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Chemistry of Anhydrous Systems Containing
Hydrogen Fluoride and Nitrogen Oxides*

MASTER

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ABSTRACT

Nitrosyl and fluoride ions are formed in liquid anhydrous hydrogen fluoride when nitric oxide, nitrogen sesquioxide, nitrogen tetroxide, or nitrosyl fluoride, are dissolved. Vapor infrared analysis was used to study the solution composition and gaseous reaction products. These solutions react with metallic uranium, plutonium, zirconium, iron, and aluminum, as well as ceramic uranium oxide and uranium carbide, forming soluble nitrosyl metal fluoride complexes and liberating nitric oxide. The uranium compound was identified as nitrosylium hexafluorouranate, NOUF_6 . This compound has been made volatile by passing nitrosyl fluoride gas over the dry salt at 500°C .

Introduction

The reprocessing of reactor fuel elements requires the dissolution and separation of uranium from its associated fuel materials. The increasing variety of cladding and matrix materials has resulted in a search for more universally reactive solvents. A particularly promising combination was found when hydrogen fluoride was mixed with nitrogen tetroxide. The complex chemistry involved has promoted the investigation upon which this paper is based.

When liquid anhydrous hydrogen fluoride reacts with certain metals such as uranium, iron, aluminum, and zirconium, a protective fluoride film is formed that prevents further reaction of the metal. The addition of nitrogen oxides to the HF produces more effective reagents, in which the complex fluoride reaction products are partially soluble.

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The compounds NO, N₂O₃, N₂O₄, and NOF have all been found to react to some extent with HF, producing solutions with similar characteristics. The increase in electrical conductivity due to addition of these compounds to HF solution has been measured; infrared analyses of the vapor in equilibrium with solvents have revealed the existence of common compounds, and the solid and gaseous reaction products of metal dissolutions have shown similar compositions.

The System NO-HF

Gaseous NO was bubbled through liquid HF. Reaction became apparent when the solution became violet in color. The solubility of NO in HF was determined to be ≈ 0.2 moles per liter at 4 atmospheres NO pressure at 25°C. At this pressure, the solution became dark blue-black, presumably due to the formation of "violet HF," N₂O₂⁺F(HF)⁻. The following equation was postulated to account for the presence of this N₂O₂⁺ ion:

and with excess NO:

The formation of N₂O as evidenced by the appearance of infrared absorption bands at 2240 and 1300 cm⁻¹ tends to confirm Eq. (1). Eq. (2) has been well established by Seel and his co-workers (1). Incidentally, the solution formed by bubbling NO through HF was found to be quite corrosive to nickel, Monel metal, and copper.

The System N₂O₃-HF

The reaction of N₂O₃ with HF was performed at dry ice temperature after first forming the blue liquid N₂O₃ from gaseous NO₂ and NO at -10°C. The resulting water-white liquid produced a vapor infrared spectrum nearly identical to that of an NOF-HF addition product which will be discussed later. (In most of these systems experimental difficulties have prevented the obtaining of good liquid-phase absorption spectra, but much useful information was obtained from the absorption of the vapor phases in equilibrium with the liquids.) A possible ionization scheme for N₂O₃ in HF is given by the following equations:

The System N_2O_4 -HF

This system is of more practical interest as a fuel solvent than the preceding two, and more information has been obtained on its properties. Absorption spectra, NMR spectra, electrical conductance, and freezing points have been measured.

The equivalent conductance of dilute solutions of N_2O_4 in HF was found to be high, suggesting complete ionization. Indeed, the value obtained by extrapolating to infinite dilution was $520 \text{ ohm}^{-1} \text{ cm}^2$, which is twice the value found by Fredenhagen for the equivalent conductance of KF and H_2O in HF. Since each of these solvents is considered to dissociate into two ions (K^+ and HF_2^- , and H_3O^+ and HF_2^-), it follows that N_2O_4 forms four. A possible ionization scheme is given by the following equation:

A similar scheme was proposed by Fredenhagen for solutions of alkali nitrates in HF, in order to account for their high conductivity (about the same as that of N_2O_4). Other workers (2,3), however, have failed to find spectral evidence of the "nitric acidium" ion, and believe that the pentavalent nitrogen is in the form of NO_2^+ or HNO_3 . In the case of N_2O_4 solutions, the equations would be:

By postulating the proper equilibrium constant for the second reaction, the total number of ions per molecule of N_2O_4 can still be made out to be four.

