The Electrochemistry of Inorganic Difluoramino Compounds. II. Solution Chemistry and Electrochemical Reduction of Difluoramine

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Abstract: The mechanism of the electrochemical reduction of difluoramine has been studied in water, protonic organic solvents, and aprotic solvents. In water and protonic solvents, such as alcohols, difluoramine undergoes a diffusion-controlled, four-electron reduction to ammonia. In aprotic solvents, such as acetonitrile and dimethyl sulfoxide, the reduction product is ammonia, but the reaction is not completely diffusion controlled. In these systems, ammonia is formed by reaction of the electrode products with the solvent. The effect of added proton donors has been studied. In aprotic systems, the mechanism of the reaction is affected by repulsion of negatively charged intermediate species at the electrode surface. The effect of the nature of the supporting electrolyte on the repulsion phenomenon has been studied. The half-wave potential of difluoramine was found to vary with the solvent used, and the values observed are correlated with the strength of solvation of HNF_2.

In the first paper of this series,[1] the mechanism of the electrochemical oxidation of HNF_2 was reported. As an extension of that work, the present paper describes an investigation of the reduction of HNF_2 at mercury cathodes.

Although the electrolytic reduction of HNF_2 in various systems has been previously demonstrated, no study of the mechanism of the reaction has been reported. The reduction of HNF_2 in aprotic systems has been investigated by means of macroscale reductions only, using nickel, zinc, and graphite electrodes in solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).[2] A complicated mixture of product gases including H_2, N_2, and N_2F_4 was observed in proportions which varied with the experimental conditions. In aqueous systems, HNF_2 has been reported to undergo a four-electron reduction at a mercury electrode, but no product analysis was given.[3]

In the present work, this reaction has been studied using polarography and controlled potential macroscale electrolysis techniques to determine the mechanism of the reduction and the reason for the apparent variation of the mechanism with the experimental conditions used.

Results and Discussion

Reduction in Water. In preliminary experiments, HNF_2 was found to give a well-defined polarographic wave in acidic aqueous buffer systems. The pH range in which the reaction was studied was limited because HNF_2 in basic systems reacts to form N_2F_2, and, at pH <2.35, the hydrogen ion reduction wave interferes.

In the pH range 2.35 to 6.65, the wave is diffusion controlled since the diffusion current (i_d) is linearly dependent on the concentration of HNF_2 in the bulk of the solution (C_{HNF_2}) and on the square root of the height of the mercury column ($h^{1/2}$). The half-wave potential ($E^{1/2}$) is constant over this pH range at -1.23 ± 0.02 v *vs.* sce. The number of electrons involved in the electrode reaction (n) was determined from the polarographic diffusion current in several buffer systems over the pH range 4.89 to 6.65 using the Ilkovic equation.

$$i_m = (7.082 \times 10^4) n m^{2/3} t_m^{1/6} D^{1/2} C_{HNF_2} \quad (1)$$

In this equation, i_m is the maximum diffusion current, m is the rate of mercury flow, t_m is the drop time, and D is the diffusion coefficient of HNF_2.[4] The value of D in this calculation was 2.1×10^{-5} cm^2/sec, determined in previous chronopotentiometric studies of the oxidation of HNF_2.[1]

The value of n obtained ranged from 3.74 to 3.85 in several trials, confirming that HNF_2 is reduced under these conditions in a four-electron process, as previously suggested.[3] The reaction is, in all probability

$$HNF_2 + 4e^- + 2H^+ \longrightarrow NH_3 + 2F^- \quad (2)$$

To confirm this hypothesis, macroscale, controlled-potential reductions of HNF_2 were carried out. The product was NH_3, and the current efficiency varied from 99 to 102%. Fluoride ion produced was determined colorimetrically and agreed with the amount expected from eq 2. A typical run is given in Table I.

Reduction in Protic Nonaqueous Solvents. When solutions of HNF_2 in methanol and ethanol were polarographed with $LiClO_4$ and $(C_2H_5)_4NClO_4$ as supporting electrolytes, a well-defined wave, similar to that observed in water, was obtained. The $E^{1/2}$ was shifted to a more negative potential and the wave was found to be diffusion controlled, since i_d was proportional to C_{HNF_2} and $h^{1/2}$.

A controlled potential, macroscale reduction of HNF_2 in anhydrous methanol showed that the reduction product was NH_3 (Table I).

Reduction of HNF_2 in Aprotic Systems. In aprotic solvents such as acetonitrile and dimethyl sulfoxide, the shape of the HNF_2 wave was found to be greatly

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[1] G. A. Ward and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 4333 (1964).

