TABLE II

$k \times 10^3$, min.$^{-1}$	Added salt	Ionic strength (approx.)	Temp., °C.
1.04	$KClO_4$	60	30.0
2.68	$KClO_4$	60	38.0
5.58	$KClO_4$	30	44.0
9.05	$KClO_4$	60	50.0

From the six possible combinations of pairs of k the activation energy in the Arrhenius expression is found to be 21.3 ± 2.7 kcal./mole, and the frequency factor is $(2.8 \pm 0.5) \times 10^{15}$ min.$^{-1}$.

This value for the activation energy is in good agreement with that reported by Brown, Ingold and Nyholm[2] for the same reaction in methanol solution, that is, 23.69 kcal./mole. The frequency factor was reported to be 3.05×10^{13} min.$^{-1}$. The close agreement of the activation energies for the reaction in different solvents is to be expected for a reaction of this type. The frequency factor, on the other hand, would be expected to be sensitive to the solvent. The small salt effect observed in methanol does not appear in 2-methoxyethanol although an effect of comparable magnitude should be discernible.

The fact that the *trans*-isomer is more stable than the *cis*-isomer can be explained by a simple electrostatic model. Two like charges located *cis* to each other on the vertices of a regular octahedron experience a greater mutual repulsion than if they are *trans* to each other. This is so even if one considers only the component of force directed along a line from the center of the octahedron through the vertex. This simple picture is shown to be inadequate, however, by the fact that 2-methoxyethanol solutions of *cis*-$[Cr(en)_2Cl_2]Cl$ do not isomerize to the *trans* form even after 30 minutes of refluxing. However, a solution of the *levo-cis*-isomer of the Cr complex, showing a rotation of +0.46° at the NaD line, was completely racemized after having been boiled for two minutes. Hence even though the bonds in the complex ion are loosened, as shown by the racemization, there are forces determining the geometry of the complex more powerful than the electrostatic repulsion between the chloride ions.

The reaction between *trans*-$[Co(en)_2Cl_2]Cl$ and 2-methoxyethanol has not been clarified. In boiling solvent it is rapid and after a short time an olive-green precipitate is formed. The solution becomes a more yellow-green in color. The precipitate is not soluble in 2-methoxyethanol, ethanol or ethyl ether. In water it is radically altered, giving a dark brown solution which yields a brown gummy material on evaporation. This brown solution will not give an AgCl precipitate with Ag^+ unless acidified. Analyses of the olive-green powder vary slightly from sample to sample and do not correspond to any rational empirical formula. Probably the material contains a polynuclear complex with some varying contaminants. A methanol solution of *trans*-$[Co(en)_2Cl_2]Cl$ in a sealed tube heated in the steam-bath for 12 hours gave no spectrophotometric evidence that a reaction had occurred.

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[2] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953); D. D. Brown and R. S. Nyholm, *ibid.*, 2696 (1953).

Reaction of Sodium Hydroxide with Methoxyfluoboric Acid and Monohydroxyfluoboric Acid

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Meerwein and Pannwitz[1] have reported the compounds sodium methoxyfluoborate, $NaBF_3OCH_3$, and sodium monohydroxyfluoborate, $NaBF_3OH$, prepared by the addition of an ether suspension of sodium methoxide and sodium hydroxide to boron trifluoride ethyl etherate. It should be pointed out that Booth and Martin[2] were incorrect in reporting the method used by Meerwein and Pannwitz in preparing these compounds. Neither compound was prepared by direct acid–base neutralization. This note reports results obtained in part of a general study of the preparation and properties of substituted fluoborates.

Experimental

Methoxyfluoboric acid and monohydroxyfluoboric acid were prepared by saturating methanol and water with boron trifluoride, after which the compounds were purified by fractional recrystallization.[3,4] Fluorine was determined by the calcium fluoride precipitation method of Ryss.[5] Boron was determined by carbonate fusion followed with mannitol–sodium hydroxide titration.

The X-ray powder diffraction photographs were made with copper radiation, filtered by nickel, using a Philips 57.3-mm. powder camera. The samples were mounted on Pyrex fibers. Intensities were estimated visually by comparison with a film of known intensity. Powder pattern data for sodium fluoborate have not been reported in the literature, although Klinkenberg[6] has reported lattice constants for this compound. Table I lists powder pattern data for sodium fluoborate.

