The Entropy of Perchloryl Fluoride.—The entropy change between 0°K. and the boiling point is summarized in Table VI.

The correction for gas imperfection was made by assuming Berthelot's equation using $T_c = 368.3°K.$ and $P_c = 53$ atm. $S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c$.

The value 62.59 cal. deg.$^{-1}$ mole^{-1} for the entropy of ideal perchloryl fluoride gas at 226.48°K. may be found by interpolation in the table of thermodynamic properties given by Lide and Mann.[5] The value of $\int_0^{226.48°K} C_p \, d \ln T$ obtained from the measurements = 60.17 cal. deg.$^{-1}$ mole^{-1}.

If the crystal showed complete inability to order the oxygen and fluorine atoms to correspond to the equilibrium crystal perfection at 0°K., the expected difference would be $R \ln 4 = 2.75$ cal. deg.$^{-1}$ mole^{-1}. The fact that the observed discrepancy is a little less than this amount indicates a small amount of ordering of the O and F atoms.

We thank J. F. Gall and the Pennsylvania Salt Manufacturing Company for supplying the perchloryl fluoride, R. E. Gerkin for assistance with the measurements and especially J. B. Ott for much assistance throughout the entire research.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Synthesis of Ammonium Fluorometallates in Methanol[1a]

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RECEIVED DECEMBER 9, 1957

A series of seventeen anhydrous ammonium fluorometallates has been prepared by reaction of methanol solutions of the metal bromides and ammonium fluoride. The products have been identified by X-ray and chemical analysis.

Introduction

The chemistry of reactions of simple inorganic compounds in organic solvents has been somewhat neglected, attention having been concentrated on organic systems containing water as one component. Comparisons of solubilities suggested to us the possibility of preparing anhydrous fluorides by metathesis in methanol, using ammonium fluoride and a metal halide. It was found, however, that in most cases an ammonium fluorometallate was produced.

Ammonium fluorometallates have long been of interest because of the structural problems they present, in themselves and in relation to fluorometallates of the alkali metals, and because of their potentialities as sources for anhydrous metal fluorides. Methods of preparation analogous to those used for the alkali complexes have not always been successful. Formation by fusion with ammonium fluoride is affected by the low decomposition temperatures of the ammonium complexes. Reactions in water or aqueous hydrogen fluoride solution often lead to hydrates, oxy- or hydroxy-compounds. The use of liquid hydrogen fluoride or bromine trifluoride as solvent and reactions with fluorine introduce obvious experimental difficulties.

Consequently, there have been some instances of failure to prepare specific compounds and other cases which appear to involve information based upon impure compounds. Cox and Sharpe,[2] for example, recently have pointed out that although several workers have reported different unit cell dimensions for ammonium hexafluoroferrate(III), $(NH_4)_3FeF_6$, none has reported analytical data. Their analyses indicate that all earlier studies, including their own, were actually made on $(NH_4)_{2.6}FeF_{5.6} \cdot 0.4H_2O$.

Experimental

Preparation of the Metal Bromides.—In each case the bromide was prepared by action of bromine on finely divided metal suspended in methanol. Excess bromine was used, except in the preparation of the iron(II) complex. The bromine was added in 1-ml. portions from a dropping funnel to a stirred suspension of 0.1 mole of metal in approximately 100 ml. of cooled "Absolute" methanol. The resultant solution was filtered to remove any insoluble residue and diluted to an approximately known molarity in a volumetric flask. The method is similar to that of Osthoff and West[3] and of Ducelliez and Raynaud.[4]

Preparation of the Complexes.—In all cases the reaction was carried out by the addition of metal bromide solution to a rapidly stirred saturated solution of ammonium fluoride in a polyethylene container. The volume of the bromide to be added was estimated from the approximate molarity of the metal bromide solution, the fluoride to metal ratio of the product expected, and the molarity (about 0.5 *M*) of the saturated ammonium fluoride solution. Generally a large excess of ammonium fluoride was used. Ammonium bromide is more soluble in methanol than is ammonium fluoride, the solubility of the latter being roughly 2 g./100 ml. of methanol.

In general the products were filtered with suction and washed on the filter with cold methanol until a test of the washings with aqueous silver nitrate showed them to be free from bromide. They were then washed with anhydrous ether, and dried in an oven at 60°. Digestion of a product was advisable to promote crystallization for better X-ray powder patterns, the samples being placed either in methanol or in a methanol solution of ammonium fluoride in a polyethylene container and kept at 40–50° for as long as a week. It was later found that running the initial reaction at about 60° greatly improved the quality of the powder patterns obtained. Negative tests for metal ions made with some filtrates indicate that precipitation is quantitative.

Analytical.—Ammonia was determined by distillation from strongly alkaline solution into cold boric acid solution, followed by titration with hydrochloric acid, using brom cresol green indicator.

Fluorine was determined by distillation from sulfuric or perchloric acid solution followed by titration of aliquots of the distillate with cerium(III) chloride, using murexide

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(1) (a) This work was supported in part by the Atomic Energy Commission. (b) National Science Foundation Predoctoral Fellow.

