

SiH<sub>2</sub>D (0.1 mmol) while the condensate in the -78° trap was mostly C<sub>2</sub>H<sub>5</sub>SiD<sub>2</sub>SiD(H)(CH<sub>3</sub>) (0.05 mmol).

The compound C<sub>2</sub>H<sub>5</sub>SiD<sub>2</sub>SiH<sub>2</sub>D was identified by a mass spectrum formed only from heavy ions of the types (with relative envelope intensities) C<sub>2</sub>Si<sub>2</sub>D<sub>2</sub>H<sub>2</sub><sup>+</sup> (29.4), C<sub>2</sub>Si<sub>2</sub>D<sub>2</sub>H<sub>2</sub><sup>+</sup> (10.5), and Si<sub>2</sub>D<sub>2</sub>H<sub>2</sub><sup>+</sup> + C<sub>2</sub>SiD<sub>2</sub>H<sub>2</sub><sup>+</sup> (100). The parent peak *m/e* 93 was large and contained 31.6% of the intensity of the C<sub>2</sub>Si<sub>2</sub> envelope. The peak at *m/e* 33 (HSiD<sub>2</sub><sup>+</sup>) was small compared to the peak at *m/e* 32 (H<sub>2</sub>SiD<sup>+</sup>) which is expected for C<sub>2</sub>H<sub>5</sub>SiD<sub>2</sub>SiH<sub>2</sub>D but not for C<sub>2</sub>H<sub>5</sub>SiH(D)SiHD<sub>2</sub>.

The condensate in the -78° trap had a mass spectrum that was very similar to that of the C<sub>2</sub>H<sub>5</sub>SiD<sub>2</sub>SiD(H)(CH<sub>3</sub>) formed in experiment 1B at high masses (*m/e* 108-83) while the mass spec-

trum had slightly more intense peaks at lower masses suggesting the presence of small quantities of methylidisilane.

**B. Pyrolysis of CH<sub>3</sub>Si<sub>2</sub>H<sub>5</sub>.**—The pyrolysis of CH<sub>3</sub>Si<sub>2</sub>H<sub>5</sub> was carried out in our flow system at 342 and 360° with the cold trap set at -45°. The ratio of CH<sub>3</sub>SiH<sub>3</sub>:SiH<sub>4</sub> produced was 1.8 at both temperatures. The less volatile products were not isolated in a pure state but the mass spectrum of our samples suggested they were mixtures of CH<sub>3</sub>Si<sub>3</sub>H<sub>7</sub> and (CH<sub>3</sub>)<sub>2</sub>Si<sub>3</sub>H<sub>8</sub>.

**Acknowledgment.**—The authors are indebted to the U. S. Army Research Office (Durham) for financial support.

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## The Raman Spectra of Molten Aluminum Trihalide-Alkali Halide Systems<sup>1a</sup>

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Received September 14, 1970

Raman spectra are presented for AlBr<sub>3</sub>-NaBr and AlI<sub>3</sub>-CsI melts in the region from 50:50 mol % to pure aluminum halide. These data are compared with previously published data for the AlCl<sub>3</sub>-NaCl system. Raman frequencies are assigned for the AlBr<sub>4</sub><sup>-</sup>, Al<sub>2</sub>Br<sub>7</sub><sup>-</sup>, AlI<sub>4</sub><sup>-</sup>, and Al<sub>2</sub>I<sub>7</sub><sup>-</sup> ions. Valence force constants have been calculated for the series of tetrahedral ions: AlCl<sub>4</sub><sup>-</sup>, AlBr<sub>4</sub><sup>-</sup>, AlI<sub>4</sub><sup>-</sup>.

In a previous paper<sup>2</sup> we presented a study of the Raman spectra of molten mixtures of AlCl<sub>3</sub>-NaCl in the concentration region from 50:50 mol % to pure AlCl<sub>3</sub>. This paper reports a similar study of the systems AlBr<sub>3</sub>-NaBr and AlI<sub>3</sub>-CsI. Comparisons are made between the different halide systems and evidence for the ionic species present is examined.

