some species such as Na_2MgH_4 might be produced in such reactions. In fact, a few weak lines in the powder patterns of the insoluble residue were observed which could not be attributed to NaCl, Na_3AlH_6, or NaH.

$$3MgCl_2 + 2Na_3AlH_6 \longrightarrow 2ClMgAlH_4 + Na_2MgH_4 + 4NaCl \quad (12)$$

While further work is required to clarify these reactions, it appears that $Mg(AlH_6)_2$ is not formed exclusively, if at all.

The major problem with K_3AlH_6 is avoidance of contamination in the dry powder. One 20-g sample, which had been stored in a screw-top sample jar for several months, exploded violently as a surface layer of oxidized material was being removed with a metal spatula in a drybox. The compound should be stored under dry, inert diluent in a firmly stoppered flask, preferably in a drybox with a good atmosphere. Residual K_3AlH_6 should be destroyed if there is any doubt as to its purity. It is not clear how this danger arises. The synthetic procedure might leave a small percentage of unhydrided, dispersed metallic potassium which can then react with oxygen on long standing to form potassium superoxide. It is possible that the hydride then reacts with the superoxide under the influence of shock or local heating caused by the spatula.

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Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Some Properties of Potassium Hexafluoronickelates(III) and -(IV). Absorption Spectra of Nickel(III) and -(IV) in Hydrogen Fluoride Solutions[1a]

By LAWRENCE STEIN, JOHN M. NEIL,[1b] and GREGORY R. ALMS[1c]

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Visible and near-ultraviolet absorption spectra have been obtained for K_3NiF_6, K_2NiF_6, and solutions of K_2NiF_6 in hydrogen fluoride. Spectra of the solutions are shown at several stages during the reduction of nickel(IV) to nickel(III) and -(II). Nickel(III) and -(IV) species have also been produced by anodic oxidation of nickel metal in hydrogen fluoride solutions. The highly reactive species may be intermediates in the fluorination of organic compounds by the Simons process, since nickel anodes are used in Simons electrolysis cells. Infrared spectra of K_3NiF_6, K_2NiF_6, and solid phases from the nickel solutions are reported. Oxygen is shown to be the chief gaseous product in hydrolysis reactions of the complex salts.

Introduction

It has been shown recently that the reaction of Na_2PrF_6 with hydrogen fluoride yields praseodymium tetrafluoride,[2,3] although the tetrafluoride cannot be obtained by direct fluorination of praseodymium trifluoride. We have studied the effect of hydrogen fluoride on the complex salts K_2NiF_6 and K_3NiF_6 and found that the first salt dissolves in this solvent, forming red solutions of nickel(IV), whereas the second partially disproportionates to nickel(II) and -(IV). A very reactive brown solid is formed in the reaction of K_3NiF_6 with liquid hydrogen fluoride, and a similar product is formed in the reduction of nickel(IV) solutions. Some spectral and chemical properties of the brown phase, the potassium hexafluoronickelate salts, and nickel(III) and -(IV) solutions are reported in the present article. It is shown that nickel(III) and -(IV) species can be formed by anodic oxidation of nickel metal in hydrogen fluoride solutions.

Experimental Section

Preparation of Complex Salts.—K_2NiF_6 and K_3NiF_6 were prepared by a modification of the method of Klemm and Huss[4], from 2:1 and 3:1 molar mixtures of potassium chloride and nickel dichloride. Potassium chloride (Baker and Adamson, reagent grade) was dried at 120° in air and nickel dichloride (Alfa Inorganics, reagent grade) was dried at 275° in an atmosphere of nitrogen and carbon tetrachloride vapor. The mixtures were intimately ground in a drybox, heated in nickel boats for 3 hr at 300° with fluorine at 300 mm pressure, and then were reground and refluorinated for 6–8 hr at 1000 mm pressure. Red, crystalline K_2NiF_6 was obtained from the 2:1 mixtures. However, the products from the 3:1 mixtures were shown by infrared analyses to contain both nickel(III) and -(IV). The latter were heated to 450° under vacuum to decompose nickel(IV) and then were reground and refluorinated until violet, crystalline K_3NiF_6 was obtained.

