide *tert.*-butoxide [probably $Hf(OMe)(OBu^t)_3$] which disproportionated on being heated, forming some hafnium tetra-*tert.*-butoxide. The boiling points of hafnium alkoxides and analogous zirconium compounds are given below:

Alkyl (R)	B. p. of $Hf(OR)_4$	B. p. of $Zr(OR)_4$
Ethyl	180—200°/0·1 mm.	180—200°/0·1 mm.
*iso*Propyl	170°/0·35 mm.	172°/0·35 mm.*
tert.-Butyl	90°/6·5 mm.	92·5°/6·0 mm.
tert.-Amyl	92°/0·1 mm. †	95°/0·1 mm.

* Calc. from 160°/0·1 mm. † Calc. from 106°/0·5 mm.

It is evident that the molecular complexity of hafnium alkoxides must be the same as that of the analogous zirconium derivatives. An important feature of this table is the fact that in no case is a hafnium alkoxide less volatile than its zirconium analogue. The data for the *tert.*-amyloxides confirm the order of volatility Hf > Zr deduced previously (*loc. cit.*, p. 4204).

As a result of b. p. measurements in the pressure range 2·0—10·0 mm. Hg on the *tert.*-amyloxide the latent heat (L_v) and entropy of vaporisation at 5 mm. pressure ($\Delta S_{5\cdot0}$) have been calculated. These results are shown below together with the density ρ (g./c.c) and molar volume (V_l c.c.) at 25°. It is not surprising to find the close similarity in latent heat, entropy of vaporisation, or molar volume for these two compounds since the chemical similarity of zirconium and hafnium is well established. However, the order of volatilities Hf > Zr demands examination. It follows from the Clausius–Clapeyron equation that the relative volatility $P_{\text{Zr}}/P_{\text{Hf}}$ over a small temperature range will take the form :

Alkoxide	$T_{5\cdot0}$	L	a	b	$\Delta S_{5\cdot0}$	ρ	V_l
$Zr(O\cdot CMe_2Et)_4$	138·4°	16·2	9·34	3550	39·5	0·975	451·1
$Hf(O\cdot CMe_2Et)_4$	136·7°	16·3	9·41	3570	39·8	1·159	454·5

$$\log_{10} P_{\text{Zr}}/P_{\text{Hf}} = (a_{\text{Zr}} - a_{\text{Hf}}) - (b_{\text{Zr}} - b_{\text{Hf}})/T$$

In the case where $b_{\text{Zr}} \simeq b_{\text{Hf}}$ the temperature-independent terms a_{Zr} and a_{Hf} will assume major importance. It is noteworthy that for the relative volatilities P_1/P_2 of solid monatomic compounds the difference between the temperature-independent terms a_1 and a_2 can be calculated by the method of statistical thermodynamics and reduces to the simple form $a_1 - a_2 = \frac{3}{2} \log_{10} M_1/M_2$, where M_1 and M_2 are the molecular weights. Hence for $b_1 = b_2$ it follows that $\log_{10} P_1/P_2 = \frac{3}{2} \log_{10} M_1/M_2$ and the substance with the greater molecular weight is the more volatile. For polyatomic molecules $a_1 - a_2$ will exceed $\frac{3}{2} \log_{10} M_1/M_2$ by an amount which is determined by a function of the ratios of the various moments of inertia, *e.g.*, $\frac{1}{2} \log_{10} (I_A \times I_B \cdots I_H/I_P \times I_Q \cdots I_2)$, and whose complexity depends on the number and arrangements of atoms in the molecule. Since molecular weight is included in the moment of inertia, it is evident that in polyatomic molecules (with $b_1 = b_2$) there is a possibility that this " molecular-weight effect " will enhance the greater volatility of the compound with higher molecular weight.

With regard to the *tert.*-amyloxides of zirconium and hafnium, our data show $b_{\text{Hf}} > b_{\text{Zr}}$ and $a_{\text{Hf}} > a_{\text{Zr}}$, which suggests that in spite of greater intermolecular attraction in the hafnium compound its higher molecular weight leads to a greater volatility. However, it is realised that a variation of 1% would reverse the orders to $a_{\text{Zr}} > a_{\text{Hf}}$ and $b_{\text{Zr}} > b_{\text{Hf}}$ and more accurate vapour-pressure determinations (now in progress) are required before a confident explanation for the observed volatility order can be advanced. It is noteworthy that in the borohydrides $M(BH_4)_4$ (Hoekstra and Katz, *J. Amer. Chem. Soc.*, 1949, **71**, 2488), which are the most volatile known compounds of zirconium or hafnium, the hafnium compound is the more volatile and again $a_{\text{Hf}} > a_{\text{Zr}}$ and $b_{\text{Hf}} > b_{\text{Zr}}$. Moreover, the relative volatility $P_{\text{Hf}}/P_{\text{Zr}}$ is greater in the borohydrides where $M_{\text{Hf}}/M_{\text{Zr}} = 1\cdot58$ than in the *tert.*-amyloxides where $M_{\text{Hf}}/M_{\text{Zr}} = 1\cdot18$, in qualitative agreement with the above theory.

EXPERIMENTAL

All-glass apparatus was used and special precautions were taken to exclude moisture. The methods of analysing the alkoxides and of purifying and drying solvent and alcohols were the same as previously described (*loc. cit.*). Boiling-point determinations were carried out in the same apparatus under the same conditions as for the zirconium compounds. A micro-dilatometer (0·65 c.c.) containing two vertical calibrated " Veridia " capillaries (bore 1 mm.) was used for density determinations. The alkoxides were collected in the dilatometer by distillation at 0·1 mm.