In this system we were successful in obtaining some liquid infrared spectra. These showed strong HNO_3 bands and weak NO_2^+ and H_3O^+ bands. The vapors in equilibrium with a 10 mole % N_2O_4 in HF solution produced strong NO_2 - N_2O_4 absorption bands in

addition to HNO_3 peaks. Upon dilution however, both the $\text{NO}_2\text{-N}_2\text{O}_4$ and HNO_3 bands disappeared. A new peak appeared at $\approx 1600\text{ cm}^{-1}$ which may be due to an NOF-HF addition compound.

It is worth noting that there is a formal similarity between solutions of N_2O_4 in HF and N_2O_4 in H_2SO_4 . There is published evidence that in the latter solvent the reaction occurs:

Mixtures of N_2O_4 with HF were examined by nuclear magnetic resonance (4), using the fluorine line. No significant deviation from the HF spectrum was observed, indicating that all the fluorine atoms in the system were equivalent. It follows that the postulated ionic and molecular species are rapidly interconvertible.

It appeared probable that the nitrosyl ion plays an important role in the aggressive character, toward metals, of $\text{N}_2\text{O}_4\text{-HF}$ solutions. To test this hypothesis, a 27 mole % solution of absolute HNO_3 in HF was prepared, since such a solution should contain all the ions which may form in $\text{N}_2\text{O}_4\text{-HF}$, except NO^+ . The rate of dissolution of zirconium in $\text{HNO}_3\text{-HF}$ was measured and found in fact to be far lower than in $\text{N}_2\text{O}_4\text{-HF}$.

Finally, a freezing point diagram was obtained for $\text{N}_2\text{O}_4\text{-HF}$ in the miscible range of 0 to 44 mole % NO_2 . A sharp minimum of 144°C was found at 10 mole % NO_2 . An incongruent point around 22 mole % appeared to exist, along with a compound at 33 mole % NO_2 . These points would indicate the formation of compounds at 4 and 2HF (5).

A similar freezing point diagram (6) is being obtained for pure NOF and HF . A minimum of -147°C was obtained at about 8 mole % NOF ; however the presence of additional $\text{NOF}\cdot\text{HF}$ compounds is indicated.

The System NOF-HF

In this system, two stable addition compounds of much lower volatility than either component have been reported to exist (7,8). The more stable is generally agreed to have the formula $\text{NOF}\cdot 3\text{HF}$ and a boiling point of 95° ; the other is $\text{NOF}\cdot 5\text{HF}$ or $\text{NOF}\cdot 6\text{HF}$, and

boils at about 65°. They can be made by the reaction of NOCl with excess HF or by direct combination of NOF with HF.

We have made rough determinations of the conductance of dilute solutions of NOF in HF. In the range 0.01 to 0.1 M, the equivalent conductance was about 220 ohm⁻¹ cm². This is what would be expected from dissociation into two ions, presumably NO⁺ and solvated F⁻.

Infrared absorption spectra were obtained on the vapors in equilibrium with various liquid mixtures obtained by bubbling gaseous NOCl through liquid HF, venting the gaseous HCl formed (it is insoluble in HF) and distilling until a constant-boiling mixture was obtained. Two conspicuous bands were found; one at 1620/1590 cm⁻¹ and one at 1804/1797 cm⁻¹. During distillation the 1800 cm⁻¹ band gradually diminished and the 1600 cm⁻¹ band increased. The latter band has also been observed in a product made by direct combination of NOF and HF. It is likely that it is due to the NOF·3HF molecule, and the 1800 cm⁻¹ band is due to the more volatile NOF·6HF.

Distillation of the NOCl-HF reaction product yields a constant-boiling material of the approximate composition NOF·3HF. According to Seel (9) this material is an azeotrope of the composition NOF·3.1 HF. In any case, it is a liquid of interesting properties from the viewpoint of reactor fuel processing, as the following section shows.

Solvent-Metal Reactions

The reaction of these solvents with various metals at 50° to 100°C produces metal fluoride-nitrosyl fluoride complexes. The nitrosyl ion is the active species, oxidizing metals by electron transfer and liberating NO gas. (NO gas is not observed in the special case of N₂O₄-HF.)