Anal. Calcd for K_2NiF_6: K, 31.17; Ni, 23.40; F, 45.43. Found: K, 31.09, 31.78; Ni, 23.04, 23.61; F, 45.6, 46.1. Calcd for K_3NiF_6: K, 40.45; Ni, 20.24; F, 39.31. Found: K, 41.28, 40.96; Ni, 19.65, 19.82; F, 39.0, 39.3.

X-Ray powder patterns of both salts were obtained with a 114.59-mm diameter Phillips camera and copper Kα radiation. These were indexed for face-centered cubic cells with lattice constants of 8.11 Å (K_2NiF_6) and 8.49 Å (K_3NiF_6). Similar constants have been reported previously by Klemm and coworkers

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[1] (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) Honors Program Participant, Alfred University. (c) Honors Program Participant, Monmouth College.

[2] J. Soriano, M. Givon, and J. Shamir, *Inorg. Nucl. Chem. Letters*, **2**, 13 (1966).

[3] L. B. Asprey, J. S. Coleman, and M. J. Reisfeld, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 122.

[4] W. Klemm and E. Huss, *Z. Anorg. Chem.*, **258**, 221 (1949).

[5] W. Klemm, *Bull. Soc. Chim. France*, 1325 (1956).

for the two compounds,[4,6a] and a smaller lattice constant has been reported by Bode and Voss[6b] for K_3NiF_6.

Reactions with Hydrogen Fluoride.—Amounts of the complex salts from 50 to 500 mg were stirred in sealed Kel-F test tubes with purified hydrogen fluoride[7] (specific conductance 2×10^{-5} to 5×10^{-7} ohm^{-1} cm^{-1}). The K_2NiF_6 samples dissolved almost completely, leaving only small amounts of brown residue, which were removed by centrifugation. The solutions were bright red at low concentrations of nickel(IV) and nearly opaque at concentrations of 0.5–1 *M* (viewed in 0.75-in. diameter tubes). Samples of K_3NiF_6 yielded large amounts of the brown phase and red supernates containing nickel(IV). The solids were washed with hydrogen fluoride, centrifuged, and dried under vacuum with heat from a hair dryer; they were then hydrolyzed and analyzed for potassium, nickel, and fluorine. In some instances, the brown phase was not washed but was dried and ground to a fine powder for infrared analysis. The nickel(IV) solutions were rapidly reduced by moisture, glass wool, and polypropylene wool and were slowly reduced by zinc, brass, nickel, and copper, with the formation of more of the brown phase. The Kel-F (polytrifluorochloroethylene) test tubes were also slowly attacked by the nickel solutions, and, on two occasions, solutions stored overnight were lost through cracks which developed in the plastic. Several attempts were made to dissolve K_2NiF_6 and K_3NiF_6 in bromine pentafluoride for spectral studies, but both salts were found to be insoluble in this solvent.

Spectral Measurements.—Infrared spectra of the complex salts and precipitates were obtained with a Beckman IR-10 spectrophotometer, either as KBr disks, CsI disks, mineral oil mulls, or dry powders between KBr windows. No interaction of K_2NiF_6 or K_3NiF_6 with KBr powder was noted during grinding in a drybox, and similar spectra were obtained for the salts in KBr disks and mineral oil mulls. However, K_2NiF_6 and K_3NiF_6 were both reduced during grinding with CsI. The brown precipitates from hydrogen fluoride solutions were very reactive and could only be examined as dry powders.

Visible and near-ultraviolet spectra of nickel solutions at several stages of reduction and of K_2NiF_6 and K_3NiF_6 in KBr disks were obtained with a Cary 14 spectrophotometer. The solutions were examined in Kel-F or platinum cells with sapphire windows over path lengths of 0.2–10.0 mm. In some instances, precipitates appeared after the cells were filled, owing to further reduction of nickel. The precipitates were allowed to settle, and the clear supernates were then examined.

Reactions with Water and KI Solutions.—Samples of K_2NiF_6 and K_3NiF_6 were hydrolyzed in capped polyethylene bottles for chemical analysis. To determine the composition of the gas liberated during hydrolysis, samples were also mixed with degassed, distilled water in Kel-F or Pyrex bulbs on a vacuum manifold. The collected gas was then analyzed with a Model 21-620 Consolidated Engineering Corp. mass spectrometer. It was found to consist of 95–99% oxygen and 1–5% water vapor and air impurities (N_2, CO, CO_2, Ar). Hydrogen fluoride was not observed, owing to its high solubility in water. Ozone was observed at very low intensity in one gas sample.

