

High Energy Oxidizers in Solution: The System $F_2/NF_3/HF$

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Introduction

The system $F_2/NF_3/HF$ has been studied as an experimental system in which it was thought possible to observe interactions leading to the formation of highly energetic ionic species. The driving force for these interactions was expected to consist primarily of the highly exothermic formation of fluoride ion in liquid HF. The system has been studied experimentally through measurements of the solubilities of F_2 , NF_3 , and mixtures of the two in liquid HF, along with nmr and epr spectra of these components and their mixtures and some conductivity measurements on NF_3 in HF.

The interactions possible between liquid HF and NF_3 or F_2/NF_3 mixtures are (1) the formation of ions, (2) the formation of complexes of NF_3 and HF, (3) decomposition of NF_3 , (4) fluorine exchange reactions among the three components, and (5) formation of unstable, solvated complexes of F_2 and NF_3 , these being precursors to ion formation.

Knowledge of the solution chemistry, the nmr and epr spectra, and the conductivities were used to determine which of the interactions occur and to support further experimental work directed toward the synthesis of ionic compounds from these oxidizers.

Results and Discussion

The interactions which are possible are more probable under certain conditions of temperature and pressure than others. Complex formation between HF and NF_3 is more likely at temperatures not much above the freezing point of HF while decomposition of NF_3 in highly purified HF may be expected at $200^\circ C$. The formation of solvated $F_2 \cdot NF_3$ or $F_2 2NF_3$ complexes followed by formation of ions is more likely to occur, if at all, at ambient or higher temperatures and pressures. All of these interactions are germane to the strict interpretation of results from the solubility and other measurements.

Solubility Measurements. The solubilities of F_2 and of NF_3 in HF are shown in Fig. 1. In addition, the solubility behavior on addition of F_2 to a known mixture of NF_3 in HF is shown in Fig. 2. For pressures up to twelve atmospheres and at $20^\circ C$, the individual solubilities are given by $p_i = k_i n_i$ where $k(NF_3) = 1.02 \times 10^{-5}$ cm of Hg·moles HF/mole NF_3 and $k(F_2) = 1.84 \times 10^{-5}$ in the same units.

The lack of an intercept indicates no appreciable compound formation, no strong interaction with the solvent, nor reaction with the vessels. The slopes show that F_2 is about half as soluble as NF_3 . This is the order to be expected from Hildebrand's ideal solubilities.

The solubility behavior in the ternary system shown in Fig. 2 shows that on addition of F_2 to NF_3 in HF, the F_2 is initially four times more soluble than when added to pure HF and about twice as soluble as NF_3 itself. Subsequently, further addition of F_2 to the ternary system proceeds according to the expected solubility of F_2 in HF alone.

There is, therefore, apparently an interaction between F_2 and NF_3 in HF. This conclusion is based on the solubility behavior as shown in Fig. 1 and on the lack of apparent interaction between F_2 and HF as well as NF_3 and HF. It has

further been shown that F_2 and NF_3 behave ideally in the gas phase and in liquid/vapor equilibrium at $-196^\circ C$. The apparent interaction can be attributed to the formation of complexes of F_2 with one or two molecules of NF_3 and, possibly, subsequent formation of ion pairs such as NF_3^+/F^- .

Solubilities were also measured in Kel-F vessels to be used as nmr tubes. In these, F_2 was 15 times more soluble than in an all metal system. This was, of course, due to interaction of F_2 with the Kel-F. As will be shown later, no evidence for products of this interaction have been observed except when decomposition of the Kel-F occurs in spontaneous, incandescent reactions.

NMR and EPR Spectra. NMR spectra of the components and mixtures of the system NF_3-F_2-HF in Kel-F, were explored as a possible means of detecting new species. These spectra showed only the F^{19} resonances of the starting materials, but the Hf/F^{19} resonance was broadened substantially on addition of NF_3 and further broadened by addition of F_2 . This resonance also shifted with temperature. The line broadening was attributed to chemical exchange with the solvent but it could not be shown what the HF was exchanging with.

The line shift with temperature was shown via epr spectra to be due to the presence of paramagnetic species. These were from a reaction of F_2 with the Kel-F and from F_2 dissolved in HF. The latter resonance disappeared on adding as much NF_3 as F_2 and was present in F_2/HF mixtures and not in any of the components alone. It was therefore evidently not related to a paramagnetic entity involving NF_3 .

Thus both nmr and epr studies gave no direct evidence for the presence of new NF species although it appeared that the NF_3 nmr line diminished appreciably on adding F_2 and, conversely, the F_2 line diminished on adding NF_3 . At the concentrations attainable, the nmr is not sufficiently sensitive while the epr, though sensitive, is most effective at temperatures at which HF is solid. At the solid transition, the HF is out-gased, and it is probable that, if present, little F_2/NF_3 adduct would be trapped in the solid.

