line in the $AlBr_3$–NaBr or AlI_3–CsI system. In the case of AlI_3–CsI, especially at 67:33 mol %, there is only a hint of a peak (AlI_4^-) observed on the side of the $Al_2I_7^-$ peak, indicating the equilibrium strongly favors the $Al_2X_7^-$ ion at this concentration.

In the $AlBr_3$–NaBr melt (67:33 mol % sample), the ratio of the intensity of the peak at 209 cm^{-1} ($AlBr_4^-$) to the peak at 198 cm^{-1} ($Al_2Br_7^-$) increased as the temperature was raised from 220 to 250°. Quantitative measurements were not made, but the effect was reproducible. Since the equilibrium constant for the reaction $2AlCl_4^- \rightleftharpoons Cl^- + Al_2Cl_7^-$ increases with temperature,[16] this equilibrium may be eliminated as the cause of the above effect. A possible explanation is the increase in dissociation of $Al_2X_7^-$ with increasing temperature: $2Al_2X_7^- \rightleftharpoons 2AlX_4^- + Al_2X_6$. At the experimental temperature, Al_2X_6 is volatile and is present in the gas phase as well as in the melt.

[16] G. Torsi and G. Mamantov, unpublished results.

CONTRIBUTION FROM THE AIR FORCE MATERIALS LABORATORY, WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433, AND THE DEPARTMENT OF MATERIALS SCIENCE AND METALLURGICAL ENGINEERING, UNIVERSITY OF CINCINNATI, CINCINNATI, OHIO 45221

Hexafluoroisopropoxides of Aluminum and of Some Group IV Elements

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Covalent, fluoro-substituted isopropoxides of aluminum, silicon, germanium, titanium, zirconium, and hafnium have been synthesized by the reaction of appropriate anhydrous metal chlorides with sodium hexafluoroisopropoxide for possible use as catalysts for specific organic and various polymerization reactions. Chemical analysis, infrared spectra, mass spectrometric fragmentation data, proton and fluorine nuclear magnetic resonance, thermal gravimetric analysis, and vapor-phase chromatography were used to characterize these compounds. The hexafluoroisopropoxides of silicon and titanium were liquid and those of aluminum, germanium, zirconium, and hafnium were white crystalline solids. Thermal and hydrolytic decomposition was quantitative to the oxides.

Introduction

No significant reports of research on aluminum and group IV fluoro-substituted metal alkoxides have appeared in the literature. However, the use of anhydrous ammonia in the preparation of nonfluorinated group IVb, group V, uranium, and iron alkoxides was demonstrated by Nelles,[1] Bradley,[2] and Brown and Mazdiyasni.[3] Jones, *et al.*,[4] and Muller and Heinrich[5] prepared some uranium and germanium fluoro-substituted alkoxides by the same method. However, no chemical or analytical results were shown to indicate the absence of ammonia. Recently the ammonia method was extended to the preparation of 2,2,2-trifluoroethoxides of some group IV and group V elements[6] and to the preparation of 1,1,1,3,3,3-hexafluoroisopropoxides[7] of the same elements in two consecutive short notes.

Attempts to synthesize either aluminum or any of the group IV metal hexafluoroisopropoxides by the method of ref 6 and 7 produced only poor yields and the products contained metal, fluorinated alkoxides, and in most instances two molecules of ammonia. It was reasoned that diammoniates of the pure metal fluoroalkoxide form instead of the uncomplexed metal fluoroalkoxides. Ammonia is apparently bonded strongly enough to prevent its loss during vacuum sublimation or fractional distillation at relatively high temperatures. Because ammoniates of the pure metal hexafluoroisopropoxides are apparently produced from the literature preparations,[6-8] the authors carried out a study designed to eliminate the problem of ammonia contamination. In this paper the results of synthesis, characterization, and thermal and hydrolytic decomposition of aluminum, silicon, germanium, titanium, zirconium, and hafnium hexafluoroisopropoxides are reported.