Oxidation states of nickel in the complex salts were measured iodometrically, using saturated KI solution rather than 0.1 *N* KI solution to minimize the reaction with water. However, oxygen was liberated as well as iodine, and the following low iodine equivalents per mole of solid were obtained: K_3NiF_6, 0.86–0.99; K_3NiF_6, 1.74–1.87.

Electrolysis Experiments.—Several electrolysis experiments were carried out with hydrogen fluoride solutions in U-shaped cells made of 0.5-in. diameter Kel-F tubing. The electrodes consisted of 0.25-in. diameter nickel rods soldered to brass plugs which sealed the flared ends of the tubes. Direct current was supplied by a rectifier unit. During electrolysis, the cells were cooled with ice to lower the vapor pressure of hydrogen fluoride, and the plugs were loosened to permit the escape of hydrogen and fluorine.

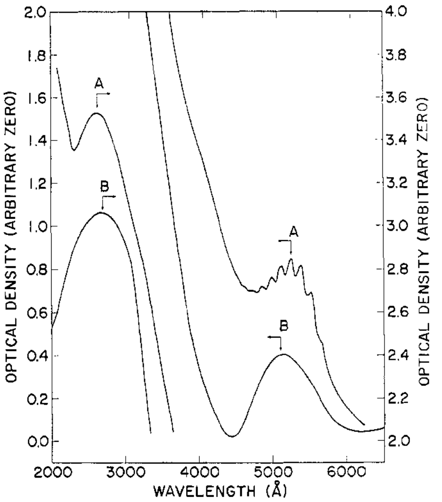

Figure 1.—Absorption spectra of K_2NiF_6 (A) and K_3NiF_6 (B) (KBr disks at room temperaure).

Solutions of hydrogen fluoride saturated with nickel difluoride were first electrolyzed for 3 hr at 10–35 V. The solutions were only slightly conducting, owing to the low solubility of the difluoride,[8] and it was necessary to increase the voltage periodically to maintain gas evolution from both electrodes. Although the solutions remained colorless throughout the electrolyses, brown deposits appeared on the anodes. The deposits liberated iodine from KI solutions and turned yellow on exposure to air.

The conductivity of the saturated nickel difluoride solutions was then increased by the addition of potassium or ammonium fluoride (concentrations of 0.2–0.5 *M*). Hydrogen and fluorine were rapidly evolved as the solutions were electrolyzed at 10 V. A brown-black deposit appeared on the anode within 10 min, and shortly thereafter brown suspended matter appeared throughout the anode leg of the cell. The suspension was found to liberate iodine from KI solution.

In the last series of experiments, nickel difluoride was omitted, and solutions 0.5–1.5 *M* in potassium fluoride or ammonium fluoride were electrolyzed at 10–12 V and 40–100 mA. The solutions near the nickel anode became brown and then red within 15 min. As the red color intensified, a stable interface was formed below the anode (top liquid red, bottom liquid colorless). Reduction occurred at the interface, and white precipitates containing nickel(II) collected at the bottom of the cell. Solids obtained by evaporation of the red solutions were shown to contain hexafluoronickelate(III) and -(IV) ions by infrared analysis.

Results and Discussion

Absorption spectra of K_2NiF_6 and K_3NiF_6 from 2000 to 6500 Å are shown in Figure 1. The two spectra are similar, each consisting of a broad band in the visible region and a more intense charge-transfer band in the near-ultraviolet region. Vibrational fine structure is present only in the spectrum of K_2NiF_6, from approximately 4600 to 5700 Å. The fine structure is shown in greater detail in Figure 2, and the intervals between bands are listed in Table I. The average interval of 492 cm^{-1} is ascribed to a stretching vibration of NiF_6^{2-} ion in an excited electronic state. Band maxima occur at 2700 and 5240 Å in the spectrum of K_2NiF_6 and at

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[6] (a) W. Klemm, W. Brandt, and R. Hoppe, *Z. Anorg. Allgem. Chem.*, **308**, 179 (1961); (b) H. Bode and E. Voss, *ibid.*, **290**, 1 (1957).

