ether–boron trifluoride to form the metal fluoborate, NBF_4, and diethyl ether. In these and other experiments reported by Schlesinger the etherate served as a reaction medium. No data appear to have been reported for boron trifluoride etherates reacting with halides other than the two fluorides mentioned above. If one were to treat chlorides, bromides and/or iodides with dimethyl ether–boron trifluoride the formation of methyl halides could result. Because of their low boiling points these alkyl halides would allow for easy removal from the reaction system, particularly in the case of methyl chloride and bromide.

Results and Discussion

Reaction of Tetramethylammonium Chloride and Bromide with Dimethyl Ether–Boron Trifluoride.—In a typical experiment 1.73 g. of tetramethylammonium chloride were reacted at 50 and 80° with an excess amount (based on an anticipated metathesis) of dimethyl ether–boron trifluoride. At the higher temperature considerable decomposition of the quaternary salt into amine was observed. When the reaction was carried out at 50° the reaction proceeded smoothly with the evolution of gas. The gas was condensed in a Dry Ice–trichloroethylene cooled trap, and the resulting liquid gave a positive chloride test indicating the formation of methyl chloride. The presence of a second component in the liquid, probably methyl borate, was indicated by the wide boiling range of the condensate, from $-25°$ to about 0°.

When the reaction mixture (from the addition of the quaternary salt to dimethyl ether–boron trifluoride) was cooled to room temperature, a fine white crystalline precipitate formed. This precipitate gave positive qualitative tests for boron, fluorine and organic matter. It also gave a positive test for a normal fluoborate with nitron reagent, m.p. of derivative 223°, corresponding to the melting point of tetramethylammonium fluoborate obtained by standard methods of preparation, *i.e.*, quaternary hydroxide with fluoboric acid.

Anal. Calcd. for $(CH_3)_4NBF_4$: F, 47.22. Found: F, 46.15, 46.28, 46.37.

The analytical data and the behavior of the compound indicated that dimethyl ether–boron trifluoride reacts with tetramethylammonium chloride to form tetramethylammonium fluoborate according to

$$4(CH_3)_2OBF_3 + 3(CH_3)_4NCl \longrightarrow 3(CH_3)_4NBF_4 + 3CH_3Cl + B(OCH_3)_3 + (CH_3)_2O$$

Since a metathetical reaction did not occur additional experiments were performed using an excess of the etherate based on the above equation. This resulted only in an increased yield of tetramethylammonium fluoborate.

The reaction of tetramethylammonium bromide with dimethyl ether–boron trifluoride was similar to the quaternary ammonium chloride reaction, with the quaternary ammonium fluoborate and methyl bromide formed. The only significant difference appeared to be in the smaller amount of fluoborate formed and an appreciable displacement of boron trifluoride from the reaction system.

Reaction of Tetraethyl- and Tetra-*n*-propylammonium Bromides and Iodides with Dimethyl Ether–Boron Trifluoride.—The reactions of the longer chain alkyl ammonium halides followed the same course as the tetramethylammonium salts. The quaternary ammonium fluoborates produced in the reactions became more soluble in the reaction media, necessitating the use of diethyl ether to throw them out of solution. This was particularly true when tetra-*n*-propylammonium fluoborate was formed.

The quaternary ammonium fluoborates were characterized by melting points and from analytical data.

Anal. Calcd. for $(C_2H_5)_4NBF_4$: F, 35.01. Found: F, 34.45, 34.69, 34.72.

Anal. Calcd. for $(C_3H_7)_4NBF_4$: F, 27.82. Found: F, 27.40, 27.53.

Melting points: $(C_2H_5)_4NBF_4$, 365–368°; $(C_3H_7)_4NBF_4$, 249°.

Reaction of Tetra-*n*-butylammonium Iodide with Dimethyl Ether–Boron Trifluoride.—Tetra-*n*-butylammonium iodide reacted with dimethyl ether–boron trifluoride to form tetra-*n*-butylammonium fluoborate and methyl iodide. In this respect the reaction was similar to the shorter chain alkyl ammonium halides. However it was extremely difficult to obtain the tetra-*n*-butylammonium fluoborate from the reaction media, large quantities of diethyl ether were needed to precipitate the fluoborate. The fluoborate was characterized by m.p. 155°, lit. value 161°,[2] and from analytical data.

Anal. Calcd. for $(C_4H_9)_4NBF_4$: F, 23.20. Found: F, 24.96, 24.29, 23.91.

Experimental

Apparatus.—The reaction chamber was a 50-ml. round-bottom two-neck flask fitted with a reflux condenser. The condenser was connected to a train of three traps. Trap 1, a safety trap; trap 2 immersed in Dry Ice–trichloroethylene bath to condense volatile reaction products; trap 3 contained saturated alcoholic silver nitrate for identification of the halides. The system was constructed in such a manner that traps 2 and 3 could be removed and used as a separate unit.