[2] Ethyl Corporation, "Research on Light Metal Fuel and Oxidizer Chemistry," Quarterly Progress Report No. 2, Part 2, Contract No. AF-04(611)-9376, Oct 1963.

[3] K. J. Martin, *J. Am. Chem. Soc.*, **87**, 394 (1965).

[4] D. Ilkovic, *Collection Czech. Chem. Commun.*, **6**, 498 (1934).

Table I. Controlled Potential, Macroscale Electrolysis of HNF_2 Solutions[a]

Electrolyte soln	Potential of cathode (*vs.* sce), v	NH_3 formed, mmoles	HNF_2 used, mmoles	Current passed, faraday	Current efficiency, %[b]
(i) 0.1 *M* HNF_2, 1.0 *M* NaOAc, 1.0 *M* HOAc, in water (pH 5.5)	−1.40	6.1	6.3	0.0242	99
(2) 0.1 *M* HNF_2, 0.75 *M* $LiClO_4$, in methanol	−1.90	2.7	2.8	0.0104	104
(3) 0.1 *M* HNF_2, 0.5 *M* $(C_2H_5)_4$-$NClO_4$, in DMSO	−2.00	3.8	4.2	0.0139	109
(4) 0.1 *M* HNF_2, 0.5 *M* $(C_2H_5)_4$-$NClO_4$, in acetonitrile	−1.80	4.8[b]	5.7	0.0177	107[c]

[a] Mercury pool cathode, 7 cm². [b] Assuming four-electron reduction. [c] A small amount of ammonia (<1 mmole) may have been lost because of difficulties in analyzing the $(C_2H_5)_4NClO_4$ acetonitrile solution. Therefore the current efficiency is a minimum value.

affected by the nature of the supporting electrolyte and the presence of traces of proton donors such as water and alcohols.

A typical polarogram for the reduction of HNF_2 in dried CH_3CN, with a supporting electrolyte of 0.1 *M* $LiClO_4$, is shown in Figure 1. In this system, the wave is not diffusion controlled, since i_d does not vary linearly with C_{HNF_2} or $h^{1/2}$. When increasing amounts of water are added to the solution, a second wave is observed, at a potential approximately 0.3 v more cathodic than the first. The size of this wave increases, and it more closely approaches diffusion-controlled behavior as the water concentration is increased. This behavior is demonstrated by the data shown in Figure 2.

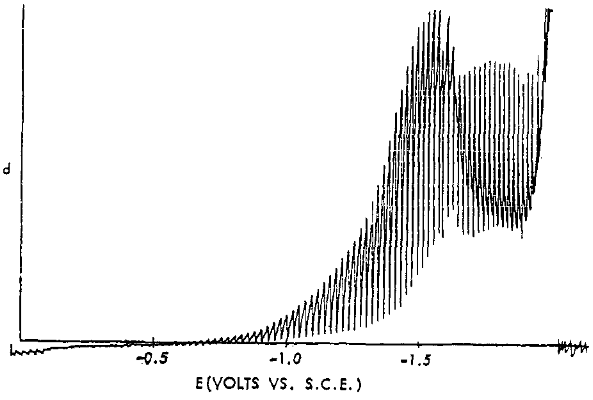

Figure 1. Polarographic wave of HNF_2 in dried acetonitrile containing 0.1 *M* $LiClO_4$.

When $NaClO_4$ was used as the supporting electrolyte, the wave observed in dried CH_3CN was quite different in appearance from the wave in $LiClO_4$ systems but was similar in behavior (Figure 3). It was not diffusion controlled and was affected by the presence of water as was the wave in $LiClO_4$. Addition of 2% water suppressed the unusually sharp wave observed in the anhydrous system. The resulting wave ($E^{1/2}$ *ca.* −1.45 v *vs.* sce) was more normal in appearance, increased in size, and more closely approached diffusion control as the water concentration was increased.

In both the $NaClO_4$ and $LiClO_4$ systems, adding other proton donors such as methanol, ethanol, and phenol produced qualitatively the same results as water.

With $KClO_4$ as the supporting electrolyte, a well-shaped wave with $E^{1/2}$ of −1.44 v *vs.* sce was observed at low ($<5 \times 10^{-4}$ *M*) concentrations of HNF_2, and for which i_d was proportional to $h^{1/2}$. As the concentration was increased, however, a dip appeared in the plateau of the wave. This dip became relatively larger as the concentration was increased. Above 5×10^{-4} *M*, i_d was not proportional to *C*.