Anal. Calcd. for $NaBF_4$: B, 9.85; F, 69.21. Found: B, 9.38, 9.52, 9.71; F, 69.11, 68.97, 69.17.

TABLE I

X-RAY POWDER DATA FOR SODIUM FLUOBORATE, "*d*" FOLLOWED IN PARENTHESES BY RELATIVE INTENSITY

3.80 (15), 3.39 (100), 3.13 (2), 2.83 (38), 2.73 (19), 2.55 (1), 2.31 (85), 2.19 (1), 2.14 (35), 2.03 (62), 1.99 (42), 1.90 (2), 1.83 (38), 1.80 (31), 1.71 (8), 1.69 (15), 1.61 (27), 1.55 (31), 1.49 (35), 1.46 (1), 1.39 (3), 1.36 (1), 1.36 (7), 1.33 (8), 1.31 (3), 1.28 (14), 1.24 (19), 1.20 (10), 1.13 (8), 1.09 (6), 1.07 (1), 1.05 (6), 1.02 (8), 1.01 (5), 0.997 (8), 0.983 (4), 0.967 (3), 0.956 (2), 0.944 (2), 0.925 (1), 0.912 (2), 0.902 (5).

Reaction of Methoxyfluoboric Acid with Sodium Hydroxide.—A saturated alcoholic (methanol) solution of sodium hydroxide was added slowly to methoxyfluoboric acid. Sufficient base was added to neutralize the acid, resulting in the formation of a precipitate. The solid product was filtered, washed and dried with acetone. A positive nitron test was obtained for the precipitate, with the nitron de-

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[1] H. Meerwein and W. Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).

[2] H. R. Booth and D. R. Martin, "Boron Trifluoride and its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 55.

[3] N. N. Greenwood and R. L. Martin, *J. Chem. Soc.*, 757 (1953).

[4] J. S. McGrath, C. G. Stack and P. A. McCusker, THIS JOURNAL, **66**, 1263 (1944).

[5] I. G. Ryss and M. M. Slutskaya, *J. Phys. Chem.* (*U.S.S.R.*), **21**, 549 (1947).

[6] L. J. Klinkenberg, *Rec. Trav. Chim.*, **56**, 36 (1937).

rivative melting at 225°, characteristic of normal fluoborates. This indicated the formation of sodium fluoborate. Fluorine and boron analyses further substantiated this observation.

Anal. Calcd. for $NaBF_4$: B, 9.85; F, 69.21. Found: B, 8.75, 9.45; F, 68.82, 69.41.

X-ray powder data for this precipitate agreed with similar data for known sodium fluoborate.

In a quantitative study of the reaction between sodium hydroxide and methoxyfluoboric acid a 90% yield of sodium fluoborate was obtained. In a typical experiment 0.0526 mole of sodium hydroxide reacted with 0.0702 mole of methoxyfluoboric acid, yielding 0.0474 mole of sodium fluoborate.

The neutralization of four moles of methoxyfluoboric acid by three moles of sodium hydroxide yields three moles of sodium fluoborate and is presumed to proceed according to the reaction

$$3NaOH + 4HBF_3OCH_3 \longrightarrow 3NaBF_4 + B(OCH_3)_3 + CH_3OH + 3H_2O$$

Reaction of Monohydroxyfluoboric Acid with Sodium Hydroxide.—The addition of a saturated aqueous solution of sodium hydroxide to monohydroxyfluoboric acid until the *p*H of the reaction mixture was about 5.5, produced boric acid. The boric acid was filtered, and identified by the X-ray powder pattern technique. Continued addition of sodium hydroxide to the filtrate from the above reaction produced sodium fluoborate, also identified by X-ray diffraction photographs.

A *p*H titration of monohydroxyfluoboric acid with standard sodium hydroxide exhibited two well-defined inflection points in plots of *p*H against ml. base. The initial inflection in the curve occurred at a *p*H of about 5 and corresponded to the neutralization of the acid to form sodium fluoborate and boric acid. The second inflection corresponded to the neutralization of the boric acid produced in the initial reaction. A poorly defined inflection was observed between the two points mentioned above. A proposed explanation for this curve suggests that partial hydrolysis of sodium fluoborate formed in the initial reaction required some additional base for neutralization. The shape of the entire curve is somewhat similar to that curve reported by Wamser[7] for the titration of mixtures of fluoboric and monohydroxyfluoboric acid with sodium hydroxide. However, Wamser explained the separate inflections by assuming the formation of sodium hydroxyfluoborate and sodium fluoride in the neutralization. Neither of these products was found to be formed in the reaction of sodium hydroxide and monohydroxyfluoboric acid by the present authors.