[7] A plastic face mask and rubber gloves were worn at all times during handling of the solutions for protection from hydrogen fluoride, and test tubes were opened in a fume hood only after cooling the solutions with liquid nitrogen.

[8] A. W. Jache and G. H. Cady, *J. Phys. Chem.*, **56**, 1106 (1952).

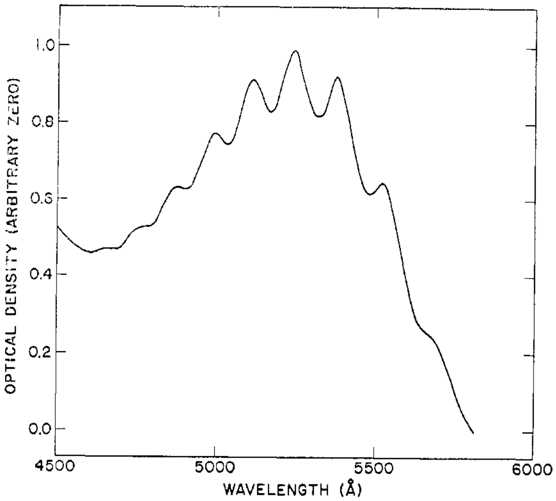

Figure 2.—Vibrational fine structure in the visible spectrum of K_2NiF_6 (KBr disk at room temperature).

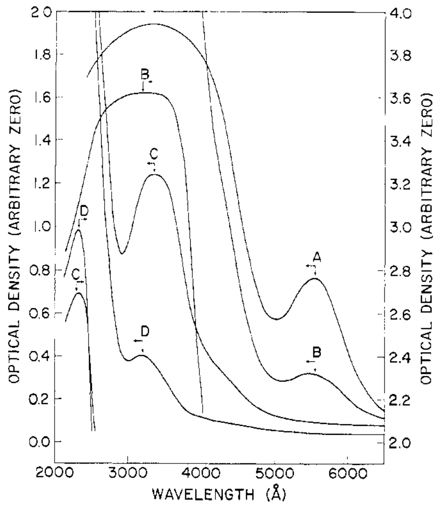

Figure 3.—Absorption spectra of nickel(IV) and reduced species in hydrogen fluoride solutions: A, solution of 0.07 *M* K_2NiF_6; B, C, and D, solutions of K_2NiF_6 at successive stages of reduction (2.0-mm cell).

2700 and 5150 Å in the spectrum of K_3NiF_6. A similar spectrum of K_2NiF_6 has recently been reported by Reisfeld, *et al.*,[9] for the compound in a mineral oil mull at 80°K. In an earlier reflectance spectrum of the compound,[10] vibrational bands were not observed. The spectrum of Reisfeld, *et al.*,[9] shows a prominent shoulder at 25,830 cm^{-1} on the charge-transfer band which is not easily discernible in our spectrum of K_2NiF_6 at room temperature (Figure 1A). We have observed a weak shoulder at approximately 4100 Å (24,390 cm^{-1}) in several spectra of the compound but have ascribed the shoulder to nickel(II) impurity, since NiF_2, $KNiF_3$, and K_2NiF_4 all absorb strongly in this region.[11-14]

Red solutions of K_2NiF_6 in hydrogen fluoride exhibit spectra of the type shown in Figure 3A, with bands at 3500 and 5520 Å. In very dilute solutions, the charge-transfer band at 3500 Å is broader than shown, with a flat top extending into the ultraviolet region. Neither of the two bands contain fine structure. Since the NiF_6^{2-} ion in solution does not have a vibronic spectrum, vibrational bands in the spectrum of solid K_2NiF_6 can be ascribed to the cubic field of the solid.

Curves B, C, and D of Figure 3 show spectra of nickel(III) and -(IV) species at several stages during reduction of the K_2NiF_6 solutions. The 3500-Å band grows narrower and more intense at the first stage of reduction (curve B), whereas the 5520-Å band grows continuously weaker. A shoulder is present at 2700 Å on the 3500-Å band at this stage and in some spectra can be noted as a separate peak. After the disappearance of the band at 5520 Å, the 3500-Å band grows weaker (curves C and D), and a new band appears at 2280 Å. No spectral bands remain after complete reduction of the solutions, owing to the low solubility of nickel difluoride. The red solutions turn brown, then yellow, and finally colorless, in the successive stages of reduction.