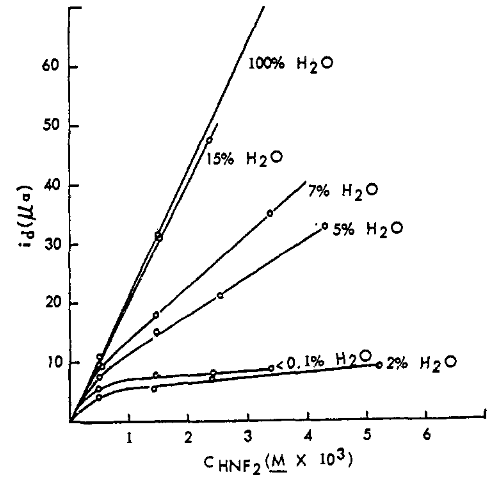

Figure 2. Effect of water concentration on HNF_2 reduction in water-acetonitrile mixtures.

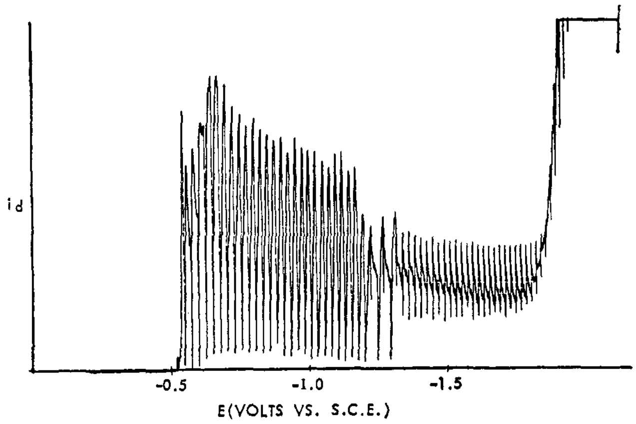

Figure 3. Polarographic wave of HNF_2 in dried acetonitrile containing 0.1 *M* $NaClO_4$.

When $(C_2H_5)_4NClO_4$ was used as the supporting electrolyte, the wave observed was normally shaped, with $E^{1/2}$ equal to −1.42 v *vs.* sce. In this case, i_d was proportional to C_{HNF_2} and $h^{1/2}$.

From a comparison of the ratio of the diffusion current to HNF_2 concentration (i_d/C) obtained in CH_3CN containing $(C_2H_5)_4NClO_4$ to that obtained in water (corrected for the difference in viscosity between the solvents), the reduction in CH_3CN appears to be a four-electron process. This conclusion is also confirmed by comparison of the i_d/C value for HNF_2 in this system with that obtained for CCl_4, for which the number of electrons involved in the reduction is known. The first wave in the reduction of CCl_4 corresponds to a two-electron reduction to remove one of the halogens. The ratio $(i_d/C_{HNF_2})/(i_d/C_{CCl_4})$ in acetonitrile containing 0.1 *M* $(C_2H_5)_4NClO_4$ was found to be 2.04; thus n_{HNF_2} is twice n_{CCl_4}, or 4, assuming D_{HNF_2} approximately equal to D_{CCl_4}.

The dried acetonitrile stock solution as well as 0.1 *M* solutions of the various perchlorate salts were analyzed for water by Karl Fischer titration. The results in Table II show that sufficient water was always present for the reduction of HNF_2 to proceed to NH_3. It appears that some effect, in addition to the lack of available protons, prevents the reduction of HNF_2 in acetonitrile from following the simple four-electron path observed in water and the alcohols. The effect is not specific to systems using acetonitrile as solvent, since the same experimental results are obtained in DMSO.

Table II. Water Content of Various Electrolyte Systems

System	Water, %	Concn, mole/l.
Acetonitrile stock	0.10	0.043
0.1 *M* $LiClO_4$ in CH_3CN	0.21	0.092
0.1 *M* $NaClO_4$ in CH_3CN	0.33	0.144
0.1 *M* $KClO_4$ in CH_3CN	0.10	0.043
0.1 *M* $(C_2H_5)_4NClO_4$ in CH_3CN	0.10	0.043

In a further attempt to determine the course of the reduction in acetonitrile and DMSO, the reduction was studied on the macroscale. Current-potential scans and controlled-potential electrolyses were run in both solvents with $(C_2H_5)_4NClO_4$ as the electrolyte. Normal current-potential scans were obtained, as would be expected from the polarography.

In the macroscale reduction of HNF_2 in DMSO, the principal reduction product was ammonia (Table I). The current efficiency (assuming a four-electron charge) was 109% and the yield of NH_3 was 90%. During electrolysis the DMSO became highly colored, indicating some attack on the solvent by intermediates in the reduction.