The neutralization of four moles of monohydroxyfluoboric acid by three moles of sodium hydroxide yields three moles of sodium fluoborate and one mole of boric acid and is presumed to proceed according to the reaction

$$3NaOH + 4HBF_3OH \longrightarrow 3NaBF_4 + H_3BO_3 + 4H_2O$$

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[7] C. A. Wamser, This Journal, **73**, 409 (1951).

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Preparation of Tetramethylammonium Monohydroxyfluoborate

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The reaction of tetramethylammonium halides with methoxyfluoboric acid was studied in an attempt to prepare quaternary ammonium methoxyfluoborates. O'Leary and Wenske[1] have reported the compound mercury (II) oxide with methoxyfluoboric acid. These authors further stated that methoxyfluoborate compounds with cations more electropositive than mercury(II) could not be prepared due to immediate decomposition into the normal fluoborate. However, no specific compounds and no experimental data were reported to substantiate this observation. Meerwein and Pannwitz[2] have reported the preparation of sodium and potassium methoxyfluoborate by an indirect method, in which the respective methylates were treated with boron trifluoride dimethyl etherate.

The addition of solid tetramethylammonium chloride, bromide or iodide to methoxyfluoboric acid, at room temperature, resulted in immediate liberation of the appropriate hydrogen halide. The reaction mixture yielded a white solid when the solution was concentrated by evaporation or upon addition of small amounts of diethyl ether. Analysis showed the compound to be tetramethylammonium hydroxyfluoborate, melting point 414°.

Anal. Calcd. for $(CH_3)_4NBF_3OH$: C, 30.19; H, 8.34; B, 6.80; F, 35.85. Found[3]: C, 29.65, 29.93; H, 7.99, 7.80; B, 7.30, 6.90; F, 35.36, 35.65.

A separate series of experiments were performed to prepare tetramethylammonium hydroxyfluoborate from different starting materials. Monohydroxyfluoboric acid was titrated with a 10% aqueous solution of tetramethylammonium hydroxide to the phenolphthalein end-point. After neutralization a white solid was again precipitated by diethyl ether. The melting point and carbon, hydrogen and fluorine analyses for this solid agreed with similar data obtained for the solid reaction product from tetramethylammonium halides with methoxyfluoboric acid.

Although the analytical data confirmed the formation of tetramethylammonium monohydroxyfluoborate, an additional characterization was made with X-ray diffraction powder data. Identical powder patterns were obtained for the solid reaction products of tetramethylammonium halides with methoxyfluoboric acid and tetramethylammonium hydroxide with monohydroxyfluoboric acid. Table I lists these data for tetramethylammonium monohydroxyfluoborate.

Table I

X-Ray Powder Data for Tetramethylammonium Monohydroxyfluoborate, "*d*" Followed in Parentheses by Relative Intensity

5.82 (6), 4.83 (10), 4.08 (100), 3.13 (20), 2.90 (1), 2.76 (10), 2.61 (1), 2.48 (40), 2.29 (20), 2.21 (6), 1.93 (20), 1.85 (1), 1.64 (18), 1.55 (3), 1.36 (1).

Nieuwland's[4] proposed ionization for methoxyfluoboric acid indicates that a metathetical reaction of the acid with quaternary ammonium halides might be expected to proceed according to the equation

$$(CH_3)_4NX + HBF_3OCH_3 \longrightarrow (CH_3)_4NBF_3OCH_3 + HX$$

Greenwood[5] has reported conductivity and viscosity data which conclusively demonstrated that

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[1] L. A. O'Leary and H. H. Wenske, This Journal, **55**, 2117 (1933).

[2] H. Meerwein and W. Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).

[3] Analyses were performed by Laboratory of Microchemistry, Dr. Carl Tiedcke, Teaneck, N. J.

[4] T. H. Vaughn, H. Bowlus and J. A. Nieuwland, *Proc. Indiana Acad. Sci.*, **40**, 203 (1931).

[5] N. N. Greenwood and R. L. Martin, *J. Chem. Soc.*, 751 (1953).