At 400° no detectable reaction occurs even when the system is evacuated. At 500° the corrosion reaction proceeds when the system is under vacuum, but is reversed when hydrogen is admitted.

The hydroxide samples used for the determinations were thoroughly degassed at or slightly above the melting point of the hydroxide being used, 319.1° for sodium hydroxide[2] and 410° for potassium hydroxide.[3] A known amount of hydrogen gas was introduced into the system and, after allowing the system to come to equilibrium, the amount of gaseous hydrogen remaining in the system was calculated. Another increment of hydrogen was then added and the procedure repeated.

Four sets of duplicate experiments were made: two blank runs with empty nickel liners at 500°; two with sodium hydroxide at 500°; two with potassium hydroxide at 500°; and two with potassium hydroxide at 410°. In every case the amount of gaseous hydrogen in the system at equilibrium was found to be the same, within the limits of the experimental error, as the amount of hydrogen added. The difference between the amount of hydrogen added and the amount of gaseous hydrogen found at equilibrium averaged 1.1, 1.0, 1.9 and 1.0% of the amount of hydrogen added for the four sets of duplicate runs in the order mentioned, and varied in a random fashion. The limits of error were such that the hydrogen solubility may be said to be less than 60 mg. hydrogen per 100 g. of hydroxide under all conditions examined.

Experimental

The sodium hydroxide and potassium hydroxide used in these experiments were specially dehydrated, low-carbonate preparations. The apparatus and experimental procedures were similar to those described in previous papers.[4,5] Screw-cap nickel liners for containing the hydroxides were fabricated from International Nickel Company Grade "L" nickel. They were pretreated at 400° by alternate 30-minute periods of hydrogen and vacuum for four hours to remove any surface oxidation and adsorbed gases.

A screw-cap nickel liner was loaded in an inert atmosphere box with approximately 25 g. of hydroxide. The liner was then placed in a stainless steel pressure vessel, which was welded gas-tight. The pressure vessel was connected by means of copper tubing to a calibrated manifold and a pressure recording gage. The volume of the copper line plus the pressure vessel were calibrated by expanding hydrogen from the unknown volume, which included a previously calibrated high-pressure manifold, into the known volume of a low-pressure manifold which had been at a flat vacuum. Corrections were made for the non-ideality of hydrogen at the pressure used.

The pressure vessel was clamped in an upright position in a molten lead-bath inside a muffle furnace. It was then degassed for one hour at or slightly above the melting point of the hydroxide being used, after which it was heated to the temperature desired for the experiment. The temperature was controlled to ±1°.

Solubility determinations were carried out by addition of a known weight of hydrogen from the high-pressure manifold to the pressure vessel system, in which was incorporated a 1000 p.s.i. recording pressure gage. Approximately 15 minutes were allowed for the system to come to equilibrium. (Exploratory experiments showed this to be a sufficient interval to establish equilibrium.) Another increment of hydrogen was then added and the procedure repeated. Hydrogen additions were made in such a way as to increase the pressure in the system by approximately 100 p.s.i. intervals to 800 p.s.i.a.

The calculations were carried out as follows. From the known pressure drop in the high-pressure manifold, the weight of hydrogen added to the system was calculated. The weight of hydrogen gas actually present above the system was then calculated in two parts, the first being the weight of hydrogen gas present in the pressure vessel at the equilibrium pressure and the operating temperature, and the second being the weight present in the copper tubing system at the equilibrium pressure and room temperature. The sum of these two values represented the weight of hydrogen gas above the hydroxide melt at equilibrium. This latter value was subtracted from the weight of hydrogen added to give the hydrogen difference (or "solubility") for the weight of sample used. Corrections for the non-ideality of hydrogen under the various conditions were derived from the data compiled by Deming and Shupe.[6]

After completing a solubility determination, the pressure vessel was cooled under approximately 800 p.s.i.a. of hydrogen, cut open, and the liner unloaded under an inert atmosphere. Samples of the resolidified melt were analyzed for total alkalinity, and a spectrographic analysis was made for trace metals. These analyses proved there had been no interaction between the hydroxide and its nickel container during the solubility determination.

In addition to these routine analyses, quantitative tests for gas evolution on dissolution of the hydroxides in degassed, distilled water were made by a modification of the method of Banus and Vetrano.[7] Because the hydroxides evolved small quantities of gas even prior to being subjected to hydrogen (presumably argon adsorbed while handling the hydroxides in an inert atmosphere box), it was necessary to determine what fraction of the evolved gas was hydrogen. This was done by sealing a platinum wire into the air chamber at the top of the gas buret, and, after the gas evolution for a sample had been completed, sparking the gas mixture with a Tesla coil until there was no further reduction of the gas volume. In every case the hydrogen found was less than 0.5 mg. per 100 g. of hydroxide. It is not known whether this small quantity of hydrogen was dissolved in or occluded by the hydroxide, and it is recognized that there is no definite relationship between this value and the hydrogen solubility under the conditions of the solubility run. It is definitely established, however, that hydrogen was present in the resolidified samples. The hydrogen evolutions are, therefore, consistent with the experimental results, although they do not afford positive confirmation of them.

The sodium hydroxide used in these experiments contained 0.07% sodium carbonate; the potassium hydroxide, 0.12% potassium carbonate. Other impurities were present in trace quantities only.

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[2] T. B. Douglas and J. L. Dever, *J. Research Natl. Bur. Standards*, **53**, 81 (1954).

[3] R. P. Seward and K. E. Martin, This Journal, **71**, 3564 (1949).

[4] T. R. P. Gibb, Jr., J. J. McSharry and R. W. Bragdon, *ibid.*, **73**, 1751 (1951).

[5] M. D. Banus, J. J. McSharry and E. A. Sullivan, *ibid.*, **77**, 2007 (1955).

[6] W. E. Deming and L. E. Shupe, *Phys. Rev.*, **40**, 848 (1932).

[7] M. D. Banus and J. B. Vetrano, *Anal. Chem.*, **25**, 1268 (1953).

CHEMICAL RESEARCH LABORATORY
METAL HYDRIDES INCORPORATED
BEVERLY, MASSACHUSETTS

Reaction of Dimethyl Ether–Boron Trifluoride with Quaternary Alkyl Ammonium Halides

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

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A consideration of the structure of dimethyl ether–boron trifluoride suggested the possibility of preparing methoxy fluoborates by a metathetical reaction of the etherate and quaternary ammonium halides. Schlesinger[1] has observed that either lithium or sodium fluorides react with diethyl

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[1] H. I. Schlesinger, H. C. Brown, J. R. Gilbreath and J. J. Katz, This Journal, **75**, 195 (1953).

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 $n^{20}\mathrm{D}$ 1.316, m.p. −14 ± 0.5°; lit. values $n^{20}\mathrm{D}$ 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
Durham, N. H.

Preparation of Substituted Quaternary Ammonium Fluoborates

By Charles M. Wheeler, Jr., and Richard A. Sandstedt

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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).