Experimental Section

Reagents.—Anhydrous $AlCl_3$ and $SiCl_4$ were obtained in 99.8% purity from the K & K Laboratories Inc. $GeCl_4$ (99.999%) was obtained from Alfa Inorganics and 99.5% $TiCl_4$, from Matheson Coleman and Bell, was used as received. Spectrograde 99.9% $ZrCl_4$ and $HfCl_4$ were obtained from Wah Chang Corp. and used as received.

Hexafluoro-2-propanol (1,1,1,3,3,3-hexafluoro-2-propanol, abbreviated hereafter as HFIP) from the Pierce Chemical Co., bp 57–58°, was distilled over sodium using a 70-cm Vigreux column. The center fraction, bp 57.5°, was collected and stored in a dark container. All other chemicals were reagent grade and were dried over Linde activated molecular sieve, Type 4A, before being used. Quantitative elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

All preparative work was carried out in glass apparatus with ground-glass joints under reduced pressure or under an atmosphere of dry helium. Compounds were handled in an inert atmosphere and were stored in an evacuated desiccator over phosphorus pentoxide. Temperatures mentioned are all uncorrected. Except for elemental analysis, all other analyses reported here were performed immediately after fractional distillation in the case of liquid compounds and sublimation or recrystallization in the case of the solid compounds.

Method of Preparation. Aluminum Tris(hexafluoroisopropox-

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(1) J. Nelles, U. S. Patent 2,187,821 (Jan 23, 1940); British Patent 512,452 (1939).

(2) D. C. Bradley, "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Wiley, New York, N. Y., 1962, pp 169–186.

(3) L. M. Brown and K. S. Mazdiyasni, *Anal. Chem.*, **41**, 10, 1243 (1969).

(4) R. G. Jones, E. Karmas, G. A. Martin, J. R. Thritle, F. A. Yoeman, and H. Gilman, *J. Amer. Chem. Soc.*, **78**, 4289 (1956).

(5) R. Muller and I. Heinrich, *Chem. Rev.*, **95**, 2276 (1962).

(6) N. P. Kapoor and R. C. Mehrotra, *Chem. Ind. (London)*, 1034 (1966).

(7) P. N. Kapoor, R. N. Rapoor, and R. C. Mehrotra, *ibid.*, 1314 (1968).

(8) J. S. Skelcey, "Synthesis and Evaluation of New and Improved Gyro Flotation Fluids," AFML-TR-67-184, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, 1967, Part I, pp 5–14.

ide).—The crude aluminum tris(hexafluoroisopropoxide), Al(HFIP)$_3$, was prepared by the reaction of 3 mol of sodium hexafluoroisopropoxide,[9] in excess HFIP, and 1 mol of anhydrous aluminum trichloride. The reactant $AlCl_3$ was added slowly to stoichiometric Na(HFIP). The mixture was refluxed for 2–4 hr and cooled to room temperature. The mixture was allowed to stand overnight and filtered and the filtrate was concentrated to a 95% yield of crude product. The crude crystalline product was purified by recrystallization from hot HFIP or by vacuum sublimation.

Group IV Metal Hexafluoroisopropoxides.—The tetrakis(hexafluoroisopropoxides) of Si, Ge, Ti, Zr, and Hf were prepared in the same way as Al(HFIP), by the reaction of 4 mol of Na(HFIP) in excess HFIP and 1 mol of anhydrous metal chloride with a 95% or higher yield. The Si and Ti compounds were colorless liquids, while those of Ge, Zr, and Hf were crystalline solids. Ge(HFIP)$_4$ was distilled to a colorless liquid which, upon standing, crystallized to white transparent crystals. Zr(HFIP)$_4$ and Hf(HFIP)$_4$ were recrystallized from hot HFIP.

The recrystallization method described above usually gives the desired product; however, it has been reported that benzene, acetone, diethyl ether, and THF are also excellent solvents for these compounds.[6–8] Our investigation indicates that the presence of benzene in the reactant mixtures lowers the yield to about 65% and diethyl ether and THF both react exothermally with the fluoroalkoxides to form diethyl etherates and tetrahydrofuranates.

