tion with 1,4-dioxane, which has frequently been used with other halides.[4]

Subsequent study has shown the formation of a 1:1 addition compound by direct reaction of antimony(III) fluoride and dioxane and by reaction in methanol solution. The complex decomposes at 143° into its components and can be used as a mild fluorinating agent.

Experimental

Antimony(III) fluoride was refluxed for 15 minutes with a 14-fold excess of dioxane, filtered and cooled. Alternatively, a mixture of 15 ml. of dioxane (0.17 mole) and 15 ml. of methanol was added slowly to a solution of 19.3 g. (0.11 mole) of the fluoride in 30 ml. of methanol. After brief refluxing the solution was cooled, the crystals removed, and dried in a stream of dry air. Samples were analyzed for antimony by titration with potassium bromate,[5] using Naphthol Blue Black.[6]

Anal. Calcd. for $SbF_3 \cdot C_4H_8O_2$: Sb, 45.62. Found: Sb, 45.47, 45.54, 45.57.

The dissociation temperature was found by determining the heating curve of a 14-g. sample in a nickel cell, using copper–constantan thermocouples and a Speedomax recorder. A sharp break occurred at 143°, and a sample heated to 305° showed a break in its cooling curve at 290°, corresponding to the m.p. of the fluoride.

Benzotrichloride was fluorinated by the complex, using the apparatus and procedures given by Henne,[7] maintaining the same fluoride–chloride ratio. Both benzotrifluoride and the chlorodifluoride were formed.

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(5) H. H. Willard and H. Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Publishing Co., Inc., New York, N. Y., 1943, p. 350.

(6) G. F. Smith and R. L. May, *Ind. Eng. Chem., Anal. Ed.*, **13**, 460 (1941).

(7) A. L. Henne in R. Adams, ed., "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 62.

DEPARTMENT OF CHEMISTRY
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Ammonium Pentafluorozirconate(IV) and its Monohydrate[1]

BY HELMUT M. HAENDLER AND DEAN W. ROBINSON

RECEIVED APRIL 8, 1953

Ammonium pentafluorozirconate(IV), NH_4ZrF_5, has been reported as one of the intermediate products of the thermal decomposition of ammonium heptafluorozirconate(IV), $(NH_4)_3ZrF_7$.[2] Attempts to grow single crystals of the pentafluorozirconate from solution for X-ray structural studies led to the discovery of its monohydrate. Both compounds crystallize from a solution of zirconium oxide in hydrofluoric acid, to which has been added 75% of the theoretical quantity of ammonium fluoride. The predominant product is controlled by the rate of crystallization. Rapid crystallization favors formation of the hydrate, slow crystallization suppresses it. The monohydrate loses water spontaneously in air of low humidity to become the anhydrous compound. Powder diffraction and Weissenberg photographs of the two compounds are distinctive.

Experimental

All crystallizations were carried out with platinum or polyethylene apparatus. To obtain the monohydrate, the solution was evaporated by heating to incipient crystallization, filtered and cooled. The hydrate crystallized in clusters of clear, colorless, six-sided right prisms. These were separated mechanically from the small crystals of the anhydrous compound, the formation of which could not be prevented completely.

Anhydrous pentafluorozirconate was produced with exclusion of hydrate by allowing the solution to evaporate slowly for 2–3 weeks, or by adding a small amount of ethanol prior to the slow evaporation. This compound crystallized in small, colorless, almost square plates, with truncated faces.

X-Ray diffraction powder photographs were taken of the products obtained by heating the hydrate at 110° and from its spontaneous decomposition in air. They were identical with the pattern of the pentafluorozirconate produced in the thermal decomposition of the heptafluorozirconate.

Ammonium ion was determined by distillation from basic solution into boric acid and titration with hydrochloric acid. Zirconium was determined by digestion with sulfuric acid and ignition to the oxide. Water was determined by heating at 110°.

Anal. Calcd. for $NH_4ZrF_5 \cdot H_2O$: NH_4, 8.12; Zr, 40.94; H_2O, 8.10. Found: NH_4, 7.64; Zr, 41.15; H_2O, 8.25.

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(1) Research supported by the Atomic Energy Commission and the Research Corporation.

(2) H. M. Haendler, C. M. Wheeler and D. W. Robinson, THIS JOURNAL, **74**, 2352 (1952).

DEPARTMENT OF CHEMISTRY
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Diazonium Fluoborates as Initiators of Vinyl Polymerization[1]

BY C. S. MARVEL, H. Z. FRIEDLANDER, SHERLOCK SWANN, JR., AND H. K. INSKIP

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In some experiments on the electrolytic generation of free radicals for the initiation of polymerization,[2] hydroquinone was added as a "shortstop" immediately after the electrolysis to prevent polymerization during the examination of the mixture. In those runs involving the electrolysis of *p*-bromobenzenediazonium fluoborate, extensive polymerization of acrylonitrile was observed after the addition of hydroquinone, but not before. Tests showed that the sulfuric acid anolyte solution and the fluoborate anion were not responsible for the polymerization. Further study demonstrated that the diazonium fluoborate in the presence of hydroquinone or ferrous ammonium sulfate caused the initiation of polymerization at 30°. In Table I are summarized the results of a number of homopolymerizations and copolymerizations initiated by substituted benzenediazonium fluoborates.

The effect of *p*H on yield and viscosity of polyacrylonitrile is demonstrated in experiments 1–6. Optimum conditions obtain at about *p*H 3. At 0° no polymer was obtained from acrylonitrile even after four days (experiments 7, 8) unless the amount of initiator was doubled over that used at 30° (experiments 9–14), and even with increase of initiator the yield and viscosity were relatively low. The effectiveness of the ferrous-salt activator in promoting polymerization of acrylonitrile at 30° is demonstrated in the 18-hour polymerizations (ex-

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(2) H. Z. Friedlander, S. Swann, Jr., and C. S. Marvel, *J. Electrochem. Soc.*, in press.