In Figure 4, infrared spectra are shown for K_2NiF_6,

Table I

Vibrational Bands in the Visible Spectrum of K_2NiF_6

Wavelength of max, Å	ν, cm^{-1}	$\Delta\nu$, cm^{-1}
4640	21,550	540
4760	21,010	520
4880	20,490	450
4990	20,040	470
5110	19,570	490
5240	19,080	490
5380	18,590	440
5510	18,150	540
5680	17,610	

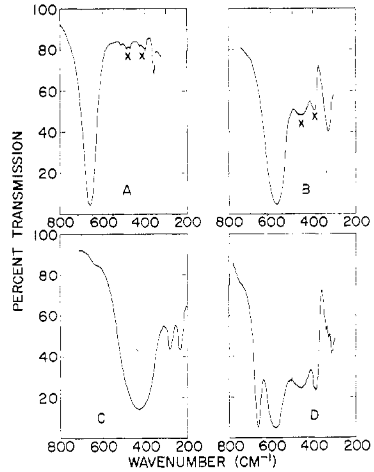

Figure 4.—Infrared spectra of several nickel fluorides: A, K_2NiF_6 (KBr disk); B, K_3NiF_6 (powder); C, NiF_2 (powder); D, potassium hexafluoronickelate salt of mixed valence state (KBr disk). X = impurity band.

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[9] M. J. Reisfeld, L. B. Asprey, and R. A. Penneman, *J. Mol. Spectry.*, **29**, 109 (1969). A copy of this article was kindly sent to us by Dr. Asprey before publication.

[10] A. D. Westland, R. Hoppe, and S. S. I. Kaseno, *Z. Anorg. Allgem. Chem.*, **338**, 319 (1965).

[11] A. Ludi and W. Feitknecht, *Helv. Chim. Acta*, **46**, 2226 (1963).

[12] W. Rudorff, J. Kandler, and D. Babel, *Z. Anorg. Allgem. Chem.*, **317**, 261 (1962).

[13] K. Knox, R. G. Shulman, and S. Sugano, *Phys. Rev.*, **130**, 512 (1963).

[14] J. Ferguson, H. L. Guggenheim, and D. L. Wood, *J. Chem. Phys.*, **40**, 822 (1964).

K_3NiF_6, anhydrous nickel difluoride, and a potassium hexafluoronickelate salt of mixed valence state, containing nickel(II), -(III), and -(IV). Salts of the latter type were frequently encountered during fluorination of the 2:1 and 3:1 potassium chloride–nickel chloride mixtures. Frequencies of the infrared bands are listed in Table II. It can be noted that the frequency of stretching vibration ν_3 in the hexafluoronickelate ions NiF_6^{4-}, NiF_6^{3-}, and NiF_6^{2-} increases progressively with the charge of the central nickel ion (+2, +3, and +4) and that the band width also narrows progressively. The band at 390 cm^{-1} in Figures 4B and 4D is an impurity band, probably of a nickel(III) compound, since it appears most often in spectra of K_3NiF_6. Infrared bands of K_2NiF_6 have been reported previously by Peacock and Sharp[15] and by Reisfeld.[16]

TABLE II

INFRARED BANDS OF POTASSIUM HEXAFLUORONICKELATES AND NICKEL DIFLUORIDE

Compound	Band freq, cm^{-1}	Approx half-width, cm^{-1}	Intens[a]	Assignment
K_2NiF_6	663	70	vs	ν_3
K_2NiF_6	349	12	w	ν_4
K_3NiF_6	580	110	vs	ν_3
K_3NiF_6	318	30	m	ν_4
$KNiF_3$	445[b]	...	vs	ν_3
NiF_2	450	180	vs	...
NiF_2	291	20	m	...
NiF_2	237	20	m	...

[a] Abbreviations: vs, very strong; m, medium; w, weak.
[b] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1950).

K_3NiF_6 was found to be stable under vacuum at 450°, whereas K_2NiF_6 partially decomposed above 350°: $3K_2NiF_6 \rightarrow 2K_3NiF_6 + NiF_2 + F_2$. Nickel(II) and -(III) were identified in the product by their infrared bands, and fluorine was identified by its reaction with mercury.

