[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Formation of Complex Fluorides in Anhydrous Liquid Hydrogen Fluoride. I. Sodium Fluocolumbates

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Complex fluorides have been synthesized commonly by crystallization from solutions of the proper ions in aqueous hydrofluoric acid. While this procedure usually is satisfactory, in many cases it yields oxy- or hydrated fluorides instead of the normal salts. The elimination of water by the use of anhydrous liquid hydrogen fluoride as the solvent should restrict the possibilities to the formation of only normal or acid complex salts. Anhydrous hydrogen fluoride has been shown to be an excellent dissociating solvent[2] for simple fluorides and many other salts and its physical properties (m. p. −83°, b. p. 19.4°) are such that it may be used conveniently. It is available commercially and the technique of handling it with safety is well understood.

Since columbium has been found almost invariably to form oxyfluorides in aqueous hydrofluoric acid, a study of the formation of fluocolumbates by crystallization from anhydrous hydrogen fluoride should test the feasibility of using this solvent for normal complex fluoride production. The univalent ionic radius ratio for columbium and fluorine is 0.735, which, according to Pauling's treatment,[3] indicates that columbium may be coördinated up to as many as eight or possibly even more fluoride ions. The formation of the ions CbF_6^-, $CbF_7^=$, $CbF_8^≡$ and perhaps $CbF_9^{≡}$ may be expected. The only normal fluocolumbates which have been reported as crystallizing from aqueous hydrofluoric acid solution are $RbCbF_6$,[4] $CsCbF_6$,[4] K_2CbF_7,[5] Rb_2CbF_7[6] and Cs_2CbF_7,[6] and the evidence for the existence of the last two could not be verified.[4] The columbium atom resembles the tantalum atom very closely, the two being almost identical in size in corresponding compounds. Since an extensive series of normal fluotantalates having TaF_6^-, $TaF_7^=$ and $TaF_8^≡$ ions are known, similar and, in fact, isomorphous compounds of columbium should be obtained.

In the present investigation the sodium fluocolumbates have been studied. Sodium fluoride and columbium pentafluoride in mole ratios varying through a wide range have been dissolved in hydrogen fluoride and the products obtained by fractional crystallization have been examined.

Experimental

Materials.—Hydrogen fluoride was available[7] stored in a stainless steel cylinder. A small amount of gas was allowed to escape to remove traces of the more volatile silicon tetrafluoride which may have been present. The liquid hydrogen fluoride to be used as solvent was collected in copper cylinders connected to the storage tank by means of copper tubing and protected from atmospheric moisture by tubes containing soda-lime. Copper or platinum apparatus was used in all subsequent handling of hydrogen fluoride and the solutions and, whenever possible, the manipulations were carried out in a chamber containing dry carbon dioxide.

The solutions of columbium pentafluoride were obtained by causing weighed amounts of columbium pentachloride to react with given volumes of liquid hydrogen fluoride, hydrogen chloride gas being evolved. The columbium pentachloride was made by the action of chlorine on powdered columbium[8] at 250°. Solutions of sodium fluoride were made by adding the dry salt to liquid hydrogen fluoride.

Formation of Sodium Fluocolumbates.—The solutions of sodium fluoride and columbium pentafluoride were mixed to give mole ratios varying between 0.5/1 and 20/1 and the mixtures were allowed to evaporate in a stream of dry nitrogen in a ceresin coated glass desiccator containing soda-lime. Fractional crystallization usually yielded three fractions of crystals in each run, but the sizes of the fractions varied considerably because the crystallization was accomplished in opaque apparatus and could not easily be controlled. The crystals were freed of excess solvent by holding them at room temperature in a stream of dry nitrogen and were then examined under the microscope. Fractions which appeared to be homogeneous were analyzed to determine the identity of the compound and the properties of each salt were established. When fractions consisted of mixtures of two or more types of crystals a rough estimate of the percentage of each compound present was made by microscopical examination. The results are summarized in Table I.

The only crystalline complex fluorides of columbium which were observed and identified were sodium hexafluocolumbate and sodium heptafluocolumbate. No octa-

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[1] Present address: Imperial Paper and Color Corporation, Glens Falls, N. Y.

[2] Ruff, "Die Chemie des Fluors," Berlin, 1920; Fredenhagen, *Z. anorg. Chem.*, **242**, 23 (1939); Simons, *Ind. Eng. Chem.*, **32**, 178 (1940).

[3] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 360.

[4] Balke and Smith, THIS JOURNAL, **30**, 1664 (1908).

[5] Marignac, *Ann. chim. phys.*, [4] **8**, 34 (1866).

[6] Pennington, THIS JOURNAL, **18**, 38 (1896); *Chem. News*, **75**, 8, 18, 31, 38 (1897).

[7] Purchased from the Harshaw Chemical Co., Cleveland, Ohio.

[8] Von Bolton, *Z. Elektrochem.*, **13**, 147 (1907).