Preparation of Pyridinium Hafnium Hexachloride from Hafnia.—Hafnium oxide (10·0 g.) was fused with potassium hydrogen sulphate (145 g.), and the cooled clear melt dissolved in water. Hafnium hydroxide (precipitated by ammonia solution, *d* 0·88) was dissolved in the minimum amount of hydrochloric acid (*d* 1·18), and hydrated hafnium oxychloride obtained by evaporation. The oxychloride (15·2 g.) in ethyl alcohol (200 c.c.) was treated with excess of hydrogen chloride followed by pyridine (8·0 g.). The crystalline *pyridinium hafnium hexachloride* (20·8 g.) was filtered off and dried at 120°/0·5 mm. [Found : Hf, 32·5; Cl, 38·4. $(C_5H_6N)_2HfCl_6$ requires Hf, 32·4; Cl, 38·6%].

Preparation of Hafnium iso*Propoxide.*—The complex hafnium chloride (20·2 g.), suspended in benzene (134 g.) and *iso*propyl alcohol (26·5 g.), was treated with excess of ammonia. After removal of ammonium chloride, the solution was evaporated to dryness, and the product heated at 120°/0·5 mm. The solid (9·4 g.) was crystallised from boiling *iso*propyl alcohol (130 c.c.), and the crystalline hafnium *iso*propoxide *solvate* (9·0 g.) obtained was dried at 40°/0·5 mm. [Found: Hf, 37·8. $Hf(OPr^i)_4,Pr^iOH$ requires Hf, 37·6%]. The foregoing product lost *iso*propanol at 120—130°/0·5 mm. and *hafnium tetra*iso*propoxide* was obtained by distillation (b. p. 170°/0·35 mm., 188°/2·5 mm.) as a colourless solid (6·0 g.) [Found: Hf, 43·1. $Hf(OPr^i)_4$ requires Hf, 43·1%].

Hafnium Tetraethoxide.—The complex hafnium chloride (11·6 g.), suspended in benzene (80 c.c.), was treated with ethyl alcohol (39·5 g.) and excess of ammonia. After removal of ammonium chloride, the solution was evaporated under reduced pressure and gave a white solid, which was heated at 160°/0·2 mm. to remove traces of pyridine. The *ethoxide* melted at *ca.* 180°/0·2 mm. and was distilled in the range 180—200°, giving a white solid distillate (7·1 g.) [Found: Hf, 50·1. $Hf(OEt)_4$ requires Hf, 49·8%].

Hafnium Tetramethoxide.—Addition of methyl alcohol (50 c.c.) to a solution of hafnium *iso*propoxide (6·7 g.) in benzene (100 c.c.) caused immediate precipitation of a white solid. The mixture was heated at 70—80° for 8 hr., and the solvent removed by evaporation. The *hafnium methoxide* was dried at 160°/0·1 mm. for 2 hr. and, like zirconium methoxide, was found to be insoluble in the common organic solvents [Found: Hf, 59·0. $Hf(OMe)_4$ requires Hf, 59·0%].

Hafnium Tetra-tert.*-butoxide.*—Hafnium methoxide (6·7 g.) was heated at 140° with *tert.*-butyl alcohol (27 g.) in benzene under an efficient fractionating column fitted with a total-condensation variable take-off still-head. The methoxide required 6 hr. to dissolve completely and fractionation was continued for a further 8 hr. After removal of solvent the remaining solid was heated at 8—9 mm. and melted at 120°. The liquid started refluxing at 200—220° and a colourless mobile liquid was distilled at 250°. This distillate was redistilled (b. p. 90°/6·5 mm.) and proved to be *hafnium* tert.*-butoxide* [Found: Hf, 38·1. $Hf(OBu^t)_4$ requires Hf, 37·9%].

Hafnium Tetra-tert.*-amyloxide.*—Hafnium tetra*iso*propoxide (9·3 g.) was treated with *tert.*-amyl alcohol (12·7 g.) in benzene (67 g.) at 140° until no more benzene–*iso*propyl alcohol azeotrope was collected by fractionation. The *hafnium* tert.*-amyloxide* which remained after the removal of solvent was distilled (b. p. 91°/0·1 mm.) and gave a colourless mobile distillate (8·6 g.) [Found: Hf, 33·9. $Hf(OC_5H_{11})_4$ requires Hf, 33·9%]; b. p.s were 106°/0·5; 123°/2·2; 125·5°/2·5; 130°/3·5; 134°/4·5; 139°/5·6; 140°/6·0; 142°/6·8; 146°/8·0; 148°/8·8; 149·5°/9·5; 150°/10·0 mm. Densities determined at 25·00° on this compound and on zirconium *tert.*-amyloxide were: $Hf(OC_5H_{11})_4$, $\rho = 1{\cdot}159 \pm 0{\cdot}003$ g./c.c. $Zr(OC_5H_{11})_4$, $\rho = 0{\cdot}975 \pm 0{\cdot}002$ g./c.c.

Spectrographic analysis showed that the sample of hafnium oxide used for this work contained: HfO_2, 98·5; ZrO_2, *ca.* 1·5%. We thank Mr. F. Hudswell, of A.E.R.E., Harwell, for conducting this analysis.

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