Infrared spectra in the 4000–200-cm^{-1} region were obtained for the first time for these fluoro-substituted alkoxides and compared with one another. The spectra were recorded with a Perkin-Elmer 521 grating infrared spectrophotometer using cesium iodide windows. The Si and Ti compounds were examined as liquid films, while the solid Ge, Al, Zr, and Hf compounds were examined in Nujol and Fluorolube oil LG160 (Fisher Scientific Co.) mulls. All sample handling and transferring to the plates were done in a drybox. The instrument was purged with dry helium during the time the spectra were recorded.

Molecular weight determinations of the fluoro-substituted isopropoxides were obtained by mass spectrometry. The mass spectrometric analysis was made with a CEC Model 21-110B double-focusing mass spectrometer using ionizing energies of 12 and 70 eV at temperatures of 140–250°. Perfluorokerosene was used as a reference.

Proton and fluorine-19 nmr spectra were measured at 60 and 56.4 MHz, respectively, at a probe temperature of 37° on a Varian Associates Model A-56/60A nmr spectrometer. Liquid hexafluoroisopropoxides were analyzed neat while the solid fluoro-substituted isopropoxides were analyzed in saturated diethyl ether solutions. The chemical shift measurements were made with both instrument and chart paper calibrated by the audio-side-band frequency technique. Tetramethylsilane and fluorotrichloromethane were used as proton and fluorine-19 internal references, respectively.

Samples of 100 mg were heated in helium or ambient air from room temperature to 800° at a rate of 5°/min under a flow of helium of 50 cm^3/min. The weight loss was continuously recorded on a Burrell Stanton Model TR-1 thermobalance. The residue was quantitative to oxide and was identified by X-ray powder diffraction analysis.

Vapor-phase chromatography was carried out using a Hewlett-Packard (F & M) Model 5754B gas chromatograph with a dual column and dual thermal conductivity detector. To minimize moisture contamination, a glove bag was attached to the injection port and continuously purged with dry nitrogen during operation of the chromatograph. Best results were obtained with a 6-ft column of 0.25-in. (o.d.) Teflon tubing containing 10% diisodecyl phthalate on Chromosorb W-AWDMSC (60–80 mesh). Temperatures for injection port, column, and thermal conductivity detector were 150, 90, and 180°, respectively. Helium flow was 60 cm^3/min; sample size was 1 μl. The solvents used were CCl_4 and diethyl ether.

For purposes of positive identification of the eluates, the material eluted from the chromatograph was trapped in a glass U tube cooled with liquid nitrogen. An infrared spectrum was recorded of the clear liquid collected in the trap and the ir spectrum was compared with the original spectrum. For all practical purposes, the two spectra were identical. The eluates were also hydrolyzed and the products were analyzed for elemental composition by emission spectroscopy and atomic absorption methods. The glass inserts in the injection port were also examined. Except for a slight discoloration of the glass tube (white to light brown) there were no signs of thermal degradation or incomplete volatilization. No residue was observed.

Discussion and Results

Chemical Analysis.—Representative elemental analyses, melting points, sublimation temperatures, boiling points, and molecular weights as determined by mass spectrometry are listed in Table I. Considering the hygroscopic nature of these compounds, with the exception of Si(HFIP)$_4$ which is insensitive to moisture, the carbon, hydrogen, fluorine, and metal analyses were in fair agreement with calculated values. Analyses for chlorine and sodium were negative. A typical elemental analysis for the diammoniate complex for the fluoro-substituted isopropoxides prepared by the ammonia method is also included for comparison.