### Experimental Section

Aluminum bromide was prepared by the reaction of high-purity, zone-refined aluminum metal (99.9999%, Cominco Products, Inc.) with purified HBr in a manner previously described<sup>3</sup> for AlCl<sub>3</sub>. Aluminum iodide was synthesized in a similar preparation by treating aluminum metal with iodine (99.99%, Alfa Inorganics, Inc.). Sodium bromide and CsI were purified by the high-temperature filtration and sparging method described<sup>4</sup> for LiCl-KCl eutectic preparation, except that for these higher melting compounds, the apparatus was constructed of quartz instead of borosilicate glass, and in the case of CsI the filtered material was sublimed under vacuum before use.

After preparation, all handling operations were conducted in a nitrogen-filled drybox with the H<sub>2</sub>O content below 10 ppm. The mixtures were placed in quartz tubes (~4-mm o.d.), evacuated to ~10<sup>-3</sup> Torr and sealed with a torch. The quartz tube containing the salt was mounted in the Raman spectrophotometer and the sample was melted by passing current through a platinum wire wrapped around the tube. The sample temperatures were in the range 200-260°.

In most cases a Spectra-Physics Model 141 argon ion laser was used to excite the Raman spectra. Observations were made

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(1) (a) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp. and under Contract AT-(40-1)-3518. (b) Chemistry Division, Oak Ridge National Laboratory. (c) Metals and Ceramics Division, Oak Ridge National Laboratory. (d) Chemistry Department, University of Tennessee.

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(3) N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).

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with the 4880- and 5145-Å laser lines. In the case of the AlI<sub>3</sub>-CsI 50:50 mol % sample, a Spectra-Physics Model-125 helium-neon laser emitting light at 6328 Å was used to excite the spectrum, since the melt was somewhat yellow. Power levels at the sample were approximately 100 mW for the 4880- and 5145-Å lines and 25 mW for the 6328-Å line. A Cary Model 81 monochromator, coupled with a cooled 9558 EMI photomultiplier tube and a photon counting system, was used to record the Raman spectra. Several confirmatory Raman spectra were also run on a Jarrell-Ash Model 25-300, Raman spectrophotometer using the 4880-Å argon ion laser line for excitation.

The samples were illuminated with the laser beam focused at right angles to the long axis of the sample tubes and at the center of the sample volume. Raman light was collected at right angles to the laser beam by a 75-mm, *f*/1.9 collimating lens and was focused on the spectrometer entrance slit by means of a 335-mm, *f*/6.5 lens. Qualitative polarization measurements were made by rotating the plane of polarization of the laser beam with a half-wave plate. Appropriate spike filters were employed in the laser beam to eliminate the background laser lines from the Raman spectra.

### Results

Figure 1 shows the Raman spectra of several mixtures of molten AlBr<sub>3</sub>-NaBr in the concentration region from 50:50 to 100:0 mol %. In the case of the AlBr<sub>3</sub>-NaBr mixture, the NaBr-saturated melt which has a composition<sup>5</sup> very close to 50:50 mol % was used for the equimolar sample. The data are recorded in Table I. The Raman spectra for three concentrations of the AlI<sub>3</sub>-CsI system are shown in Figure 2, and the data for these melts are given in Table II. We observed the AlI<sub>3</sub>-CsI system rather than the AlI<sub>3</sub>-NaI system because samples of the former materials were already available. In addition, for the cesium-containing system, it was possible to prepare the solid compound CsAl<sub>2</sub>I<sub>7</sub> in crystalline form, indicating a greater stability for the Al<sub>2</sub>I<sub>7</sub><sup>-</sup>

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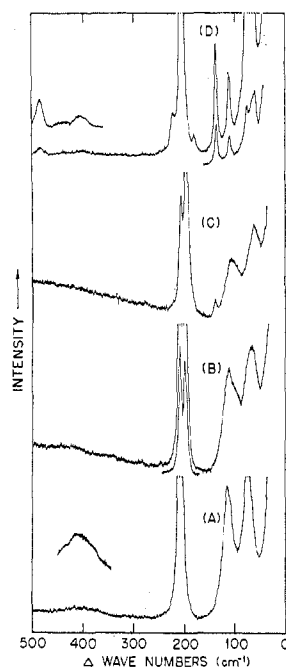


Figure 1.—Raman spectra of molten  $\text{AlBr}_3\text{-NaBr}$  at  $\sim 220^\circ$  and  $4880\text{-}\text{\AA}$  laser excitation: (A) 50:50, (B) 62:38, (C) 75:25, (D) 100:0 mol %.