Hydrogen fluoride vapor at 100–300 mm pressure was slowly absorbed by K_2NiF_6 and K_3NiF_6 at room temperature. No color change was observed in the reaction with K_2NiF_6, but K_3NiF_6 turned a darker violet color. The products showed infrared bands of the original hexafluoronickelate ions and very strong bands of bifluoride ion (1230 and 1525 cm^{-1}). It is probable that complex acid salts similar to those of titanium, tin, and lead[17] were formed. The reaction was reversible for K_3NiF_6, since hydrogen fluoride could be removed by heating the product under vacuum at 400°. However, the salt formed by K_2NiF_6 partially decomposed to K_3NiF_6 at approximately 350°.

In contrast to K_2NiF_6, which dissolved without appreciable decomposition in liquid hydrogen fluoride, K_3NiF_6 yielded large amounts of brown precipitate containing nickel difluoride. Red supernates containing nickel(IV) were also obtained. Both products are ascribed to a partial disproportionation of K_3NiF_6 in liquid hydrogen fluoride: $2K_3NiF_6 \rightarrow 6K^+ + NiF_6^{2-} + NiF_2 + 4F^-$.

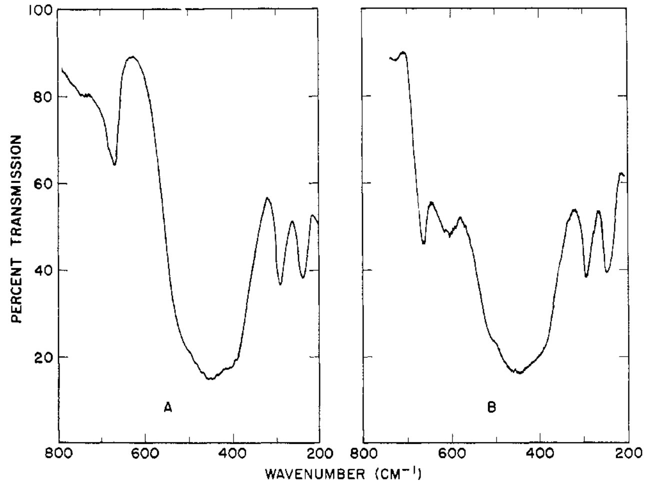

Figure 5.—Infrared spectra of precipitates obtained by partial reduction of a solution of 0.3 *M* K_2NiF_6 in hydrogen fluoride with water: A, first precipitate; B, second precipitate (dry powders).

The brown precipitates from K_3NiF_6 and from reduced solutions of K_2NiF_6 were found to have appreciable oxidizing power (0.30–0.48 equiv of iodine per mole of nickel) and were found to be much less stable than either of the potassium salts.

Figure 5 shows infrared spectra of precipitates obtained by progressively reducing solutions of K_2NiF_6 in hydrogen fluoride with minute amounts of water. Nickel difluoride was the chief component of each of the solids, as indicated by the bands at 450, 291, and 237 cm^{-1}. The first precipitate (Figure 5A) also contained nickel(IV), as shown by the band of the NiF_6^{2-} ion at 673 cm^{-1}. Nickel(IV) may have been present as coprecipitated K_2NiF_6 or an acid species, such as $KHNiF_6$ or H_2NiF_6. The latter would be expected to be much more reactive than K_2NiF_6.

The second precipitate (Figure 5B) exhibited infrared bands of both nickel(III) and -(IV) species, at 610 and 673 cm^{-1}, respectively. The shift of the nickel(III) frequency, from 580 to 610 cm^{-1}, indicates that nickel(III) was present as a new compound and not as K_3NiF_6. The bands at 610 and 673 cm^{-1} have also been observed in precipitates from solutions reduced with zinc.