Similar results were obtained for the reduction in acetonitrile. The principal reduction product was again ammonia (Table I), and the solvent turned bright orange in color, indicating attack by the reaction intermediates. The colored material was found to be a tarry substance containing amine and nitrile groups and no fluorine.

Conclusions from this work are that the main product of the reduction of HNF_2 at a mercury cathode is ammonia, even in solvents of low proton availability. The reaction can apparently proceed partially through steps that involve abstraction of a hydrogen atom from the solvent, since, in solvents of low proton availability, a current efficiency of greater than 100% is obtained and the solvent is severely attacked.

The Solvation of HNF_2 and Its Effect on the Reduction Potential. Solutions of HNF_2 and Rb^+ in several solvents were polarographed, using $(C_2H_5)_4NClO_4$ as the supporting electrolyte. The data obtained (Table III) show that the solvent has a considerable effect on the reduction potential of HNF_2. The $E^{1/2}$ for the reduction of Rb^+ in the various solvents was also measured and was found to vary slightly from one solvent to the next (Table III). The effect of liquid junction potentials on $E^{1/2}$ for HNF_2 can be estimated from the $E^{1/2}$ of the Rb^+ ion which has previously been established as a good reference standard for comparing reduction potentials in various solvent systems[5] since it is very little affected by solvation. The effect of traces of water on the $E^{1/2}$ of HNF_2 in the various solvents was determined by adding water to the solvents. No significant effect was observed at water concentrations five times greater than those given in Table II. The variation of $E^{1/2}$ for HNF_2 may be caused by solvation, which changes the electron density on the HNF_2 nitrogen atom and affects the rate of the potential-determining, electron-transfer step of the reduction.

Table III. Effect of Solvent on the Polarographic Reduction of HNF_2

Solvent	$E^{1/2}_{HNF_2}$ (±0.03 v), v *vs.* sce	$E^{1/2}_{Rb^+}$ (±0.03 v), v *vs.* sce
H_2O[a]	−1.23	−2.13
CH_3OH	−1.55	...
C_2H_5OH	−1.50	−2.05
CH_3CN	−1.42	−1.98
Dimethylformamide (DMF)	−1.61	−2.01
Dimethyl sulfoxide (DMSO)	−1.64	−2.06

[a] $(CH_3)_4NCl$ was used as the supporting electrolyte because of the insolubility of $(C_2H_5)_4NClO_4$ in H_2O; $(C_2H_5)_4NClO_4$ was used in all other solvents.

The strength of association of HNF_2 with acetonitrile, methanol, dimethylformamide, dimethyl sulfoxide, and water was investigated by determining the total enthalpy for the dissociation of 1:1 complexes of HNF_2 with these solvents. The assumption that the solvated species would involve a ratio of one molecule of HNF_2 to one solvent molecule was not made on theoretical considerations, but rather as a point of reference. The association of HNF_2 with DMF and DMSO was so strong that very little (~5 mm) dissociation pressure was observed even at 0° (the boiling point of HNF_2 is −23°). Thus, no equilibrium expression could be obtained for these complexes. At the other extreme, the association of HNF_2 with water is so weak that no good equilibrium expression was obtainable. The strengths of association of HNF_2 with methanol and acetonitrile are in the intermediate range. The enthalpy of dissociation of $HNF_2 \cdot CH_3OH$ over the range −47.7 to 0.0° was found to be 8.24 kcal mole^{-1}, and

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(5) J. F. Coetzee, D. K. McGuire, and J. L. Hedrick, *J. Phys. Chem.*, **67**, 1814 (1963).