The moles of NO liberated in the U and Zr reactions were measured as 4.60 and 3.63, respectively. Since some NO reacts with solvent, the nearest integers, 5 and 4, were selected for the equation. Plutonium metal also dissolves but its compound has not been characterized.

In addition to the NO gas liberated, a relatively small amount of N₂O was observed in the vapor infrared spectrum of the reaction products. This is undoubtedly due to the NO-HF side reaction mentioned in Eq. (1). As the NO pressure increased over the liquid, "violet HF" was produced in the solution.

In the reactions of 10 mole % N₂O₄-HF, some N₂O was observed in the vapor in addition to NO₂-N₂O₄. Apparently the NO released reacts completely with both the HF (Eq. (1)) and the NO₂ to form N₂O₃. The N₂O₃ can then react with the HF in the solvent to yield nitrosyl ions (Eqs. (3) and (4)). The uranium salts were identified as NOUF₆ by chemical as well as x-ray diffraction analyses and the solubility determined to be 25 g/l at 25°C in 10 mole % N₂O₄-HF.

Some other metals which readily dissolve in the N₂O₄-HF solution include niobium, molybdenum, beryllium, tantalum, 304 SS, and the oxides of beryllium and aluminum. The dissolving rates for most of the materials are greatly in excess of 5 mg/cm²-min at 100°C. The salts of these have not been characterized.

The UO₂-NOF-HF Azeotrope Reaction

The reaction of the NOF-HF azeotrope with UO₂ produces NO₂ in addition to NO and some N₂O. The uranium compound was again identified as NOUF₆ by its x-ray powder diffraction pattern. Reactions may be postulated to produce five, three, or less moles of gas. The moles of gas may be reduced further by considering the N₂O₃ NO₂ + NO equilibrium and the NO₂ solubility in the azeotrope. The stoichiometry of this reaction was difficult to determine because of the complex equilibrium and solubility phenomena of NO₂ in this system.

Eq. (14) is consistent with previous reactions in that only the nitrosyl ion is reactive. Eq. (15) assumes the hydrogen fluoride is a competing reactant for the oxide, forming H_2O .

The Salt $NOUF_6$

The uranium salt formed in all these Corporation reactions was first identified by workers at Goodyear Atomic (10). Its formula was established as nitrosylium hexafluorouranate, $NOUF_6$. At Brookhaven, the salt was subjected to electron paramagnetic resonance measurement and found to have no magnetic moment. The pure salt was formed by combining the gases NO and UF_6 at room temperature in vacuo. The NO molecule has a magnetic moment of 1.3×10^{-3} emu due to the single uncoupled electron, whereas the magnetic moment of the UF_6 is practically zero (0.12×10^{-6} cm).

Further experiments are contemplated to determine if the lack of magnetic moment is due to the dimerization of $NOUF_6$, rapid electron exchange, or merely due to the short relaxation time of the paramagnetic state of the molecule.

Uranium Volatility

The formation of volatile uranium hexafluoride is well known in chemical separation techniques (11). Its production from $NOUF_6$ is accomplished readily by fluorination with gaseous fluorine or the interhalogen fluorides; however an interesting method has been found of producing a "volatile $NOUF_6$." The dry powder can be made volatile simply by heating to $500^\circ C$ and passing NOF or $NOF \cdot 3.1 HF$ vapor over the salt. The uranium salt will redeposit in another zone at a temperature of $390^\circ C$ with an efficiency of close to 100%. If helium is substituted for the NOF gas, no volatilization will occur.

The pure salt, NOUF_6 , when heated in vacuo from 400° to 500°C decomposes to UF_4 without any uranium becoming volatile, therefore the presence of NOF in the gas phase apparently prevents decomposition. The NOUF_6 is presumably evaporated and then condensed at the lower temperature of 390°C , at which point the salt decomposes to UF_4 .

Summary

The results of this study indicate that solutions of nitrosyl fluoride as well as solutions of nitrogen oxides in hydrogen fluoride produce reactive nitrosyl ions. These solutions have been shown to be versatile solvents for many materials. The high reactivity of these solvents is directly attributable to the oxidizing power of the nitrosyl ion. The reactions of these solvents with other compounds as well as studies of the nitrosyl fluoride-hydrogen fluoride system itself, offer a large area for further investigation.

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