TABLE I

ANALYTICAL DATA FOR ALUMINUM AND SOME GROUP IV METAL HEXAFLUOROISOPROPOXIDES, $M[OCH(CF_3)_2]_n$

Compounds[a]		Carbon %	Hydrogen %	Fluorine %	Metal %	Molecular weight	b.p. °C/mm Hg m.p. Sub. Temp °C
Al(HFIP)$_3$	Calcd	20.48	0.57	64.75	5.11		m.p. 185°
	Found	20.17	0.72	63.80	5.50		Sub. 75/0.08
Si(HFIP)$_4$	Calcd	20.69	0.58	65.48	4.03	696	b.p. 158°
	Found	20.78	0.69	66.90	5.12	677	
Ge(HFIP)$_4$	Calcd	19.46	0.54	61.52	9.80	742	b.p. 145°
	Found	19.07	0.75	61.32	10.08	723	m.p. 35°
Ti(HFIP)$_4$	Calcd	20.12	0.56	63.66	6.69	716	b.p. 35°/0.15
	Found	19.90	0.72	64.67	6.65	697	
Zr(HFIP)$_4$	Calcd	19.02	0.53	60.19	12.04	758	m.p. 111°
	Found	19.07	0.69	59.40	12.08	739	
Hf(HFIP)$_4$	Calcd	17.02	0.48	53.80	21.08	848	m.p. 110°
	Found	16.04	0.63	53.55	21.00	848	
Zr(HFIP)$_4$·2NH$_x$**	Calcd	18.12	1.02	57.32	11.47		b.p. 110/0.8
	Found	18.00	1.07	57.33	11.52		

[a] Analysis for chlorine and sodium were negative

** Prepared by Ammonia method, N cal. 3.52%, found 3.92%

Infrared Spectra.—The absorption frequencies of the M(HFIP)$_n$, n = 3 or 4, are given in Table II. The spectra for the two liquid compounds Si(HFIP)$_4$ and Ti(HFIP)$_4$ are almost identical except for the bands at 735 and 590 cm^{-1} for silicon and a band at 783 cm^{-1} for titanium. Some small frequency shifts also occur, such as the major band at 1158 cm^{-1} for silicon and at 1150 cm^{-1} for titanium. The similarity of the spectra of the fluorinated isopropoxides of aluminum, silicon, germanium, titanium, zirconium, and hafnium is seen in Table II.

Characteristic absorptions appear at 1090–1110, 880–895, and 835–865 cm^{-1}. In part these are assigned to skeletal vibrations. The frequency absorptions appearing at 1160–1210 cm^{-1} are assigned to C–F stretching.[9] The CF_3 band is observed at 1225 and 1250 cm^{-1}. The bands at 1350–1380 and at 1435 cm^{-1} are assigned to C–CH stretching and the bands at 2900–2960 cm^{-1} are due to C–H splitting.[9] The aluminum, zirconium, and hafnium fluoroisopropoxides, in addition to the expected absorptions, exhibit an additional absorption band in the carbonyl region, 1655–1720 cm^{-1}. This is due to the partial oxidation of the fluoroalkoxide to the fluoroalkoxy carboxylate.[8,10]

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[9] H. J. Koetzsch, *Chem. Ber.*, **99**, 1143 (1966).

[10] E. E. Glagg, J. E. Rumminger, and J. S. Skelcey, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 211.

TABLE II

INFRARED SPECTRA OF ALUMINUM AND SOME GROUP IV METAL HEXAFLUOROISOPROPOXIDES (CM^{-1})

$Al(HFIP)_3$	2920	1655	1395sh	1378	1295	1260	1230	1185	1150sh	1100	940	892	855	805	725		687	570		535	522		460	400	
$Si(HFIP)_4$	2965			1382	1306	1265	1235	1208	1158	1112	938	903	862		735		688	'59		538	522	475	458		
$Ge(HFIP)_4$	2950		1390sh	1375	1298	1268	1230	1205		1108		902	865	795		717	685		558	534	522		450	400	
$Ti(HFIP)_4$	2930			1378	1300	1258	1230	1200	1150	1108		897	848	783		721	685		552	532	516			400	
$Zr(HFIP)_4$	2905	1720	1390sh	1370	1280	1250	1225	1175	1125sh	1093		882	848		748	718	685	590	547	531	520				378
$Hf(HFIP)_4$	2905	1697	1361sh	1348	1260	1230	1210	1160	1120sh	1090		884	848	800	747	718	682	585	548	530	519				370