TABLE I

Expt.	Mole ratio NaF/CbF$_5$ used	Fraction	% Compounds present, approximate
1	0.5/1	1	65% NaCbF$_6$, 35% unidentified crystals
		2	90% CbF$_5$
2	1/1	1	100% NaCbF$_6$
		2	100% NaCbF$_6$
		3	100% NaCbF$_6$
3	1.2/1	1	100% NaCbF$_6$
		2	80% NaCbF$_6$, 20% NaHF$_2$
		3	60% NaCbF$_6$, 40% NaHF$_2$
4	3/1	1	95% NaCbF$_6$, 5% NaHF$_2$
		2	15% NaCbF$_6$, 5% Na$_2$CbF$_7$, 80% NaHF$_2$
		3	100% NaHF$_2$
5	6/1	1	50% NaCbF$_6$, 50% Na$_2$CbF$_7$
		2	10% Na$_2$CbF$_7$, 90% NaHF$_2$
		3	100% NaHF$_2$
6	12/1	1	100% Na$_2$CbF$_7$
		2	50% Na$_2$CbF$_7$, 50% NaHF$_2$
		3	100% NaHF$_2$
7	20/1	1	100% Na$_2$CbF$_7$
		2	95% Na$_2$CbF$_7$, 5% NaHF$_2$
		3	100% NaHF$_2$

fluocolumbate was formed, even in Expt. 7 where the high concentration of sodium fluoride was most favorable for its formation. Sodium bifluoride was obtained instead, indicating that in liquid hydrogen fluoride the bifluoride ion probably is more stable than the octafluocolumbate ion. Indeed the appearance of NaHF$_2$ crystals in all of the experiments where the mole ratio was greater than 1/1 indicates the high relative stability of this substance compared to the higher fluocolumbates in the presence of hydrogen fluoride. The relative solubilities of the various salts also undoubtedly favor bifluoride formation. The use of hydrogen fluoride as a solvent apparently does not favor a high coördination number for columbium toward fluorine, because of the strong tendency to use up the fluoride ions to give bifluoride ions, and therefore the octafluocolumbate is not obtained, even though from the radius ratio standpoint its formation is possible.

In the first fraction in Expt. 1 there were elongated crystals having parallel extinction and with a refractive index between 1.44 and 1.495. This refractivity is much higher than that observed for sodium bifluoride or sodium hexafluocolumbate and it is extremely unlikely that they were the heptafluocolumbate. They probably were crystals of an acid sodium fluocolumbate such as NaHCbF$_7$ but it was impossible to isolate them for analysis to establish their identity.

Sodium hexafluocolumbate is readily obtained by using the 1/1 mole ratio and it may be recrystallized from this solvent. The mole ratio of 12/1 gives a first fraction of pure sodium heptafluocolumbate. This salt dissolves in hydrogen fluoride but reacts, and the hexafluocolumbate and sodium bifluoride are obtained when the solution is evaporated, which is in line with the data of Experiments 3 and 4.

Analysis.—Sodium was determined as sulfate and columbium as the pentoxide according to the method of Balke,[9] and fluorine was determined as calcium fluoride following the procedure established by Ruff and Schiller.[10]

Anal. Calcd. for NaCbF$_6$: Na, 10.00; Cb, 40.14; F, 49.59. Found: Na, 9.78; Cb, 39.93; F, 49.95. Calcd. for Na$_2$CbF$_7$: Na, 16.92; Cb, 34.18; F, 48.90. Found: Na, 16.59; Cb, 34.53; F, 49.29.

The slightly low results observed for sodium and columbium and the high values for fluorine are probably due to the fact that it is very difficult to completely free the crystals of solvent.

Properties of the Sodium Fluocolumbates.—Sodium hexafluocolumbate has a density of 2.71 ± 0.01 at 25°, determined pycnometrically in benzene. The colorless crystals were small and poorly formed, with a refractive index of less than 1.328, the value for sodium bifluoride. The refractive index could not be determined exactly because of the difficulty of finding a standard liquid for immersion tests which would not react with the sample. Sodium hexafluocolumbate is not stable in the air, being hydrolyzed rapidly. Water takes it into solution with hydrolysis. It reacts with absolute ethyl alcohol and is insoluble in benzene. When dry nitrogen was passed over it and the temperature was raised 2° a minute the salt was stable up to 480°, but above this temperature it decomposed without melting into sodium fluoride and columbium pentafluoride.

Sodium heptafluocolumbate has a density of 3.47 ± 0.01 at 25°. The crystals were poorly formed and were biaxial, probably being either monoclinic or orthorhombic. The principal view obtained showed slightly oblique extinction and gave a refractive index of 1.460 ± 0.004. It is unstable in the air and is rapidly hydrolyzed by water. It is insoluble in benzene. When heated in dry nitrogen it melted at 530 ± 10° and then decomposed into sodium fluoride and columbium pentafluoride, the latter vaporizing.

