Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916, and the Air Force Rocket Propulsion Laboratory, Edwards, California 93523, U.S.A.

Reactions of Aluminum Monofluoride with Covalent Fluorides

F. Q. Roberto and G. Mamantov

Received August 22, 1968

Introduction

Recent success in using high temperature species, silicon difluoride[1-4] and boron monofluoride,[5] as reagents prompted us to investigate the reactions of aluminum monofluoride with several covalent fluorides. The formation of aluminum monofluoride in the reaction between aluminum and aluminum trifluoride was demonstrated in 1943 by Klemm and Voss;[6] it was shown that aluminum monofluoride disproportionates to the reactants upon condensation. Recently the infrared spectrum of aluminum monofluoride in an argon matrix was reported by Snelson.[7]

The reactions of aluminum monofluoride and monochloride vapors with several carrier gases, such as oxygen, water, nitrogen, and carbon monoxide, and refractory materials (primarily oxides and carbides) have been studied by Semenkovich.[8] In nearly all reactions, compounds of trivalent aluminum (usually Al_2O_3) were obtained. In a few cases, elemental aluminum was also produced.

In this work, we attempted to produce new aluminum-containing species by reacting aluminum monofluoride with silicon tetrafluoride, boron trifluoride, phosphorus trifluoride, and carbon tetrafluoride.

Experimental Section

Equipment. Most of the studies were carried out in a reactor consisting of 1″ o.d.×13″ long AD99 high-vacuum alumina tube (Coors Porcelain Company) which was conected to a liquid nitrogen-cooled trap by means of 1″ o.d. Swagelok unions. The reactor-trap system could be isolated and transferred to a dry box to remove solid products formed. The trap was connected to an all-metal vacuum system for pressure measurements using a Wallace and Tiernan Model FA 145 pressure gauge and NRC Model 720 vacuum gauge. The reactor was heated with a multiple unit furnace (Hevi-Electrical Equipment). The temperature was controlled with a Model 292 Capacitrol and measured with a platinum/platinum—13 per cent rhodium thermocouple, placed in the center of the furnace. The operating temperature was varied from 600° to 800°C.

Procedure. In a typical experiment the gaseous reactant was passed over a mixture of AlF_3 to aluminum (mole ratio 1:2), contained in an alumina combustion boat, located inside the high-vacuum alumina tube. Preliminary experiments in which no gaseous reactant was used and the reactor was evacuated to $\sim 5 \times 10^{-3}$ torr, resulted in a solid in the trap, which corresponded to the elemental analysis expected for $AlF_3 + 2Al$. X-ray diffraction patterns indicated only aluminum and AlF_3. Thus, in this reactor the reactions were presumably between gaseous AlF vapors and the second gaseous reactant, the products being condensed in the cold trap, or collected downstream in the alumina tube. The use of another reactor, in which AlF was deposited on top of the second reactant, previously condensed on a cold finger, was also explored; only the starting materials were observed in these experiments.

Materials. Aluminum powder and AlF_3 were obtained from Matheson, Coleman and Bell. AlF_3 was dehydrated by heating to 400°C under vacuum. BF_3, SiF_4, and CF_4, obtained from Matheson Company, were used without further purification. PF_3, obtained from Ozark-Mahoning Company, was purified by low-temperature distillation.

Analysis. The volatile products were analyzed by infrared spectroscopy, using a nickel cell with silver chloride windows. X-ray diffraction patterns and elemental analyses were obtained on a number of solid samples.

Reaction of AlF with SiF_4. SiF_4 was passed over the AlF_3—Al (1:2) mixture at the average flow rate of 15 cc/min. at 600-700°C. A white-yellow polymeric material that burned in moist air was observed in the cold trap. The material appeared to be the same as that obtained by Timms, Kent, Ehlert, and Margrave,[1] namely $(SiF_2)_x$. A brown solid, found ~½″ from the alumina boat, contained aluminum (24-28%), fluorine (41-60%), and silicon (10-20%) (the elemental analysis varied depending on the temperature at which the reaction was conducted). X-ray

---

(1) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, *87*, 2824 (1965).
(2) P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckman, T. C. Farrar, and T. D. Coyle, *J. Am. Chem. Soc.*, *87*, 3819 (1965).
(3) J. C. Thompson, J. L. Margrave, and P. L. Timms, *Chem. Comm.*, 566 (1966).
(4) P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Am. Chem. Soc.*, *88*, 940 (1966).
(5) P. L. Timms, *J. Am. Chem. Soc.*, *89*, 1629 (1967).
(6) W. Klemm and E. Voss, *Z. Anorg. Allg. Chem.*, *251*, 233 (1943).
(7) A. Snelson, *J. Phys. Chem.*, *71*, 3202 (1967).
(8) S. A. Semenkovich, *Zhurnal Prikl. Khim.*, *33*, 552 (1960).

diffraction patterns of the brown solid showed the presence of aluminum trifluoride and silicon.

Reactions of AlF with BF_3, PF_3, and CF_4. The reactions were conducted in the manner described above. With BF_3, the solid material, deposited 1½" from the alumina boat, contained aluminum (30-43%), boron (3-6%), and fluorine (48-57%) (as above, the composition depended on the experimental temperature). X-ray diffraction patterns indicated only aluminum and aluminum trifluoride. The presence of amorphous boron was indicated by emission spectroscopy. In one run, a polymeric material was found in the trap; however, there was not enough sample to obtain elemental analysis. It is believed that boron trifluoride was not completely reduced to boron, and some $(BF)_x$ polymer[5] was formed from the condensation of BF on the cold trap.

With PF_3, the products collected in the trap were complex; attempts to separate them completely, using fractional codistillation,[9] failed. Partial separation resulted in the identification of PF_5 and POF_3 from the infrared spectra. A crumbly polymeric material, that smoked when the reactor was opened in the dry box, was also produced. The color of the material changed from yellow to brown after 72 hours in the dry box. A sample burned upon exposure to air. Attempts to analyze the material by hydrolysis resulted in unidentified gases; only 40 per cent of the sample could be accounted for by elemental analysis (P, 29.9; F, 5.4; Al, 4.6). Because of the problems encountered in the characterization of the solid, and the lack of volatile species containing aluminum, the study of the reaction of AlF with PF_3 was abandoned.

In the reaction with CF_4, only the disproportionation products of AlF ($Al + AlF_3$) and CF_4 were observed.

Results and Discussion

Gaseous aluminum monofluoride, produced at 600-800°C, is a powerful reducing agent, as evidenced by its reactions with silicon tetrafluoride and boron trifluoride.

$$AlF + SiF_4 = SiF_2 + AlF_3 \quad (1)$$

$$xSiF_2 = (SiF_2)_x \quad (2)$$

$$2AlF + SiF_4 = 2AlF_3 + Si \quad (3)$$

$$3AlF + 2BF_3 = 3AlF_3 + 2B \quad (4)$$

$$AlF + BF_3 = BF + AlF_3 \quad (5)$$

$$xBF = (BF)_x \quad (6)$$

The reaction of AlF with phosphorus trifluoride was found to be complex; complete characterization of the products was not possible.

Carbon tetrafluoride was found to be inert to AlF, under the experimental conditions employed.

---

(9) G. H. Cady and D. P. Siegworth, *Anal. Chem.*, *31*, 618 (1959).