TABLE III

MASS SPECTROMETRIC ANALYSIS OF TETRAKIS(HEXAFLUOROISOPROPOXIDES) OF Si, Ge, Ti, Zr, AND Hf

$Si[OCH(CF_3)_2]_4$		$Ge[OCH(CF_3)_2]_4$		$Ti[OCH(CF_3)_2]_4$		$Zr[OCH(CF_3)_2]_4$		$Hf[OCH(CF_3)_2]_4$	
Measured m/e	Identity[a]	Measured m/e	Identity[b]	Measured m/e	Identity[c]	Measured m/e	Identity[d]	Measured m/e	Identity[e]
677	$SiO_4C_{12}F_{23}H_4$	723	$GeO_4C_{12}F_{23}H_4$	697	$TiO_4C_{12}F_{23}H_4$	739	$ZrO_4C_{12}F_{23}H_4$	848	$HfO_4C_{12}F_{24}H_4$
627	$SiO_4C_{11}F_{21}H_4$	673	$GeO_4C_{11}F_{21}H_4$	647	$TiO_4C_{11}F_{21}H_4$	689	$ZrO_4C_{11}F_{21}H_4$	829	$HfO_4C_{12}F_{23}H_4$
529	$SiO_3C_9F_{18}H_3$	575	$GeO_3C_9F_{18}H_3$	549	$TiO_3C_9F_{18}H_3$	665	$ZrO_4C_9F_{21}H_4$	779	$HfO_4C_{11}F_{21}H_4$
381	$SiO_2C_6F_{13}H_2$	525	$GeO_3C_8F_{16}H_3$	499	$TiO_3C_8F_{16}H_3$	591	$ZrO_3C_9F_{18}H_3$	681	$HfO_3C_9F_{18}H_3$
299	$SiO_2C_4F_{10}H$	443	$GeO_3C_6F_{13}H_2$	401	$TiO_2C_6F_{13}H_2$	541	$ZrO_3C_8F_{16}H_3$	631	$HfO_3C_8F_{16}H_3$
233	$SiOC_3F_8H$	427	$GeO_2C_6F_{13}H_2$	381	$TiO_2C_6F_{12}H$	443	$ZrO_2C_6F_{13}H_2$	533	$HfO_2C_6F_{13}H_2$
217	SiC_3F_8H	407	$GeO_2C_6F_{12}H$	350	$TiO_2C_5H_{11}H$	393	$ZrO_2C_5F_{11}H_2$	483	$HfO_2C_5F_{11}H_2$
181	C_4F_7	299	$GeO_2C_5F_7$	252	$TiOC_3F_8$	295	$ZrOC_3F_8H$	316	$HfOC_2F_5H$
169	C_3F_7	199	$GeO_2C_3F_3$	202	$TiOC_2F_6$	245	$ZrOC_2F_6H$	277	$HfOC_2F_3$
151	C_3F_6H	151	C_3F_6H	181	C_4F_7	226	$ZrOC_2F_5H$	129	OC_3F_4H
129	OC_3F_4H	129	OC_3F_4H	151	C_3F_6H	167	C_3F_6OH	110	OC_3F_3H
110	OC_3F_3H	110	OC_3F_3H	129	OC_3F_4H	149	C_3F_5O	101	C_2F_4H
101	C_2F_4H	101	C_2F_4H	110	OC_3F_3H	129	OC_3F_4H		
				101	C_2F_4H	110	OC_3F_3H		
						101	C_2F_4H		

[a] Mass numbers based on ^{28}Si
[b] " " " " ^{74}Ge
[c] " " " " ^{48}Ti
[d] Mass numbers based on ^{90}Zr
[e] " " " " ^{180}Hf

The oxidation of the freshly sublimed product is not uncommon in these compounds if oxygen is not excluded in sample recovery or in sample preparation for infrared studies. The infrared spectra of aluminum, zirconium, and hafnium hexafluoroisopropoxides recrystallized from diethyl ether also exhibit an additional band at 1000–1030 cm^{-1}, not shown in Table II, assigned to carbon–oxygen–metal vibrations[11,12] from an apparent reaction of these fluoroalkoxides with diethyl ether to form the etherated analog. The ir spectra of all the compounds prepared by the ammonia method exhibit a major band in the 3270–3400-cm^{-1} region due to N–H stretching (also not reported here).