Conductivity Measurements. These were carried out only on the NF_3/HF system. The conductivity of the NF_3 in HF was not greater than that of the HF alone. This was 3×10^{-5} /ohm cm at $0^\circ C$. The upper limit for the ionization of NF_3 was estimated to be 10^{-7} and is probably much lower since this implies a degree of ionization of 10^{-3} . If this were true, ionic derivatives of NF_2^+ would be easily prepared.

Experimental

Apparatus. The vacuum systems used in this work were assembled from copper and/or monel tubing, vessels and bellows valves. Valve gaskets, conductivity cells, nmr and epr tubes were of Kel-F plastic. All permanent joints were silver soldered or heliarc welded. Demountable joints were $\frac{1}{8}$ inch pipe fittings sealed with Teflon tape. There were no leaks detectable by means of a helium leak detector. Pressures were measured with Wallace and Tiernan gauges equipped with resistant metal capsules. Thermocouple gauges were used to monitor low pressures in the vacuum system but were isolated from the system to prevent destruction of the gauge by F_2 and HF contamination of the system by reaction products. The systems were passivated with respect to F_2 and HF after any exposure to the atmosphere.

Materials. Anhydrous HF was prepared by distillation through an 80 plate plastic column. Its specific conductivity before exposure to metal parts of the vacuum system was 10^{-4} /ohm-cm or less.

Fluorine, which contains about 2% impurities composed mainly of air, HF, CO_2 , and CF_4 , was purified in two steps. The less volatile impurities were frozen out

at about -187°C in a metal trap charged with the desired quantity of the gas. Air was removed by extracting the supernatant gases above the liquid condensed in a cold finger at -196°C .

Nitrogen trifluoride was obtained in 99.9% purity from Air Products and Chemicals, Inc., and used without further purification for solubility studies but was passed through liquid HF at -80°C , condensed and pumped on at -196°C for use in conductivity studies.

Solubility Measurements. Solubilities were determined in the apparatus shown in Fig. 2. For the system NF_3/HF , 50 gm of HF were charged into the 450 ml monel pressure vessel, Vs, and, successively, quantities of NF_3 (Pvm) were condensed quantitatively into the vessel cooled to -196°C . The resulting pressure in Vm was 0.0 mm and the valve on the monel vessel was closed. The vessel and its contents were allowed to equilibrate at 20°C in a water bath. The HF was stirred magnetically. The mixture of HF and NF_3 gases was admitted to Vm, and the system, Vs and Vm, was allowed to reach equilibrium at P_1 .

For the F_2/HF system, the procedure was the same except that F_2 was transferred quantitatively at about 55°K with the aid of a solid nitrogen/liquid oxygen bath. Solid nitrogen was prepared by pumping on the dewar, filled with liquid nitrogen and cooling the 450 cc pressure vessel. Subsequently, the solid nitrogen sublimed away from the vessel and liquid oxygen was added to maintain efficient heat transfer from the vessel to the solid nitrogen.

For the $\text{F}_2/\text{NF}_3/\text{HF}$ system, the behavior was observed two ways. Successive quantities of F_2 were added to the vessel containing a known quantity of NF_3 and HF. Secondly, successive quantities of NF_3 were added to a known F_2/HF system.

In addition, the composition of the mixture of gases above the liquid phase was determined. HF was separated from F_2 and NF_3 and its pressure was measured. F_2 and NF_3 were determined from their total pressure both at room temperature and at liquid nitrogen temperature where they behave as an ideal solution. Temperature control was achieved by means of a nitrogen thermometer.

NMR Spectra. NMR spectra of components and mixtures were obtained in Kel-F tubes of two types. Spinnable tubes were made by heat sealing both ends of a tube machined to resemble standard 200 ml glass tubes. Tubes to which components were added successively in order to observe changes in spectra were made from $\frac{1}{2}$ inch rod and equipped with a valve. A Varian A-60 Spectrometer was used.

EPR Spectra of components and mixtures were obtained in Kel-F capillaries drawn from $\frac{1}{4}$ inch tubing. Spectra were observed at temperatures down to -190°C .

Conductivity Studies were carried out in an all Kel-F vacuum system and conductivity cell with platinum electrodes. The cell constant was .03/cm determined by calibration with KCl solutions at ice temperature.

