Volatile Double Alkoxides of Hafnium

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Volatile double ethoxides and isopropoxides, $MHf_2(OR)_9$ and $M_2Hf_3(OR)_{14}$, of hafnium with alkali metals (M = Li, Na, or K) and $KHf(OBu^t)_5$ have been synthesised. Alcoholysis reactions of the double isopropoxides have been studied. Volatile double isopropoxides, $HfM(OPr^i)_7$ and $HfM_2(OPr^i)_{10}$, have also been prepared (M = Al or Ga). The i.r. and n.m.r. spectra of the compounds have been recorded.

ALTHOUGH double alkoxides of zirconium with alkali metals, $MZr_2(OR)_9$ and $M_2Zr_3(OR)_{14}$ (M = Li, Na, or K) have been synthesised,[1,2] the corresponding hafnium compounds have not been reported. In view of the greater stability of tantalum double alkoxides $MTa(OR)_6$ compared with those of niobium,[3] it was of interest to synthesise the hafnium double alkoxides.

RESULTS AND DISCUSSION

Hafnium isopropoxide reacted with alkali-metal isopropoxides (M = Li, Na, or K) in 2 : 1 and 1 : 1 molar ratios to give $MHf_2(OPr^i)_9$ and $M_2Hf_3(OPr^i)_{14}$ respectively.

All the compounds sublimed at 180—200°/0·5 mmHg and were monomeric in boiling benzene. Since the molar conductivities of $Hf(OPr^i)_4,Pr^iOH$, $NaHf_2(OPr^i)_9$, $Na_2Hf_3(OPr^i)_{14}$, and $NaOPr^i$ in isopropyl alcohol were *ca.* 0·05, 0·2, 1·0, and 25 Ω^{-1} respectively, we carried out conductometric titrations of hafnium isopropoxide in isopropyl alcohol. Addition of alkali isopropoxide (Na or K) in isopropyl alcohol hardly affected the conductance until the molar ratio of the added alkali isopropoxide was half that of the hafnium isopropoxide in solution; this confirmed the covalent nature of the product $MHf_2(OPr^i)_9$. Beyond this point, the conductivity curve rose sharply. Neither the Na or K reaction showed an inflexion corresponding to $MHf_3(OPr^i)_{14}$. Hafnium ethoxide reacted with potassium ethoxide in ethanol to give similar volatile products which were monomeric in boiling benzene. In contrast hafnium t-butoxide on reaction with potassium t-butoxide in 2 : 1 or 1 : 1 molar ratio gave a volatile product with the formula $KHf(OBu^t)_5$; it showed an average association of 1·5 in refluxing benzene.

Both $KHf_2(OPr^i)_9$ and $K_2Hf_3(OPr^i)_{14}$ exchanged all their isopropoxy-groups on treatment with an excess of butanol. In contrast, on treatment with an excess of t-butyl alcohol in the presence of benzene only partial exchange took place; the products had analyses corresponding to $KHf_2(OPr^i)_4(OBu^t)_5$ and $K_2Hf_3(OPr^i)_6(OBu^t)_8$. The t-butoxy-compounds tended to disproportionate when heated under reduced pressure.

Reaction of hafnium isopropoxide with aluminium isopropoxide in 1 : 4 molar ratio in isopropyl alcohol and removal of solvent gave upon distillation under reduced pressure $Al(OPr^i)_3$, followed by a mixture of $HfAl_2(OPr^i)_{10}$ and $Al(OPr^i)_3$, and then $HfAl_2(OPr^i)_{10}$.

Reaction of hafnium and aluminium isopropoxides in 2 : 1 molar ratio gave upon work-up crystalline $Hf(OPr^i)_4,Pr^iOH$; this when treated gave $HfAl(OPr^i)_7$ (b.p. 151°/0·3 mmHg). Hafnium isopropoxide and gallium isopropoxide reacted similarly in isopropyl alcohol.

The 1 : 1 products appear to be almost dimeric whereas the 1 : 2 products show monomeric behaviour in boiling benzene.

Hafnium compounds, in general, are slightly more volatile than the corresponding zirconium analogues (*cf.* zirconium and hafnium alkoxides [4]).

N.m.r. and i.r. Spectra.—The n.m.r. spectra of hafnium isopropoxide–isopropyl alcohol and some typical double isopropoxides have been recorded in anhydrous carbon tetrachloride. The positions (in Hz from internal tetramethylsilane) of methyl proton peaks are summarised below:

Alkoxide	A	B	C	D	E	F	Area of the peaks
$Hf(OPr^i)_4,Pr^iOH$					74	68	1 : 1
$KHf_2(OPr^i)_9$			79	*a*	73	67	1 : 1 : 2 : 2
$LiHf_2(OPr^i)_9$			81	*a*	74·5	68	1 : 1 : 2 : 2
$K_2Hf_3(OPr^i)_{14}$			81	*a*	74·5	68	1 : 1 : 2·5 : 2·5
$Li_2Hf_3(OPr^i)_{14}$			81	*a*	75	69	1 : 1 : 2·5 : 2·5
$HfAl_2(OPr^i)_{10}$	84	78	75	*a*	65	62	2 : 2 : 1 : 1 : 2 : 2

[a] Peak D appears to be coincident with the obscured peak E.

The n.m.r. spectral characteristics can be interpreted in terms of bridged structures, similar to those proposed for other group III alkoxides,[5,6] which contain both bridging and terminal alkyloxy-groups.

The i.r. spectra of the new compounds were recorded and are deposited with the N.L.L. as Supplementary Publication No. 20362 (6 pp.).