Mass Spectrometric Analysis.—Due to the hygroscopic and thermal instability of these compounds, conventional vapor pressure osmometry could not be utilized for molecular weight determinations. However, the mass spectra of the hexafluoroisopropoxides of Si, Ge, Ti, Zr, and Hf were recorded only to obtain molecular complexity for these compounds. The measured molecular ion peaks listed in Table III indicate that these compounds are monomeric in the vapor state. It is interesting to note that the first weak peak observed in these fluoro-substituted isopropoxides corresponds to the loss of one fluorine from the parent $M(HFIP)_4$ species. A similar loss of fluorine in fluoro-substituted β-diketonates has been reported previously.[13] However, for the $Hf(HFIP)_4$ species, a weak parent peak is observed at an *m/e* ratio of 848 which corresponds to a molecular ion peak. For the fluoro-substituted isopropoxides, the *m/e* values at high mass numbers indicate the general instability of the molecular ion which leads to successive losses of low mass number fragments corresponding to CF_3, CF_2, and C_2F_3 groups. The next most significant peak observed in these compounds corresponds to the loss of one hexafluoroisopropoxy group from the parent compound. It should be noted that in general the *m/e* fragment peaks reported here are the strongest of a cluster of peaks having an isotopic abundance ratio corresponding to the one metal atom. Many more peaks were observed with $Zr(HFIP)_4$ than with any of the other fluoro-substituted alkoxides studied. Attempts to obtain the mass spectra of $Al(HFIP)_3$ were unsuccessful because of rapid volatilization and the excessive back pressure created as the sample was introduced into the instrument chamber for analysis.

Nuclear Magnetic Resonance.—The results of the proton and fluorine nmr studies of hexafluoro-2-pro-

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[11] H. Kaesz and F. Stone, *Spectrochim. Acta*, **15**, 360 (1959).

[12] C. T. Lynch, K. S. Mazdiyasni, J. S. Smith, and W. J. Crawford, *Anal. Chem.* **36**, 2332 (1964).

[13] C. Chattoraj, C. T. Lynch, and K. S. Mazdiyasni, *Inorg. Chem.*, **7**, 2501 (1968).

panol and the fluoro-substituted isopropoxides are given in Table IV. The fluorine nmr results show that the metal hexafluoroisopropoxides all give one doublet which is due to the equivalence of the two $-CF_3$ groups. The pmr spectra of the compounds contain a low-intensity multiplet due to the α hydrogen coupled with six fluorines in the species. This was observed as a very sharp, low-intensity quintet for the liquid Si and Ti compounds and the liquid Ge compound, a supercooled melt obtained by distillation from the solid. However, the resonance peaks for the solvated $Al(HFIP)_3$, $Zr(HFIP)_4$, and $Hf(HFIP)_4$ were broad and of low intensity. Both the $-CH$ and $-CF_3$ shifts are equally sensitive to the change of elements. It is also noted that, except for $Ti(HFIP)_4$, the $-CH$ and $-CF_3$ shifts follow the order of electronegativity of the Pauling scale.[14] The progressive lower field chemical shifts from Si to Hf shown in Table IV may be due to the degree of covalency of the metal ions and/or an increase in the mass of the central metal atoms.