Conclusions

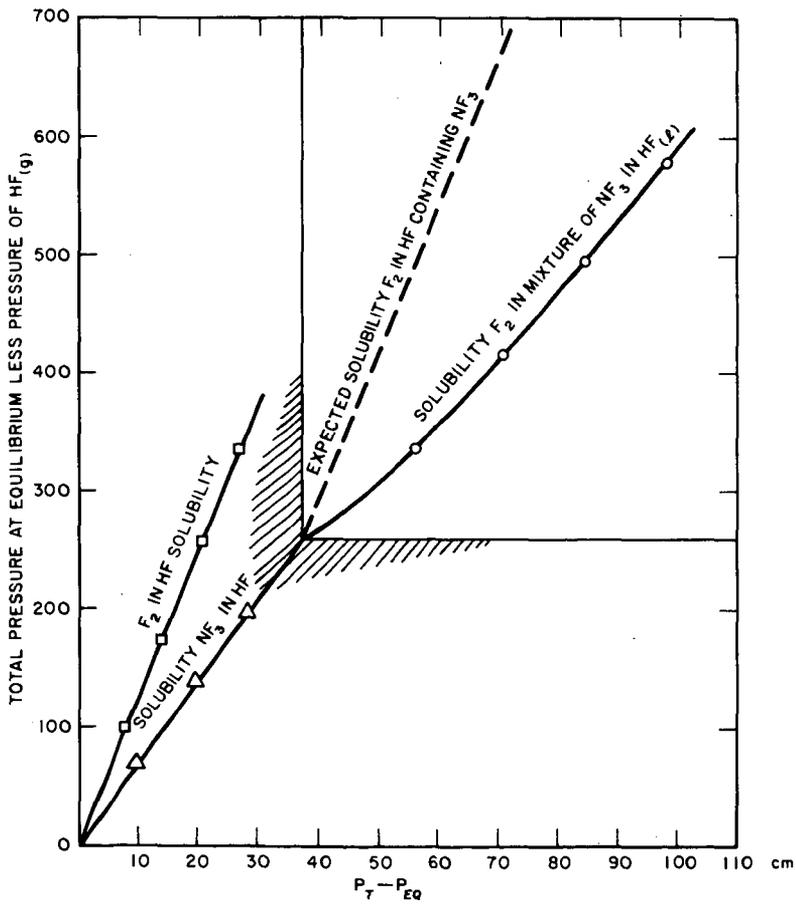
The existence of the interactions justified some speculation on its nature. There are three reactions of interest which could occur in this system:

1. $\text{NF}_3 \xrightarrow{\text{HF}} \text{NF}_2^+ \text{F}^-$
2. $\text{NF}_3 + \frac{1}{2}\text{F}_2 \xrightarrow{\text{HF}} \text{NF}_3^+ \text{F}^-$
3. $\text{NF}_3 + \text{F}_2 \xrightarrow{\text{HF}} \text{NF}_4^+ + \text{F}^-$

None of these violate valence rules but the extent of reaction (1) is small from its conductivity while (2) and (3) may very well proceed through the proposed unstable $F_2 \cdot NF_3$ and $F_2 \cdot 2NF_2$ complexes. It is planned to determine whether any ions of interest can be derived from this system by addition of SbF_5 in order to obtain a solid derivative.

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FIG 1 SOLUBILITY OF F_2 AND NF_3 IN HF

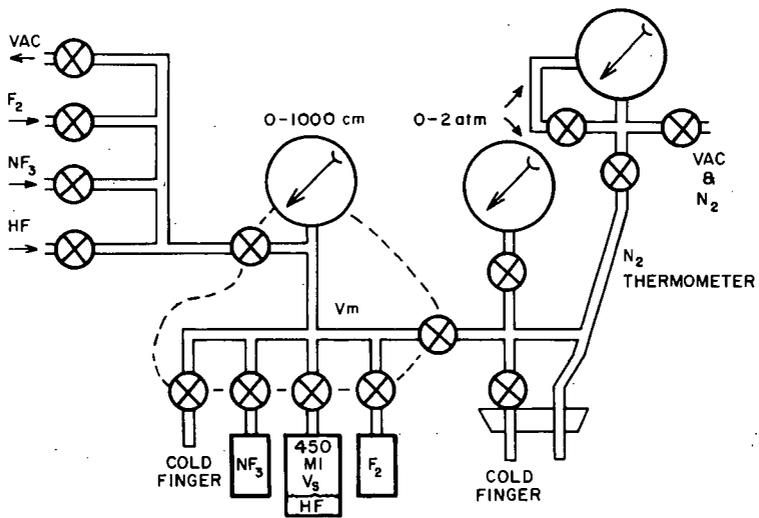


FIG 2 SOLUBILITY APPARATUS