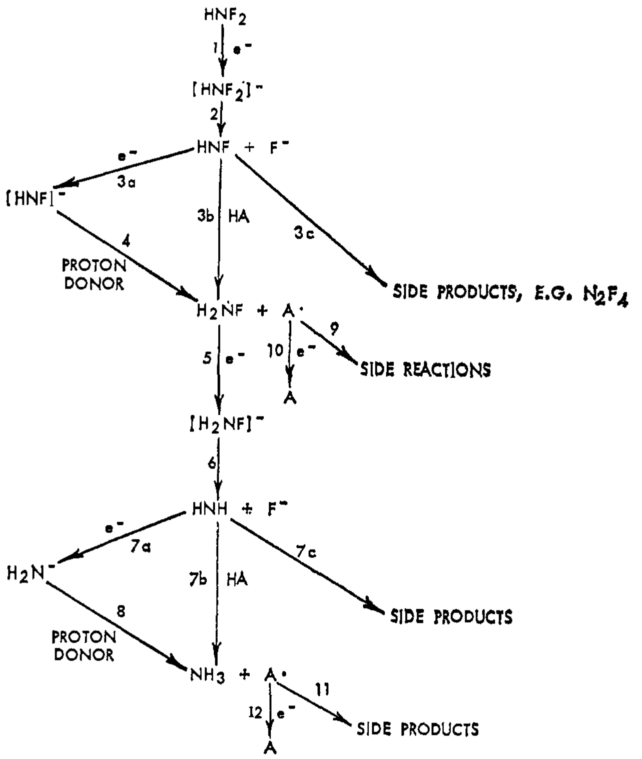


Figure 4. Possible pathways for the reduction for HNF_2.

that of $HNF_2 \cdot CH_3CN$ over the range −56.6 to −1.2° was found to be 13.01 kcal mole^{-1}. The strength of association thus decreases in the order $HNF_2 \cdot DMF \sim HNF_2 \cdot DMSO > HNF_2 \cdot CH_3CN > HNF_2 \cdot CH_3OH > HNF_2 \cdot H_2O$. This order of strength of association is in agreement with observed solubility of HNF_2 in these solvents.

The infrared spectra of various solvated HNF_2 species were investigated in the liquid and solid states (Table IV). The N–H stretching frequency in the complexes of HNF_2 with CH_3CN, DMF, DMSO, and CH_3OH appears at approximately the same location, while that of $HNF_2 \cdot H_2O$ is considerably higher. The assignment of the N–H stretch in $HNF_2 \cdot H_2O$ to either 2800 or 2975 cm^{-1} is not possible. At these locations, the spectrum shows two strong bands which could be caused by both a shift in the N–H stretching frequency of HNF_2 and a change in an O–H vibration of the water.

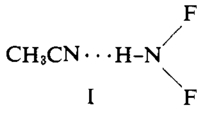
Table IV. Infrared Absorption Maxima of HNF_2 Complexes

Complex	N–H stretch	N–H asym bend	N–H sym bend	N–F sym stretch	N–F asym stretch
HNF_2 (solid)[a]	3110	1450	1350	972	880
$H_2O \cdot HNF_2$ (solid)[a]	2800 2975	1390	1320	973	875
$CH_3CN \cdot HNF_2$ (solid)[a]	2710	1424	*c*	960	860
1 *M* HNF_2 in CH_3OH (liquid)[b]	2725	*c*	1325[c]	955	855
$DMF \cdot HNF_2$ (solid)[a]	2725	*c*	*c*	952	850
1 *M* HNF_2 in DMSO (liquid)[b]	2740	*c*	*c*	*c*	855

[a] At −160°. [b] At 25°. [c] Solvent interference.

Difluoramine appears to be more strongly hydrogen bonded to the nonaqueous solvents than to water. The N–F vibrations are less strongly affected by solvation but do indicate that the degree to which the fluorines are involved in intermolecular bonding increases in the order $HNF_2 \cdot H_2O < HNF_2 \cdot CH_2CN < HNF_2 \cdot CH_3OH < HNF_2 \cdot DMSO < HNF_2 \cdot DMF$.

Spectra of 1 *M* solutions of HNF_2 in DMF and acetonitrile were also obtained but were of value only for the N–F vibrations. Dilution of the solutions with CCl_4 or $CHCl_3$ did not improve the spectra. The N–F stretching frequencies occurred at approximately the same location as in the respective solid-state spectra. Attempts to balance out the solvent bands with reference cells to enhance the N–H frequency were unsuccessful. The addition of 1 *M* amounts of $LiClO_4$, $KClO_4$, $HClO_4$, H_2O, and $(C_2H_5)_4NClO_4$ to these solutions had no effect on the N–F bands. Little or no interaction appears to occur between HNF_2 and these supporting electrolytes. The HNF_2 is probably bonded to these solvents in structures of type I. However, it appears that contributions of bonding with the fluorines cannot be neglected, *e.g.*, structure II.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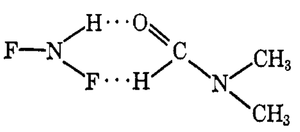
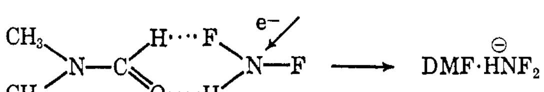

II

The addition of an electron to the nitrogen of solvated HNF_2 should be more difficult than in less solvated systems if solvation causes a greater charge separation between the hydrogen and the nitrogen. Thus, solvation of HNF_2 as species such as I and II will cause a decrease in the ease with which reduction will occur. The initial reduction step may be exemplified as


III

The strength of solvation of the fluoride ion also plays an important role in determining the reduction potential. The ease of decomposition of the intermediate species III to yield a fluoride ion also depends on the solvation of that ion. Since the solvation of F^- by water is greater than by the nonaqueous solvents, the effects of solvation of the HNF_2 and the F^- are complementary and are in agreement with the corresponding shifts in reduction potential with changes in solvent in going from water to nonaqueous solvents.