Thus far, we have been unable to identify the nickel(III) compound in the complex mixtures by chemical or crystallographic methods. X-Ray powder patterns of the solids have shown only diffuse lines of NiF_2 and KHF_2. The solids liberate hydrogen fluoride below 200° when heated under vacuum and liberate small amounts of fluorine at higher temperatures. Nickel trifluoride is one product which might be expected from the reduction of nickel(IV) solutions and from the decomposition of K_3NiF_6 in hydrogen fluoride, by analogy with the decomposition of Na_2PrF_6 in hydrogen fluoride.[2] However, H_3NiF_6 and other acid species are equally probable. In further studies of this system, Raman spectra and fluorine-19 nmr spectra may prove

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(15) R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1950).
(16) M. J. Reisfeld, *J. Mol. Spectry.*, **29**, 120 (1969).
(17) M. F. A. Dove, *J. Chem. Soc.*, 3722 (1959).

useful for identification of nickel(III) and -(IV) ions in the solutions. Raman bands of solid K_2NiF_6 are known,[16] and an nmr line has been observed for NiF_6^{2-} ion in hydrogen fluoride solutions.[18]

The mass spectrometric analyses indicate that K_2NiF_6 and K_3NiF_6 react chiefly as follows with water

$$K_2NiF_6 + H_2O \longrightarrow 2K^+ + 2F^- + NiF_2 + 2HF + 0.5O_2$$

$$K_3NiF_6 + 0.5H_2O \longrightarrow 3K^+ + 3F^- + NiF_2 + HF + 0.25O_2$$

Ozone is a secondary product. The odor of ozone is very strong above samples of K_2NiF_6 or K_3NiF_6 exposed to moist air or hydrolyzed in open beakers, and a blue ring of ozone also appears occasionally above solutions of K_2NiF_6 in hydrogen fluoride when the latter are frozen with liquid nitrogen. This is attributed to the partial hydrolysis of nickel(IV) by traces of water in the solvent. Klemm and Huss[4] suggested that oxygen difluoride might be formed in the hydrolysis of K_2NiF_6, but no oxygen difluoride was observed in the mass spectrometric analyses.

Absorption spectra of the nickel(III) and -(IV) solutions formed by electrolysis were found to be similar to those shown in Figures 3A and 3B. During the first 10–15 min of electrolysis, when the solutions remained colorless, water and other reducing impurities probably were being oxidized by fluorine in the vicinity of the anode. The solutions became slightly turbid as the brown species appeared, possibly from saturation with nickel difluoride, and became clear again as the very soluble, red nickel(IV) species were formed. Colored nickel ions have been observed previously by Asprey and coworkers at Los Alamos Laboratory in electrolysis experiments with hydrogen fluoride solutions.[19] The stability of the interface between the red and colorless solutions and the absence of any migration of colored ions to the cathode indicate that only anionic or neutral nickel(III) and -(IV) species such as NiF_6^{3-}, $HNiF_6^{2-}$, $H_2NiF_6^-$, H_3NiF_6, NiF_6^{2-}, $HNiF_6^-$, and H_2NiF_6 were present in the anode region.

The Simons process[20,21] has been used extensively to produce fluorocarbons through electrolysis of such compounds as carboxylic acids, alcohols, ethers, amines, and hydrocarbons in hydrogen fluoride solutions. Cells used in the Simons process are generally made of iron or steel, with one or more nickel anodes. Several authors[22–25] have suggested that nickel(III) or -(IV) fluorides might be involved as intermediates in the cell reactions, since nickel difluoride has frequently been observed in deposits on the anodes and in residues from the cells. It is probable that the brown and red nickel(III) and -(IV) species described in the present article behave as such intermediates in Simons cells operated under anhydrous conditions. The nickel species have high oxidation potentials since they liberate oxygen from water and undoubtedly act as vigorous fluorinating agents in reactions with organic molecules.

Acknowledgment.—We are indebted to K. Jensen, I. M. Fox, and J. Sha for chemical analyses, B. Tani for X-ray powder photographs, and L. Quarterman for the supply of purified hydrogen fluoride.

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(18) N. A. Matwiyoff, L. B. Asprey, E. Fukushima, M. J. Reisfeld, and W. E. Wageman, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March–April 1968, No. S 205.

(19) L. B. Asprey, private communication.

(20) J. H. Simons, *J. Electrochem. Soc.*, **95**, 47 (1949).

(21) J. H. Simons, "Fluorine Chemistry," Vol. 1, Academic Press, New York, N. Y., 1950, pp 414–422.

(22) T. Gramstead and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).

(23) R. N. Haszeldine and F. Nyman, *ibid.*, 2684 (1956).

(24) J. Burdon and J. C. Tatlow, *Advan. Fluorine Chem.*, **1**, 129 (1969).

(25) S. Nagase, "Fluorine Chemistry Reviews," Vol. 1, P. Tarrant, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, pp 77–106.