Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Thermolysis of tetramethylammonium iodotrimethylaluminate

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(Received December 8th, 1971)

The reaction of aluminum alkyls with alkali metal or ammonium halides was first investigated by Ziegler *et al.* in 1960[1]. Two principal types of compounds were formed as the preparation of the iodides illustrates:

$$\mathrm{Al(C_2H_5)_3 + N(C_2H_5)_4I \longrightarrow [N(C_2H_5)_4]\ [Al(C_2H_5)_3I]}\ \text{(m.p. 50°)}$$
$$\mathrm{2\ Al(C_2H_5)_3 + N(C_2H_5)_4I \longrightarrow [N(C_2H_5)_4]\ [Al_2(C_2H_5)_6I]}\ \text{(liquid at room temp.)}$$

More recently the synthesis and properties of a number of analogous pseudohalide complexes have been reported[2,3,4]. $\mathrm{K[Al_2(CH_3)_6SCN]}$ has been shown to undergo a thermal decomposition which involves the splitting of the thiocyanate ion[3]:

$$\mathrm{K[Al_2(CH_3)_6SCN]} \xrightarrow{130^\circ} \mathrm{[(CH_3)_2Al{\cdot}NC(CH_3)_2]_2} + \begin{array}{l}\text{unidentified}\\ \text{decomposition}\\ \text{products}\end{array}$$

As part of a general study of the thermolysis of anionic organoaluminum compounds we now report the preparation and thermal behavior of $\mathrm{[N(CH_3)_4]\ [Al(CH_3)_3I]}$, and the crystal structure of the major thermal decomposition product.

The white crystalline compound $\mathrm{[N(CH_3)_4]\ [Al(CH_3)_3I]}$ (m.p. 252–254°) was prepared by the sealed tube reaction of 0.01 mole of trimethylaluminum with 0.005 mole $\mathrm{N(CH_3)_4I}$. Complexation readily occurred at 90°, and although different reaction times were tried, in all cases 0.005 mole of trimethylaluminum was later recovered. (Found: C, 28.78; H, 7.49; Al, 10.15; I, 45.00; N, 4.91. $\mathrm{C_7H_{21}AlIN}$ calcd.: C, 30.78; H, 7.69; Al, 9.88; I, 46.50; N, 5.13%.)

Thermal decomposition of $\mathrm{[N(CH_3)_4]\ [Al(CH_3)_3I]}$ was accomplished by heating the substance at 280° for several hours in a sealed tube. A white crystalline sublimate was obtained in 60% yield; subsequent investigations have shown the material to be $(CH_3)_3N \cdot Al(CH_3)_2I$. (Found: Al, 11.38; N, 5.74. $C_5H_{15}AlIN$ calcd.: Al, 11.08; N, 5.76%.)

$$[N(CH_3)_4][Al(CH_3)_3I] \xrightarrow{280^\circ} (CH_3)_3N \cdot Al(CH_3)_2I + C_2H_6$$

The presence of ethane was confirmed by a mass spectroscopic analysis of the gaseous contents of the reaction vessel. Some of the properties of the new compound are shown in Table 1.

TABLE 1

DATA FOR $(CH_3)_3N \cdot Al(CH_3)_2I$

Crystal system:	orthorhombic
Space group:	$Pna2_1$ or $Pnma$
Lattice constants:	a = 12.59±0.01Å
	b = 10.75±0.01Å
	c = 7.58±0.01Å
	ρ_{calc} = 1.58 g/cm^3
Melting point[a]:	124–126°
NMR spectrum[b]:	τ 8.15 (3), τ 10.20 (2)

[a]Sealed capillary, uncorrected. [b]Benzene solution

The crystal structure has been obtained, and the molecular geometry is shown in Fig. 1. At present the R value based on 696 independent observed reflections is 11%. The aluminum, iodine, nitrogen, and one of the nitrogen-methyl carbon atoms of the molecule lie on a crystallographic mirror plane. The trimethylamine and iododimethylaluminum groups are in a staggered configuration about the aluminum-nitrogen bond.

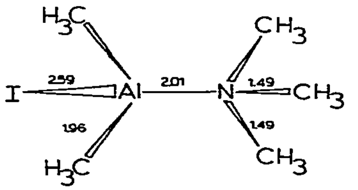

Fig. 1. Molecular structure of iododimethylaluminum–trimethylamine complex.

The aluminum–iodine bond distance (2.59Å) is the first to be determined crystallographically for an organometallic compound, but seems to be reasonable on the basis of a sum of covalent radii. The nitrogen–aluminum (2.01Å), aluminum–carbon (1.96Å) and nitrogen–carbon (1.49Å) bond lengths are normal for a donor–acceptor complex of this type[5,6]

From Fig. 1 it is apparent that the thermolysis product can be viewed as the neutral addition complex of trimethylamine and dimethylaluminum iodide. In fact, the analogous chloride compound has been prepared by the straight-forward addition of trimethylamine to dimethylaluminum chloride[7]. In the present situation, the trimethylamine was generated from the tetramethylammonium cation in a manner apparently similar to the decomposition of tetramethylammonium iodide itself:

$$N(CH_3)_4I \xrightarrow{230^\circ} N(CH_3)_3 + CH_3I$$

However, a detailed knowledge of the mechanism of interaction of the anion $[Al(CH_3)_3I]^-$ with the cation $[N(CH_3)_4]^+$ must await further investigations.

ACKNOWLEDGEMENTS

We are grateful to the National Science Foundation under Grant GP-24852 for support of this research.

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