Conclusions

Based on the experimental results presented above, a general picture of the mechanism of the electrolytic reduction of HNF_2 in nonaqueous solvents is schematically represented in Figure 4.

The initial step in the mechanism is addition of an electron to HNF_2, as in step 1, followed by (or perhaps occurring practically simultaneously with) loss of a fluoride ion as in step 2.

The HNF radical can then undergo several reactions, including further reduction, as in 3a; abstraction of a hydrogen atom from an available proton donor, as in 3b; or combination with a like radical to give side products, such as in 3c. Reaction 3c seems relatively unimportant since product analyses of macroscale electrolyses in all systems have shown that almost all of the fluorine present occurs as F^- and most of the nitrogen occurs as NH_3. Both reactions 3a and 3b are likely to predominate, with the relative amounts of the products formed depending on the nature of the solvent and electrolyte. The formation of negatively charged species, such as HNF_2^-, HNF^-, and H_2NF^-, in various steps of the reaction, accounts for the repulsion effect observed in $LiClO_4$ solutions in acetonitrile and DMSO. The radical anion extracts a proton from the solvent, or from an added proton donor, to produce H_2NF, the same product as in 3b. Further reduction of H_2NF must occur at a potential no more cathodic than that of the reduction of HNF_2, since NH_3 is the final product of the reaction.

The predominant reaction path in aqueous and alcoholic solvents, which provide a ready source of protons, is most likely the one in which the steps 1, 2, 3a, 4, 5, 6, 7a, and 8 are involved. In the aprotic systems studied, pathways involving 3b, 3c, 7b, 7c, 9, 10, 11, and 12 are more important and lead to reaction with the solvent and high current efficiencies.

The reason the four-electron reduction is observed only in the presence of $(C_2H_5)_4NClO_4$ in polarographic work may be explained with a theory which has evolved from numerous studies of the polarographic reduction of negatively charged species such as $S_2O_8^{2-}$, $PtCl_4^{2-}$, $PtCl_6^{2-}$, $IrCl_6^{2-}$, $RhCl_6^{3-}$, and $Fe(CN)_6^{3-}$. This work has recently been reviewed in detail by Parsons.[6] In the reduction of such species, a dip is observed on the plateau of the polarographic wave. The current in the region of this dip is not diffusion controlled and is greatly affected by the nature and concentration of the supporting electrolyte.

While the dip is usually not amenable to quantitative treatment, it is well understood qualitatively. The dip is due to repulsion of the negatively charged, reducible species by the electrode, which becomes increasingly negative with respect to the solution surrounding it as the voltage scan proceeds to more cathodic values. The potential at which this effect occurs and the depth of the dip are affected by the nature and concentration of the supporting electrolyte. For example, the dip in the wave for the reduction of $S_2O_8^{2-}$ becomes less pronounced as the supporting electrolyte cation used is changed to one of increasing atomic weight in the series Li^+, Na^+, K^+, Rb^+, Cs^+.[7] In addition, the size of the dip for $S_2O_8^{2-}$ has been shown to be reduced by the addition of specifically adsorbed cations to the system[8] and increased by specifically adsorbed anions.[9]

HNF_2, of course, is not initially a negatively charged species. In the first steps of the reduction, however, a radical-anion intermediate appears to be produced. In systems of high proton availability, this species is rapidly protonated, and the neutral species thus formed is further reduced, finally resulting in the formation of NH_3. In systems of low proton availability, the anion radical has a lifetime sufficient for it to be repelled by the negative charge on the electrode since protonation is slow. Thus, the reduction is no longer diffusion controlled. The effect of adding proton donors is explained by the fact that these species increase the rate of protonation.

The effect of the change in alkali metal cation of the supporting electrolyte is similar to that discussed above for $S_2O_8^{2-}$, in which a variation of the effectiveness of these cations in producing a negative maximum is observed.

When the tetraalkylammonium ion is used, the supporting electrolyte cation is specifically adsorbed on the electrode surface and decreases the effective negative charge on the electrode. This decrease eliminates the repulsion of the negatively charged reaction intermediates and prevents the occurrence of a dip in the current–potential curve.