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Ammonium Fluorometallates from Methanol Solution

Formula	Anal., calcd. %	Anal., found %	Metal method	Color	Ref.
NH_4BiF_4	NH_4, 5.95	NH_4, 5.89, 5.90	Phosphate	White	8
	Bi, 68.97	Bi, 68.63, 68.80			
	F, 25.08	F, 26.70, 26.69			
NH_4CdF_3	NH_4, 9.62	NH_4, 9.41, 9.41	Anthranilate	White	8
	Cd, 59.96	Cd, 59.76, 59.68			
	F, 30.42	F, 31.11, 30.96			
NH_4CoF_3	NH_4, 13.45	NH_4, 13.97, 14.09	Electrolysis	Pink	..
	Co, 44.00	Co, 42.36, 42.40			
	F, 42.55	F, 41.21, 41.42			
NH_4CuF_3	NH_4, 13.00	NH_4, 13.22, 13.26	Electrolysis	Blue-white	..
	Cu, 45.87	Cu, 45.72, 45.49			
	F, 41.13	F, 40.58, 40.61			
NH_4MnF_3	...	[a]	....	Light pink	10
NH_4ZnF_3	NH_4, 12.84	NH_4, 12.80, 12.89	Anthranilate	White	..
	Zn, 46.54	Zn, 46.53, 46.59			
	F, 40.62	F, 40.67, 41.10			
NH_4MgF_3[b]	NH_4, 18.15	NH_4, 16.80, 16.20	8-Quinolinol complex	White	..
	Mg, 24.48	Mg, 20.70, 20.80			
	F, 57.37	F, 55.20, 55.30			
NH_4FeF_3	...	[c]	Oxide	Buff	11
$(NH_4)_2NiF_4$[d]	NH_4, 21.13	NH_4, 20.60, 20.67	Electrolysis	Yellow and white	12
	Ni, 34.37	Ni, 32.26, 32.38			
	F, 44.50	F, 44.29, 44.30			
$(NH_4)_2GeF_6$	NH_4, 16.20	NH_4, 15.30, 15.98	Oxide	White	2
	Ge, 32.60	Ge, 33.10			
	F, 51.20	F, 50.81, 51.26			
$(NH_4)_2SnF_6$	NH_4, 13.41	NH_4, 13.08, 13.25	Oxide	White	13
	Sn, 44.16	Sn, 44.20, 44.55			
	F, 42.43	F, 42.80, 42.33			
$(NH_4)_2ThF_6$	NH_4, 9.43	NH_4, 8.68, 8.57	Oxide	White	..
	Th, 60.75	Th, 59.90, 59.85			
	F, 29.82	F, 29.09, 28.84			
$(NH_4)_2TiF_6$	NH_4, 18.21	NH_4, 18.09, 18.19	Cupferron	White	9
	Ti, 24.21	Ti, 23.95, 24.08			
	F, 57.58	F, 56.75, 56.70			
$(NH_4)_3AlF_6$	...	[a]	....	White	2, 7, 14
$(NH_4)_3FeF_6$	NH_4, 24.16	NH_4, 24.16, 24.18	Oxide	White	2, 7, 14
	Fe, 24.94	Fe, 25.00, 24.82			
	F, 50.90	F, 51.00, 50.95			
$(NH_4)_3InF_6$	NH_4, 19.12	NH_4, 19.11, 19.15	Oxide	White	14
	In, 40.57	In, 40.67, 41.29			
	F, 40.31	F, 40.94, 40.08			
$(NH_4)_3ZrF_7$	...	[a]	....	White	15

[a] Identified by powder pattern. [b] Composition varies with method and duration of washing. X-Ray diffraction shows only lines attributable to a cubic substance with a = 4.07 Å. and similar to $KMgF_3$. [c] X-Ray pattern shows contamination with $(NH_4)_3FeF_6$. The remaining lines are completely analogous to the patterns for NH_4MnF_3 and NH_4CoF_3, indicating NH_4FeF_3. Analysis for NH_4^+ and Fe^{++} also indicates this, although values found differ somewhat from the theoretical due to contamination with $(NH_4)_3FeF_6$. Bromide solution was prepared with large excess of iron and inert atmosphere. [d] Two nickel compounds appear to form, determined by reactant in excess, as shown by difference in powder patterns; thermal decomposition of the yellow form indicates that an intermediate NH_4NiF_3 exists.

indicator,[5] and subsequently by titration with thorium nitrate, using the oscillometric method of Grant and Haendler.[6]

Metal was determined by a suitable standard analytical procedure, as indicated in the table.

Results

The ammonium fluorometallates prepared in this research are listed in the accompanying table. Analytical data are listed except for those compounds

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which were identified by reference to known X-ray diffraction patterns. In cases where a compound of apparently similar nature has been reported, the reference is given. As suggested by Cox and Sharpe,[2] however, some of these may be open to question. Preliminary tests, for example, indicate some differences in color and infrared spectra between the iron(III) complexes prepared from water and from methanol.