Materials.—The quaternary ammonium halides were Eastman Kodak C.P. grade and used without further purification.

Dimethyl ether–boron trifluoride was prepared by direct vapor phase reaction according to the method of Laubengayer and Finlay.[3] The dimethyl etherate was purified by repeated fractional crystallization. Physical constants for the fraction used were $n^{20}D$ 1.316, m.p. $-14 \pm 0.5°$; lit. values $n^{20}D$ 1.302, m.p. $-14°$.[4] Fluorine was determined by the nitron precipitation method.[5]

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[2] C. R. Witschonke and C. A. Kraus, This Journal, **69**, 2472 (1947).

[3] A. W. Laubengayer and G. R. Finlay, *ibid.*, **65**, 884 (1943).

[4] H. Meerwein, *Ber.*, **66B**, 411 (1933).

[5] W. F. Hillebrand, *et al.*, "Applied Inorganic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 321.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW HAMPSHIRE
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Preparation of Substituted Quaternary Ammonium Fluoborates

BY CHARLES M. WHEELER, JR., AND RICHARD A. SANDSTEDT

RECEIVED NOVEMBER 4, 1954

The preparation of three quaternary ammonium fluoborates, tetramethyl-, tetraethyl-[1] and tetra-*n*-butylfluoborate[2] have been reported. Reaction of tetraalkylammonium chloride and hydroxide with an aqueous solution of fluoboric acid was the method of preparation.

In a systematic study of the properties and reactions of methoxyfluoboric and monohydroxyfluoboric acids we have had the occasion to treat a number of quaternary ammonium halides and hydroxides with these acids. The reaction of tetramethylammonium halides with monohydroxyfluoboric and methoxyfluoboric acids has been reported previously.[3]

Tetraethyl-, tetra-*n*-propyl- and tetra-*n*-butylammonium fluoborates were prepared by the reaction of the appropriate quaternary ammonium halide or hydroxide with monohydroxyfluoboric and methoxyfluoboric acids. The formation of normal fluoborates in these reactions is in contrast to the formation of monohydroxyfluoborate in the reaction of a tetramethylammonium halide

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[1] E. Wilke-Dorfurt and G. Balz, *Ber.*, **60B**, 115 (1927).

[2] C. R. Witschonke and C. A. Kraus, This Journal, **69**, 2472 (1947).

[3] C. M. Wheeler, Jr., R. D. Beaulieu and H. W. Burns, *ibid.*, **76**, 6323 (1954).

with monohydrofluoboric and methoxyfluoboric acids. It is also of interest to note the decrease in melting points with increased carbon chain length; tetramethyl-, 417–419°; tetraethyl-, 365–367°; tetra-*n*-propyl-, 249–251° and tetra-*n*-butylammonium fluoborate, 153–155°.

Experimental

Preparation and Characterization of Tetramethylammonium Fluoborate.—In order to obtain the melting point, 418 ± 1°, a sample of this compound was prepared by reaction of tetramethylammonium hydroxide with 40% fluoboric acid.

Anal.[4] Calcd. for $(CH_3)_4NBF_4$: C, 29.84; H, 7.51; F, 47.22. Found: C, 30.12, 29.94; H, 7.59, 7.49; F, 47.61, 47.27.

Preparation of Tetraethylammonium Fluoborate.—The addition of fluoboric, monohydroxyfluoboric and methoxyfluoboric acid to either an aqueous solution of tetraethylammonium bromide or the solid salt resulted in the liberation of hydrogen bromide and the formation of tetraethylammonium fluoborate. The reactions with monohydroxyfluoboric and methoxyfluoboric acid were carried out at 10°, with fluoboric acid at room temperature. It was necessary in each instance to concentrate the reaction solution, followed by addition of ether to the solution, precipitating tetraethylammonium fluoborate, m.p. 365–367°. Analytical data are presented below for the fluoborate formed from the reaction of tetraethylammonium bromide with methoxyfluoboric acid.

Anal. Calcd. for $(C_2H_5)_4NBF_4$: C, 44.29; H, 9.23; F, 35.03. Found: C, 44.72, 44.50; H, 9.54, 9.70; F, 35.08, 34.74.

Preparation of Tetra-*n*-propylammonium Fluoborate.—Although the preparation of tetra-*n*-propylammonium fluoborate has not been previously reported it was assumed that the quaternary hydroxide would react with fluoboric acid, to produce the quaternary fluoborate. The addition of tetra-*n*-propylammonium hydroxide to excess fluoboric acid resulted in immediate precipitation of white crystals. Recrystallization from hot methanol yielded tetra-*n*-propylammonium fluoborate, m.p. 249–250°.