Since the reaction with which we are concerned is a complicated one, with a number of possible reactive intermediates which may interact at the electrode surface, the explanation for the various effects given above can only be qualitative. It does, however, account for most of the observed phenomena, including the effect of supporting electrolyte, protonic and aprotic solvents, and added proton donors, and is thus useful.

Experimental Section

Chemicals. Difluoramine was prepared by hydrolysis of trityldifluoramine,[10] and stock solutions were prepared by dissolving sufficient HNF_2 in deaerated, freshly purified solvent. This stock solution was stored in glass under nitrogen and standardized immediately prior to use by reacting an aliquot with excess KI in 0.1 M H_2SO_4 and titrating the liberated iodine with standard sodium thiosulfate solution. Acetonitrile was purified by distillation from P_2O_5. Other solvents were reagent grade materials and were purified by passing them through a Linde Molecular Sieve 5A column prior to use.

$LiClO_4$, $NaClO_4$, and $KClO_4$ were standard anhydrous reagent grade materials. $(C_2H_5)_4NClO_4$ was prepared by the procedure of Kolthoff and Coetzee.[11]

Polarographic Apparatus. The instrument used in all polarographic work was a modular instrument based on operational amplifier circuitry as described by DeFord.[12] Polarograms were recorded with either a Mosely Autograph X-Y recorder or a Sargent multirange recorder, Catalog No. S-72150.

The cell used was a standard polarographic H-cell, which was immersed in a constant-temperature water bath. A three-electrode system was used, with the dme mounted between the reference and auxiliary electrodes to minimize voltage drop effects. The reference electrode was a Beckman No. 1170 fiber-type, saturated calomel electrode. The auxiliary electrode was 1.0 cm² of platinum foil welded to a platinum contact wire sealed in glass.

Macroscale Electrolysis Apparatus and Procedure. The instrument used in all macroscale, controlled potential electrolyses was an Anatrol Model 4100 research controller. The HNF_2 solution (100 ml) to be reduced was transferred, under a nitrogen blanket,

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(6) R. Parsons, *Advan. Electrochem Electrochem. Eng.*, **1**, 1 (1961).

(7) A. N. Frumkin and N. V. Nikolaeva-Fedorovich, *Vestn. Mosk. Univ.*, 169 (1957).

(8) N. V. Nikolaeva-Fedorovich and L. A. Fokiva, *Dokl. Akad. Nauk SSSR*, **118**, 987 (1958).

(9) T. V. Kolish and A. N. Frumkin, *Zh. Fiz. Khim.*, **28**, 473 (1954).

(10) W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963).

(11) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870 (1957).

(12) D. D. DeFord, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 1958.

to a 150-ml titration flask which was to serve as the cathode compartment of the electrolysis cell. Mercury was added to a depth of *ca.* 0.5 in. (surface area, 17 cm^2), a magnetic stirrer bar was added, and a Teflon cap was placed on the cell. The cap was fitted with a nitrogen inlet and outlet, a saturated calomel reference electrode, a cathode connection, and a 30-ml alundum cup which was positioned in the center of the cell, its bottom ~1 in. from the mercury. The alundum cup served as the anode compartment. The cell was made airtight. A few milliliters of electrolyte solution were added to the anode compartment and a platinum gauze anode inserted. The appropriate electrical connections were made to the Anatrol potential controller.

The current-voltage relationship of the system was determined by increasing the electrode potential in steps and recording the current. The cathode solution was magnetically stirred during these measurements. The cell was immersed in an ice bath, the magnetic stirrer was started, nitrogen was passed over the cathode solution, and the controlled potential electrolysis was carried out at an appropriate voltage.

During the electrolysis, the cathode compartment was continuously swept with N_2, and the sweepings were passed into a conventional glass, high-vacuum system and condensed in liquid nitrogen. These sweepings were then fractionated by low-temperature distillation *via* −78, −126, and −196° baths. The various fractions and the cathode solution were analyzed for NH_3, HNF_2, and F^- as required.

Formation and Decomposition of Complexes. All work was carried out in a conventional glass, high-vacuum system. Equimolar quantities (~3 mmoles) of HNF_2 and the solvent to be studied were measured separately and condensed together in a cold finger at −126°. The reagents were further mixed by allowing them to warm to room temperature and recooling to −126°. The dissociation pressures of the complexes were measured as they were allowed to warm slowly from −96 to 0°. Three or four points were taken on cooling the mixtures back to −96° at the end of each experiment to determine if the dissociation was completely reversible. Temperatures were measured to ±0.1° with an iron-constantan thermocouple, and pressures were read to ±0.2 mm. Equations were obtained through simple regression analysis of the data on a Bendix G-15 computer.