TABLE I  
RAMAN FREQUENCIES ( $\text{cm}^{-1}$ ) OF THE  
 $\text{AlBr}_3\text{-NaBr}$  SYSTEM AT  $\sim 220^\circ$

Compn, mol % $\text{AlBr}_3$								Polar- izn
50	52	54	62	67	75	80	100	
				60 m	61 m, b	65 m	65 s	P
75 s	73 s	73 s	66 s, b			80 m	79 m	D
114 s	114 s	113 s	108 m, b	104 m	109 m, b	112 m	113 m	D
					140 w	141 m	140 m	P
							183 w	P
			198 s	198 vs	199 vs	199 s		P
209 vs	209 vs	209 vs	209 s	209 s	208 s	208 vs	208 vs	P
						224 w	224 w	D?
409 w	408 w						405 w	?
							434 w	?
							489 w	D

<sup>a</sup> Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; P, polarized; D, highly depolarized.

ion in this case. The corresponding sodium compound is not known. The Raman spectrum of polycrystalline  $\text{CsAl}_2\text{I}_7$  is shown in Figure 3 and the data are recorded in Table II.

### Discussion

The Raman spectra of fused  $\text{AlBr}_3(\text{Al}_2\text{Br}_6)$  and fused  $\text{AlI}_3(\text{Al}_2\text{I}_6)$  have been reported previously.<sup>6-8</sup> Our data agree quite well with the literature values. We were not able to observe the 284- or 340- $\text{cm}^{-1}$  peaks reported<sup>8</sup> for  $\text{Al}_2\text{Br}_6$  but observed several weak unreported<sup>8</sup> peaks for  $\text{Al}_2\text{I}_6$ .

It is clear that, in the 50:50 mol % mixtures, the  $\text{AlBr}_3\text{-NaBr}$  and  $\text{AlI}_3\text{-CsI}$  systems are similar to the  $\text{AlCl}_3\text{-NaCl}$  system and that the dominant species is the tetrahedral  $\text{AlX}_4^-$  ion, where X is Cl, Br, or I. In the  $\text{AlCl}_4^-$  case at 50:50 mol %, a small peak was seen<sup>2</sup> at 306  $\text{cm}^{-1}$  which was assigned either as an overtone or as due to the 313- $\text{cm}^{-1}$   $\text{Al}_2\text{Cl}_7^-$  peak. We now believe that this peak is due to  $\text{Al}_2\text{Cl}_7^-$  resulting from a small

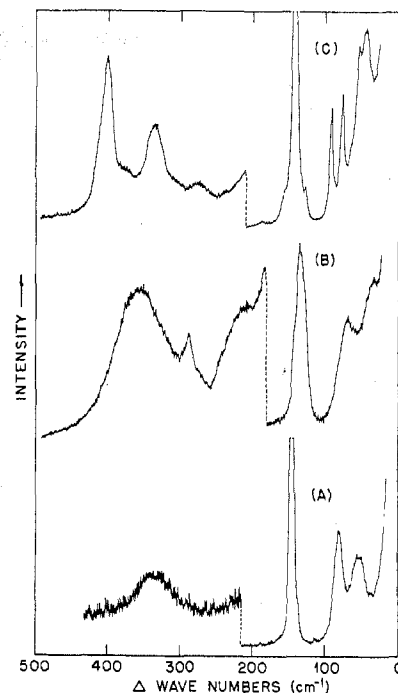


Figure 2.—Raman spectra of molten  $\text{AlI}_3\text{-CsI}$  at  $250^\circ$  and  $6328\text{-}\text{\AA}$  (A) and  $4880\text{-}\text{\AA}$  (B and C) laser excitation: (A) 50:50, (B) 67:33, (C) 100:0 mol %.

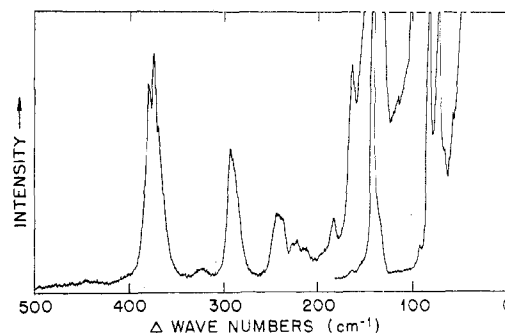


Figure 3.—Raman spectrum of polycrystalline  $\text{CsAl}_2\text{I}_7$  at  $\sim 25^\circ$  and  $4880\text{-}\text{\AA}$  laser excitation.