A number of metals did not produce fluorometallates. Barium, strontium and calcium precipitated the corresponding metal fluoride. Thallium, selenium, tellurium and antimony bromide solutions gave no precipitate with ammonium fluoride. Mercury(II) appears to form a complex bromide, and lead bromide is too insoluble in methanol. Some metals, such as vanadium, niobium, molybdenum and uranium, produce ammonium oxy- complexes which will be discussed separately.

All complexes give usable X-ray powder patterns, but in some cases only after digestion. Analytical data were also found to improve following digestion either in pure methanol, or in a methanol solution of ammonium fluoride.

Little as yet is known as to the mechanism of the bromination of metal in methanol, or as to the species present in the methanol solutions of the metal bromides. The work of Bradley, Caldwell and Wardlaw[7] with tin(IV) chloride in various alcohols suggests the presence of species such as $SnCl_x(OR)$-ROH, a suggestion which also appears valid for work we are doing with niobium and vanadium.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The *cis–trans* Isomerization of Dihydroxo- and Diaqua-bis-ethylenediamine-cobalt(III) Ions

BY JAMES YING-PEH TONG AND PETER E. YANKWICH

RECEIVED OCTOBER 24, 1957

The rate of isomerization of dihydroxo-bis-ethylenediamine-cobalt(III) ions is independent of hydroxide concentration at hydroxide concentration greater than 0.01 *M* and increases rapidly as hydroxide concentration becomes less than 10^{-3} *M*. The total rate constant of isomerization, $(k_c + k_t)$, of the dihydroxo ions in solutions 1 *M* in ionic strength and 0.01 *M* or greater in hydroxide concentration has been determined at 35.03° to be 0.155 $(\text{hr.})^{-1}$. The total rate constant of isomerization of the diaqua-bis-ethylenediamine-cobalt(III) ions in 1 *M* perchloric acid has been determined at 24.84° to be 0.0249 $(\text{hr.})^{-1}$. Since the reaction rates were reported by others to be irreproducible when different preparations were used, synthetic procedures have been modified and the preparations have been tested for kinetically active impurities. The rates have been found to be reproducible when different preparations of purified reactants were used.

Introduction

During a recent study of the alkaline hydrolysis of *cis*-carbonato-bis-ethylenediamine-cobalt(III) ion,[1] we were unable to isolate the intermediate of the hydrolysis reaction. In seeking to elucidate the second step of the alkaline hydrolysis a straight forward approach would be to investigate the reaction between carbonate ion and the dihydroxo-bis-ethylenediamine-cobalt(III) ions. Before such a study is attempted, however, it is necessary to have detailed knowledge of the *cis–trans* isomerization of the dihydroxo ions, possibly the isomerization of the aqua-hydroxo ions, and of the second acid dissociation constants of the diaqua ions.

Bjerrum and Rasmussen[2] determined the first and second acid dissociation constants of the diaqua ions and estimated the half-life of isomerization to be about 25 hours at 25° in a solution 0.5 *M* in sodium hydroxide and 0.5 *M* in sodium nitrate. The rate of isomerization of the aqua-hydroxo ions is much higher[3] and has not been measured quantitatively.

In this paper we report quantitative studies on the hydroxide ion dependence of the rates of isomerization of the dihydroxo ions, the rate of isomerization of the diaqua ions, together with modified synthetic procedures and tests of starting materials for kinetically active impurities.

Experimental

Syntheses.—*trans*-Dichloro-bis-ethylenediamine-cobalt (III) chloride was prepared according to reported method,[4] which was modified as follows: (a) the ethylenediamine solution was added to the cobaltous chloride solution under nitrogen atmosphere and with vigorous stirring, (b) the product was thoroughly washed with ice-cold concentrated hydrochloric acid before it was washed with alcohol and ether. (The duration of air oxidation was found to be greatly reduced by the use of an efficient bubbler.) The product was reprecipitated from an aqueous solution by addition of cold concentrated hydrochloric acid and dried at 100°.

trans-Dichloro-bis-ethylenediamine-cobalt(III) perchlorate was precipitated from an ice-cold solution of the *trans*-dichloro chloride with dilute perchloric acid; the precipitate was washed with ice-cold perchloric acid, alcohol and ether.

Carbonato-bis-ethylenediamine-cobalt(III) perchlorate was prepared from freshly precipitated *trans*-dichloro perchlorate by the method of Linhard and Stirn.[5] The preparation was analyzed for cobalt volumetrically,[6] a weighed sample first being converted to cobalt sulfate for this purpose by a rapid method outlined below (Co, exp. 17.44%; theo. 17.41%). The carbonate content was analyzed by treating a known amount of the compound with a slight excess of standard 0.1 *M* perchloric acid and back titrating the excess acid after the mixture was boiled gently to expel carbon dioxide ($CO_3^=$, exp. 17.75%; theor. 17.72%). The perchlorate content was measured by exchanging the perchlorate ions for chloride ions on an Amberlite IR-400 resin column in the chloride form and determining the chloride content of the eluent gravimetrically (Cl, exp. 10.47%; theo. 10.47%).

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