$HNF_2 + H_2O$. Some association of HNF_2 with H_2O was observed below −23°, but a true equilibrium expression was not obtainable.

$HNF_2 \cdot CH_3OH$. This complex exerts little or no measurable vapor pressure up to −55°. The reversible dissociation over the range −47.7 to 0.0° is described by the equation $\ln Kp = (-4143.2/T) + 23.22$, where $Kp = P^2/4$; $\Delta H = 8.24$ kcal mole^{-1}.

$HNF_2 \cdot CH_3CN$. This complex exerts little or no measurable vapor pressure up to −62°. The reversible dissociation over the range −56.6 to −1.2° is described by the equation $\ln Kp = (-6538.2/T) + 31.461$; $\Delta H = 13.01$ kcal mole^{-1}.

$HNF_2 + (CH_3)_2SO$ and $HNF_2 + (CH_3)_2NC(H)O$. These mixtures exerted little vapor pressure up to 0°. No equilibrium expressions were obtained: vapor pressure of $HNF_2 \cdot DMF$ at 0°, 5.0 mm; of $HNF_2 . DMSO$ at 0°, 5 mm.

Infrared Spectra. Spectra of the solvation complexes in the solid state at −196° were obtained by techniques similar to those described earlier.[13] The 1 *M* HNF_2 solutions were examined in conventional liquid cells. The spectra were obtained with a Perkin-Elmer Model 137 spectrometer.

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Trifluoromethylarsinophosphinoamines[1]

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Abstract: The new-type compounds $(CF_3)_2As(NH)P(CF_3)_2$ (mp −44°, bp estd 110°) and $(CF_3)_2As(NCH_3)P(CF_3)_2$ (mp −30°, bp estd 127°) are easily cleaved by HCl or NH_3, in contrast to the analogous P–N–P compounds. The point of cleavage is the As–N bond, which lacks π stabilization. BCl_3 is less effective than HCl for As–N–P cleavage and BF_3 still less; however, $[(CF_3)_2As]_2NH$ is more easily attacked than the As–N–P compounds. The novel compound $(CF_3)_2AsN[P(CF_3)_2]_2$ (mp 26°, bp estd 161°) also is cleaved at the As–N bond by HCl or NH_3, to form the well-stabilized $HN[P(CF_3)_2]_2$. The iminobisarsine $[(CF_3)_2As]_2NH$ with $(CF_3)_2PCl$ and $(CH_3)_3N$ catalyst exchanges groups to make $(CF_3)_2As(NH)P(CF_3)_2$ and finally $HN[P(CF_3)_2]_2$. The cacodyl oxide $[(CF_3)_2As]_2O$ with excess $(CF_3)_2PCl$ goes to $(CF_3)_2AsCl$ and $[(CF_3)_2P]_2O$ or with less $(CF_3)_2PCl$, to $[(CF_3)_2As]_2$ and oxidized phosphorus compounds; the unstable $(CF_3)_2AsOP(CF_3)_2$ probably is an intermediate in both cases. Accurate infrared spectra are reported for the three new arsinophosphinoamines.

Compounds containing the As–N–P chain should offer good opportunities for direct comparison of the π-acceptor strength of As_{4d} *vs.* P_{3d} orbitals, especially if fluorocarbon groups are placed on As and P to enhance their π-acceptor character. Accordingly, we have made the new arsinaminophosphines $(CF_3)_2As(NH)P(CF_3)_2$ and $(CF_3)_2As(NCH_3)P(CF_3)_2$ for a comparison of their chemical behavior with the previously known analogous As–N–As and P–N–P compounds. The syntheses were accomplished in a quantitative manner, by the established method whereby trimethylamine removes HCl from the appropriate mixture of reactants.[2,3] For the tertiary amine $(CF_3)_2AsN[P(CF_3)_2]_2$, however, it was necessary to employ the sodium salt $NaN[P(CF_3)_2]_2$ with $(CF_3)_2AsCl$—a process like that used for $N[P(CF_3)_2]_3$.[3] Attempts to make an As_2NP or As_3N compound did not succeed: like the phosphorus case, the As_2NH compound failed to react with $(CF_3)_2AsCl$ even in the presence of $(CH_3)_3N$; and attempts to make the sodium salt $NaN[As(CF_3)_2]_2$ failed for lack of protic acid character in the As_2N–H

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