TABLE IV

PROTON AND FLUORINE NMR DATA FOR HFIP AND FOR ALUMINUM AND SOME GROUP IV METAL HEXAFLUOROISOPROPOXIDES

Compound	CH Proton Chemical Shift δ PPM	Fluorine Chemical Shift δ PPM
$(HFIP)^a$	-4.17 Quintet	76.8 Doublet
$Al(HFIP)_3^{bcd}$	-4.35 "	73.6 "
$Si(HFIP)_4^a$	-4.70 "	76.4 "
$Ge(HFIP)_4^a$	-4.80 "	76.1 "
$Ti(HFIP)_4^a$	-4.92 "	75.8 "
$Zr(HFIP)_4^{bc}$	-4.82 "	74.2 "
$Hf(HFIP)_4^{bc}$	-4.83 "	74.1 "

Internal Standard TMS and $CFCl_3$

a Neat

b Saturated Solution of sublimed product in diethyl ether.

c Additional proton peak for ether was observed

d Spectrum shows that compound contains coordinated ether.

Thermogravimetric Analysis.—The thermal decomposition in a helium atmosphere was studied by tga. The liquid silicon and titanium hexafluoroisopropoxides and the liquid Ge analog, the supercooled melt of the solid compound, gave identical results. The samples lose weight immediately after being introduced into the balance chamber. The weight loss from 25 to 160° is approximately 78% for Si and 70% for the Ge and Ti compounds, an indication of partial decomposition at relatively low temperature. The thermograms of the solid Al, Zr, and Hf compounds, however, are significantly different from those of the liquid compounds. $Al(HFIP)_3$ weight loss occurs in two consecutive steps, one at 25–100° and another at 100–190°, corresponding to 25 and 75% of the total weight loss, respectively. Similarly the $Zr(HFIP)_4$ and $Hf(HFIP)_4$ weight losses occur in multisteps at approximately 80, 120, and 200°, corresponding to approximately 20, 30, and 65% of the total weight loss, respectively. It is noted that some of the breaks in the thermogram coincide reasonably well with the melting point or boiling point of these compounds. The thermal hydrolysis in ambient air resulted in a decreased volatility as expected; the first inflection appeared at about the same temperature range as it did in the helium atmosphere, but a much lower weight loss was observed in the air atmosphere. The decomposition of known quantities of the compound heated to 750–800° was quantitative to the oxides. The oxides were identified by X-ray diffraction. No attempt was made to investigate the mechanisms of decomposition of the fluoro-substituted alkoxides to the corresponding oxides.

Gas Chromatography.—Under the stated experimental conditions, the fluoro-substituted isopropoxides of the group IV elements were successfully chromatographed. The $Si(HFIP)_4$ was considerably more volatile than the other compounds and gave a very sharp peak with an average retention time of 1 min. The hexafluoroisopropoxides of Ge, Ti, Zr, and Hf all gave moderately sharp peaks with average retention times of 4 min. Therefore, the $Si(HFIP)_4$ could easily be separated from any of the other four compounds; however, various combinations of the Ge, Ti, Zr, and Hf compounds always gave only one peak and no separation could be achieved under these conditions.

Conclusion

Aluminum, silicon, germanium, titanium, zirconium, and hafnium hexafluoroisopropoxides are moisture sensitive (with the exception of the silicon compound which is insensitive to moisture) with considerable volatility. Chemical, infrared, and nmr analyses show that the previously reported technique (ammonia method) used to prepare these compounds results in an ammoniate complex and impure product. Mass spectra show that they are monomeric. Thermogravimetric analysis data indicate that the liquid $Si(HFIP)_4$ is the most volatile compound. Each compound gives a single peak when injected separately in a gas chromatograph. Well-resolved peaks have been obtained with a mixture of $Si(HFIP)_4$ and any one of the group IV metal hexafluoroisopropoxides.

Acknowledgment.—The authors thank Daniel Dyer and Lee D. Smithson of the Analytical Branch of the Physics Division, AFML, for help in obtaining nmr and mass spectra, respectively, and Miss Sally Allen and Mrs. Jean Gwinn for typing the manuscript.

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(14) L. Pauling "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 88.