TABLE II  
RAMAN FREQUENCIES ( $\text{cm}^{-1}$ ) OF THE  
 $\text{AlI}_3\text{-CsI}$  SYSTEM AT  $250^\circ$  AND OF SOLID  $\text{CsAl}_2\text{I}_7^a$

Compn, mol % $\text{AlI}_3\text{-CsI}$ melt		Polycrystalline $\text{CsAl}_2\text{I}_7$
50:50	67:33	
	100:0	
	35 m	
51 m		48 m
		57 m
		56, 60, 65 w
		72 s
82 m	69 m	82 s
		80 m
		95 m, P
		132 w
	137 s, P	
146 s, P	145 w, sh	142 vs
		145 s, P
		158 w, sh
		164 w
		189 w, b
		183 w
	220 w, b	213, 221 w, b
		240 m, b
	288 w, P	277 vw
		292 m
336 w, b		325 w
	360 m, b	339 w
		370, 373, 380 m
		380 vw, sh
		404 w, b

<sup>a</sup> Abbreviations: w, weak; m, medium; s, strong; v, very; sh, shoulder; b, broad; P, polarized.

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(8) I. R. Beattie, T. Gilson, and G. A. Ozin, *J. Chem. Soc. A*, 813 (1968).

excess of aluminum chloride in the sample. This assignment is supported by the Raman spectra we observed with the aluminum chloride-thallos chloride system,<sup>9</sup> which, like  $\text{AlCl}_3\text{-NaCl}$ , shows a peak in the  $310\text{-cm}^{-1}$  region with the 50:50 mol % sample. However, at the  $\text{AlCl}_3\text{-TiCl}_4$  48:52 mol % composition, this peak is not observed. It may be noted that with the  $\text{AlCl}_3\text{-NaCl}$  system the liquidus temperature is near  $500^\circ$  for a melt with such a high concentration of alkali chloride.<sup>5</sup> In the case of  $\text{AlBr}_4^-$  and  $\text{AlI}_4^-$ , only the four characteristic Raman peaks of the tetrahedral ion are seen, and it is clear that any other species present at 50:50 mol % are in low concentrations. Table III lists the frequencies we have observed for the  $\text{AlX}_4^-$  ions and the assignments made to the vibrational modes assuming tetrahedral symmetry.

TABLE III  
VIBRATIONAL FREQUENCIES OF  
ALUMINUM TETRAHALIDE IONS ( $\text{CM}^{-1}$ )

Ion	$\nu_1$ (A <sub>1</sub> )	$\nu_2$ (E)	$\nu_3$ (F <sub>2</sub> )	$\nu_4$ (F <sub>2</sub> )
$\text{AlCl}_4^-$ <sup>a</sup>	351	121	490	186
$\text{AlBr}_4^-$	209	75	409	114
$\text{AlI}_4^-$	146	51	336	82

<sup>a</sup> Reference 2.

Using the symmetry coordinates of Meister and Cleveland,<sup>10</sup> we calculated valence force constants for  $\text{AlCl}_4^-$ ,  $\text{AlBr}_4^-$ , and  $\text{AlI}_4^-$ . The Wilson *F* and *G* matrix method<sup>11</sup> was used and solutions were arrived at by a machine-iterative, least-squares process similar to that of Overend and Scherer.<sup>12</sup> The Al-X distances were assumed to be 2.13, 2.27, and 2.55 Å for  $\text{AlCl}_4^-$ ,  $\text{AlBr}_4^-$ , and  $\text{AlI}_4^-$ , respectively. The  $\text{AlCl}_4^-$  distance is taken from crystal data<sup>13</sup> while the  $\text{AlBr}_4^-$  and  $\text{AlI}_4^-$  distances are averages taken from electron diffraction data<sup>14</sup> for gaseous  $\text{Al}_2\text{Br}_6$  and  $\text{Al}_2\text{I}_6$ . This procedure for estimating the bond distances was used since no data were available for  $\text{AlBr}_4^-$  and  $\text{AlI}_4^-$ , and it was found that the average of the two different Al-Cl distances in gaseous  $\text{Al}_2\text{Cl}_6$  was close to the Al-Cl distance in crystalline  $\text{AlCl}_3$ . It was possible to fit the frequencies to within a few tenths of a wave number of various combinations of valence force constants; one of the simplest sets is given in Table IV. The nonzero force constants used were:  $f_d$ , stretching;  $f_a$ , bending;  $f_{aa'}$ , bend-bend interaction between opposite angles;  $f_{da}$  and  $f_{da'}$ , stretch-bend interactions. The force constants clearly illustrate the progressive weakening of the Al-X bond as the size of the halide increases.