Anal. Calcd. for $(C_3H_7)_4NBF_4$: C, 52.75; H, 10.33; F, 27.82. Found: C, 52.28, 52.37; H, 10.05, 10.12; F, 27.18, 27.28.

Solid tetra-*n*-propylammonium iodide added to methoxyfluoboric acid yielded hydrogen iodide and tetra-*n*-propylammonium fluoborate. It was necessary to add ether to precipitate the quaternary fluoborate from the reaction mixture. The precipitated fluoborate was recrystallized from hot methanol. Addition of ether aided in crystallization. The purified tetra-*n*-propylammonium fluoborate melted at 251° in good agreement with the sample prepared as described above.

Anal. Calcd. for $(C_3H_7)_4NBF_4$: C, 52.75; H, 10.33; F, 27.82. Found: C, 53.24, 53.09; H, 10.66, 10.45; F, 27.47, 27.14.

Subsequent reactions of tetra-*n*-propylammonium iodide with monohydroxyfluoboric and fluoboric acid and tetra-*n*-propylammonium hydroxide with monohydroxyfluoboric and methoxyfluoboric acids produced tetra-*n*-propylammonium fluoborate, identified by melting point.

Preparation of Tetra-*n*-butylammonium Fluoborate.—The addition of fluoboric, monohydroxyfluoboric and/or methoxyfluoboric acid to tetra-*n*-butylammonium hydroxide resulted in the immediate precipitation of a white solid, tetra-*n*-butylammonium fluoborate, m.p. 153–155°, lit.[2] 161°, which gave a positive nitron test.

Anal. Calcd. for $(C_4H_9)_4NBF_4$: C, 58.36; H, 11.03; F, 23.08. Found: C, 58.05, 58.24; H, 11.02, 10.84; F, 23.34, 23.06.

Hydroxyfluoboric acid was added to a solution of tetra-*n*-butylammonium iodide with immediate precipitation of tetra-*n*-butylammonium fluoborate. An attempt was made to recrystallize the salt from methanol; however, due to the high solubility of the salt in the alcohol it was necessary to add water and concentrate the solution on a steam-bath. Subsequent cooling produced crystalline tetra-*n*-butylammonium fluoborate, m.p. 156°, positive nitron test.

Methoxyfluoboric acid was added to solid tetra-*n*-butylammonium iodide. It was necessary to extract the fluoborate with chloroform, followed by evaporation of the solvent. The fluoborate was recrystallized from a 50% water–methanol solution yielding crystals melting 155°, positive nitron test.

Anal.[5] Calcd. for $(C_4H_9)_4NBF_4$: F, 23.08. Found: F, 22.92, 22.85, 22.74.

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[4] Unless otherwise noted all analyses were performed by Laboratory of Microchemistry, Dr. Carl Tiedcke, Teaneck, New Jersey.

[5] Fluorine detn. by nitron ppt. method: W. F. Hillebrand, *et al.*, "Applied Inorganic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 321.

DEPARTMENT OF CHEMISTRY
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COMMUNICATIONS TO THE EDITOR

THE PRODUCTION OF A FLAME TEMPERATURE OF 5000°K.

Sir:

We have recently measured the temperature of the $(CN)_2$–O_2 flame at the stoichiometric point (*i.e.*, 1:1 mole)[1] and found that it produces the highest temperature obtainable by a chemical reaction. This is due to its high exothermicity coupled with the fact that the products of combustion, *i.e.*, CO and N_2, are the most thermally stable molecules known. Our experimental flame temperature measurement (4640 ± 150°K.) checks the calculated temperature, *i.e.*, 4835 ± 50°K., within the error of both methods.

In order to produce higher temperatures we have recently operated this flame at pressures up to 100 p.s.i.a., as described below. Under pressure the dissociation of CO and N_2 is suppressed and the temperature of the flame is increased.

The pressure effect can be calculated with a high degree of reliability due to the precision of the heat content data now being published by the National Bureau of Standards,[2] coupled with W. M. Latimer's revised tables[3] of the free energy functions and dissociation constants of the CO and N_2 molecules up to 5000°K. Using the above data we

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[1] J. B. Conway, R. H. Wilson, Jr., and A. V. Grosse, THIS JOURNAL, **76**, 499 (1953).

[2] Circular of the National Bureau of Standards C-461, Washington, D.C., 1947, p. 228.

[3] W. M. Latimer, "Tables of Free Energy Functions for Elements and Compounds in the Range of 2000–5000°K.," MDDC-1462, revised 1952.