EXPERIMENTAL

Materials.—Anhydrous hafnium chloride (Research Organic/Inorganic Chemical Corporation) and gallium chloride (Dr. Theodor Schuchardt) and aluminium isopropoxide (N.C.L., Poona) were used. Benzene (B.D.H.), isopropyl alcohol (B.D.H.), t-butyl alcohol (B.D.H.), n-butanol (B.D.H.), and ethanol were dried by usual techniques. The reactions were carried out with exclusion of moisture.

Preparations of Hafnium and Gallium Isopropoxide.—Gallium isopropoxide was prepared by the sodium method [7] (b.p. 130°/0·3 mm). Hafnium isopropoxide was prepared

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[3] R. C. Mehrotra and M. M. Agarwal, *J. Chem. Soc.* (*A*), 1968, 2673.

[4] D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 1953, 1634.

[5] V. J. Shiner (jun.), D. Whittaker, and V. P. Fernandez, *J. Amer. Chem. Soc.*, 1963, **85**, 2318.

[6] J. G. Oliver, P. K. Philips, and I. J. Worrall, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1609.

[7] S. R. Bindal, V. K. Mathur, and R. C. Mehrotra, *J. Chem. Soc.* (*A*), 1969, 863.

by the ammonia method[4] and purified by recrystallization. Hafnium was estimated as its oxide after ignition of the precipitated mandelate. Aluminium and gallium were estimated as their oxinates. The alkoxy-groups were estimated by oxidation with potassium dichromate.[8] A semimicro Gallenkamp ebulliometer with thermistor sensing was used for molecular-weight determinations. N.m.r. spectra were recorded with a Varian A-60 instrument, using anhydrous carbon tetrachloride as solvent.

Reaction of Hafnium Isopropoxide with Potassium Isopropoxide in 2 : 1 *Molar Ratio.*—Potassium isopropoxide [4·09 mg-atom of K in Pr^iOH (10 ml)] was added to a hafnium isopropoxide (8·40 mmol) solution. The clear solution was refluxed for 1 h; the solvent was removed and the residue was dried under reduced pressure. The white solid obtained sublimed at 180—190°/0·2 mmHg (75% yield).

Details of other reactions with various alkali metals and in different molar ratios which were carried out similarly (and analytical data, volatility, and molecular weights) have been deposited with the N.L.L. as Supplementary Publication no. 20362 (6 pp).*

Reactions of $KHf_2(OPr^i)_9$ *and* $K_2Hf_3(OPr^i)_{14}$ *with Butanol in an Excess of Benzene.*—Butanol (*ca.* 20 ml) was added to each of the double isopropoxides (*ca.* 1 g) dissolved in benzene (*ca.* 30 ml) and the solutions were continuously fractionated. Solvent was removed and the white solids which were obtained were dried; they sublimed at *ca.* 230—250° at 0·7 mmHg to give white sticky sublimates (82 and 60% respectively) [Found for $KHf_2(OBu^n)_9$: Hf, 33·9 (Calc. 33·9); and $K_2Hf_3(OBu)_{14}$: 32·75 (Calc. 32·7)].

Reaction of $KHf_2(OPr^i)_9$ *with an Excess of t-Butyl Alcohol in Benzene.*—An excess of t-butyl alcohol (*ca.* 30 ml) was added to a solution of potassium hafnium isopropoxide (1·58 g, 1·70 mmol) in benzene (*ca.* 40 ml) and the mixture was refluxed for 7 h; the isopropyl alcohol liberated was removed azeotropically until the distillate showed the absence of any alcohol. Excess of solvent was removed under reduced pressure; the residue was dried (yield 1·72 g, 1·73 mmol). Amount of isopropyl alcohol liberated was 0·50 g (8·37 mmol); the amount required for replacement of five isopropoxy-groups per mole of the double alkoxide is 0·51 g (8·48 mmol) [Found for $KHf_2(OPr^i)_4(OBu^t)_5$: Hf, 35·85; OPr^i, 23·0. Calc. for: Hf, 35·8; OPr^i, 23·7].

Reaction of $K_2Hf_3(OPr^i)_{14}$ *with an Excess of t-Butyl Alcohol in Benzene.*—An excess of t-butyl alcohol (*ca.* 20 ml) was added to a solution of potassium hafnium isopropoxide (1·05 g, 0·73 mmol) in benzene (*ca.* 70 ml) and the alcoholysis was carried out as above.

The yield of product was quantitative; the amount of isopropyl alcohol released corresponded to replacement of eight isopropoxy-groups [Found: Hf, 34·5; OPr^i, 22·8. Calc. for $K_2Hf_3(OPr^i)_6(OBu^t)_8$: Hf, 34·5; OPr^i, 22·85].

Reaction of Hafnium Isopropoxide with Aluminium Isopropoxide in 2 : 1 *Molar Ratio in Isopropyl Alcohol.*—Hafnium isopropoxide (4·16 mmol) and aluminium isopropoxide (2·08 mmol) were heated under reflux for 1 h in isopropyl alcohol (*ca.* 20 ml). Hafnium isopropoxide crystallized out (1·82 mmol) [Found: Hf, 38·75; OPr^i, 62·6. Calc. for $Hf(OPr^i)_4,Pr^iOH$: Hf, 37·6; OPr^i, 62·4]. The supernatant liquid was decanted off and then the solvent was removed; the residue was pumped under reduced pressure to leave a thick viscous liquid which slowly solidified (b. p. 151°/0·3 mmHg; 72% yield).

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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