It should be pointed out that Table IV should be used for intercomparison purposes only, since the values of the diagonal force constants depend on which interaction terms are included. The metal-halide stretching force constants are somewhat lower in the cases where  $f_{da}$  (stretch-stretch interaction term) is included. For example, when the constants  $f_d$ ,  $f_a$ ,  $f_{da}$ , and  $f_{aa'}$  were used, the values calculated for  $f_d$  were 1.71, 1.34, and 0.81 mdyne/Å for  $\text{AlCl}_4^-$ ,  $\text{AlBr}_4^-$ , and  $\text{AlI}_4^-$ , respectively. This case, however, did not converge as well or produce as good a fit of the frequencies as that of Table IV.

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(14) K. J. Palmer and N. Elliott, *J. Amer. Chem. Soc.*, **60**, 1852 (1938).

TABLE IV  
VALENCE FORCE CONSTANTS FOR  $\text{AlCl}_4^-$ ,  $\text{AlBr}_4^-$ , AND  
 $\text{AlI}_4^-$  IONS (MDYN/Å)

Ion	$f_d$	$f_a/d^2$	$f_{aa'}/d^2$	$(f_{da} - f_{da'})/d$
$\text{AlCl}_4^-$	2.58	0.14	-0.04	0.30
$\text{AlBr}_4^-$	2.06	0.10	-0.02	0.17
$\text{AlI}_4^-$	1.59	0.08	-0.02	0.15

In the fused  $\text{AlCl}_3\text{-NaCl}$  system, we observed Raman lines which we assigned<sup>2</sup> to the  $\text{Al}_2\text{Cl}_7^-$  ion. Cyvin, *et al.*,<sup>15</sup> independently obtained similar results and made the same interpretation. In the spectra of  $\text{AlBr}_3\text{-NaBr}$  and  $\text{AlI}_3\text{-CsI}$  mixtures, a similar effect may be seen with the appearance of a strong polarized line and several other weaker lines which are probably due to the  $\text{Al}_2\text{Br}_7^-$  and  $\text{Al}_2\text{I}_7^-$  ions, respectively. This assignment is strengthened by the similarity between the spectrum of solid  $\text{CsAl}_2\text{I}_7$  (Figure 3) and that of the 67:33 mol %  $\text{AlI}_3\text{-CsI}$  melt. In solid  $\text{CsAl}_2\text{I}_7$  the peaks occur at nearly the same frequencies as in the melt but they are considerably sharper and some splittings occur. We were not able to analyze the solid spectrum further since crystal structure data are not yet available.

In all three cases we found the strongest, polarized, symmetrical stretching vibration of the  $\text{AlX}_4^-$  ion to be very close to the similar vibration of the  $\text{Al}_2\text{X}_6$  dimer. The greatest difference occurred with  $\text{AlCl}_4^-$ - $\text{Al}_2\text{Cl}_6$  where the two frequencies observed are 351 and 341  $\text{cm}^{-1}$ , respectively. Similar values for  $\text{AlBr}_4^-$ - $\text{Al}_2\text{Br}_6$  and  $\text{AlI}_4^-$ - $\text{Al}_2\text{I}_6$  are 209, 208 and 146, 145  $\text{cm}^{-1}$ . The frequency most characteristic of the  $\text{Al}_2\text{X}_7^-$  ion, a strong, polarized band, is found to be lower than the symmetrical stretching frequency for either the  $\text{AlX}_4^-$  ion or the  $\text{Al}_2\text{X}_6$  dimer. This characteristic frequency occurs at 313, 198, and 137  $\text{cm}^{-1}$  for  $\text{Al}_2\text{Cl}_7^-$ ,  $\text{Al}_2\text{Br}_7^-$ , and  $\text{Al}_2\text{I}_7^-$ , respectively. Table V lists the lines we have assigned to the  $\text{Al}_2\text{X}_7^-$  ions in the melt.