Summary

The formation of sodium fluocolumbates by crystallization from solutions in anhydrous liquid hydrogen fluoride of sodium fluoride and columbium pentafluoride in mole ratios varying between 0.5/1 and 20/1 has been studied. The use of liquid hydrogen fluoride as solvent effectively prevents the formation of oxy- or hydrated complexes and it is thus possible to synthesize normal fluocolumbates which cannot be obtained by the use of aqueous solutions. Pure sodium hexafluocolumbate is obtained when the mole ratio is 1/1. With higher ratios sodium heptafluocolumbate and sodium bifluoride also form. When the ratio is 12/1 or higher the first fractions are pure sodium heptafluocolumbate. Even with very high ratios no octafluocolumbate was observed, sodium bifluoride being formed instead. The tendency to form bifluoride ion in these solutions in hydrogen fluoride is so great that the coördination number of eight is not realized by columbium, although the univalent ionic radius ratio of columbium and

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[9] Balke, THIS JOURNAL, **27**, 1143 (1905).

[10] Ruff and Schiller, *Z. anorg. Chem.*, **72**, 348 (1911).

fluorine is favorable. With mole ratios of less than 1/1 some crystals which could not be isolated but which may have been an acid sodium fluocolumbate were observed.

The properties of sodium hexafluocolumbate and sodium heptafluocolumbate have been examined.

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Preparation of Constant Boiling Hydrochloric Acid. Rate of Approach to Equilibrium

BY ALBERT C. TITUS AND DONALD E. SMITH

In the first precise paper on constant boiling hydrochloric acid Hulett and Bonner[1] pointed out that starting with acid of density 1.09 to 1.15 and distilling 75% of the starting volume resulted in the remaining distillate being well within the constant boiling region. They also showed, however, that equilibrium was attained after only 60% of a solution of density 1.10 had been distilled. The attainment of constant distillate density served to indicate equilibrium.

In view of the importance of the preparation of constant boiling hydrochloric acid for use as a primary standard in analytical chemistry, it was considered desirable to extend the above study over a larger range of starting densities, and to follow the course of density change during complete distillations in each case. It has been found that not only are the statements given in the first paragraph confirmed but furthermore when starting with acid of density about 1.06 attainment of equilibrium is extremely slow, whereas with acid of density about 1.14 it is fairly rapid in spite of these two density values being about equidistant from the equilibrium value. The results are given in Figs. 1 and 2. The last fractions are again represented in the latter, along with the check values, all on a very large scale.

Experimental

All hydrochloric acid was pre-distilled and its density precisely determined after appropriate dilution. In the regular runs 300 ml. was distilled using a 1-liter distilling flask with the side-arm fitting into a straight condenser, forming an acid seal. Sintered quartz kept the acid boiling smoothly and collection was made in nine fractions in 25-ml. Erlenmeyer flasks, leaving about 6 ml. of residue. There was a loss of about 10 ml. which was considered as distributed evenly and so was ignored. The first few ml. of each ninth of the approximately 294 ml. actually distilled (32.7 ml. should be a fraction) was used for rinsings and the 28 ml. used for density determinations was then separately collected. In Fig. 2 there are horizontal lines for the typical ninth fraction and for the residue, as well as for the analyzed portion of the ninth fraction. Samples were collected without use of an adapter although this entailed a small but negligible amount of evaporation and density change.

Densities were determined at 24.97° (to less than 0.10°) in glass-stoppered volumetric flasks made especially for the work and used alternately for succeeding fractions. They each had a capacity of about 27 ml., calibrations in each case agreeing to less than 0.0010 ml. A proper counterpoise was employed for the glass, and the buoyancy effects on the contents and weights were corrected for, using the density 0.0010 gram per milliliter for air in Salt Lake City.

Separate samples of twice redistilled water were used in check work. Results from these were not plotted in Fig. 1 where the complete distillations are represented, but for the last five fractions dotted lines in Fig. 2 represent the checks. An average of run and check run values in Fig. 2 gives a density not over 0.00015 different from either, this value being considered as the precision here. Corrections were made here for the small barometric pressure differences between runs, all values being reduced to 647 mm. by means of the findings of Bonner and Titus,[2] who found in this range that 7 mm. pressure induced a density change of 0.0001 unit, increased pressure giving a lower density. Since the attempted precision in Fractions 6 and beyond for all curves except C and c, and for Fractions 8 and 9 of these last, was to several parts in the 5th decimal place, the values in Fig. 2 were plotted to that place. All other densities in both Fig. 1 and Fig. 2, as well as the unplotted check densities, were determined with an attempted precision of two parts in the fourth decimal place or better.

The first four fractions did not agree nearly so closely with their checks as the later fractions. The worst case was in Curve E, where Fraction I was 0.011 lower than its check although the starting density was 0.0005 higher. The other variations were smaller, being less than 0.002 after the first fraction except in Curve E and Curve e. All starting densities in the check runs were within 0.0010 density unit (gram per milliliter) of the values in the runs with which they were being compared. No check was made on Fraction 3 of Curve B but the fractions on each side checked satisfactorily. There was loss of gas in the first fraction in each of the higher curves, and this occurred into the second fraction for Curves E and e. This would cause a lowering of the plotted density from its true value in each case but would not affect the later densities of

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[1] Hulett and Bonner, THIS JOURNAL, **31**, 390 (1909).

[2] Bonner and Titus, *ibid.*, **52**, 633 (1930).