TABLE V  
VIBRATIONAL FREQUENCIES FOR  $\text{Al}_2\text{X}_7^-$  IONS ( $\text{CM}^{-1}$ )<sup>a</sup>

$\text{Al}_2\text{Cl}_7^-$	$\text{Al}_2\text{Br}_7^-$	$\text{Al}_2\text{I}_7^-$
435 w		360 w
		288 w, P
		220 w
313 s, P	198 s, P	137 s, P
165 m	104 m	69 m
100 m	60 m	35 m

<sup>a</sup> Abbreviations: P, polarized; s, strong; m, medium; w, weak.

Since many of the lines tend to overlap with lines of the  $\text{AlX}_4^-$  or  $\text{Al}_2\text{X}_6$  species, band centers were difficult to determine. It is likely that the small number of observed Raman lines for the  $\text{Al}_2\text{X}_7^-$  ions is due to weak spectra or to coincidences with  $\text{AlX}_4^-$  or  $\text{Al}_2\text{X}_6$  lines. However, we have certainly observed the major Raman lines of  $\text{Al}_2\text{X}_7^-$ . A linear Al-Cl-Al bridge with a staggered ethane-like structure ( $D_{3d}$ ), as assumed by Cyvin, *et al.*,<sup>15</sup> will fit the data better than a less symmetric structure which would have more Raman-active frequencies. Force constant calculations were not made because of the uncertainty of the assignments.

In the case of the  $\text{AlCl}_3\text{-NaCl}$  system, we found an additional line at the higher  $\text{AlCl}_3$  mole ratio. We tentatively attributed this line<sup>2</sup> to the presence of a complex ion, such as  $\text{Al}_3\text{Cl}_{10}^-$ . We did not observe such a

(15) S. J. Cyvin, P. Klaboe, E. Rytter, and H. Øye, *J. Chem. Phys.*, **52**, 2776 (1970).

line in the  $\text{AlBr}_3\text{-NaBr}$  or  $\text{AlI}_3\text{-CsI}$  system. In the case of  $\text{AlI}_3\text{-CsI}$ , especially at 67:33 mol %, there is only a hint of a peak ( $\text{AlI}_4^-$ ) observed on the side of the  $\text{Al}_2\text{I}_7^-$  peak, indicating the equilibrium strongly favors the  $\text{Al}_2\text{X}_7^-$  ion at this concentration.

In the  $\text{AlBr}_3\text{-NaBr}$  melt (67:33 mol % sample), the ratio of the intensity of the peak at  $209\text{ cm}^{-1}$  ( $\text{AlBr}_4^-$ ) to the peak at  $198\text{ cm}^{-1}$  ( $\text{Al}_2\text{Br}_7^-$ ) increased as the temperature was raised from 220 to  $250^\circ$ . Quantitative measurements were not made, but the effect was repro-

ducible. Since the equilibrium constant for the reaction  $2\text{AlCl}_4^- \rightleftharpoons \text{Cl}^- + \text{Al}_2\text{Cl}_7^-$  increases with temperature,<sup>18</sup> this equilibrium may be eliminated as the cause of the above effect. A possible explanation is the increase in dissociation of  $\text{Al}_2\text{X}_7^-$  with increasing temperature:  $2\text{Al}_2\text{X}_7^- \rightleftharpoons 2\text{AlX}_4^- + \text{Al}_2\text{X}_6$ . At the experimental temperature,  $\text{Al}_2\text{X}_6$  is volatile and is present in the gas phase as well as in the melt.

(18) 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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Received September 28, 1970

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,<sup>1</sup> Bradley,<sup>2</sup> and Brown and Mazdiyasni.<sup>3</sup> Jones, *et al.*,<sup>4</sup> and Muller and Heinrich<sup>5</sup> 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<sup>6</sup> and to the preparation of 1,1,1,3,3,3-hexafluoroisopropoxides<sup>7</sup> 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,<sup>6-8</sup> 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  $\text{AlCl}_3$  and  $\text{SiCl}_4$  were obtained in 99.8% purity from the K & K Laboratories Inc.  $\text{GeCl}_4$  (99.999%) was obtained from Alfa Inorganics and 99.5%  $\text{TiCl}_4$ , from Matheson Coleman and Bell, was used as received. Spectrograde 99.9%  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  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  $57\text{--}58^\circ$ , was distilled over sodium using a 70-cm Vigreux column. The center fraction, bp  $57.5^\circ$ , 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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