

Anal. Calcd. for $C_{28}H_{40}N_6S_4Pt$: C, 39.4; H, 5.4; N, 11.4; Pt, 26.5. Found: C, 39.1; H, 5.5; N, 11.3; Pt, 27.1.

Tetraethylammonium Bis(1,2-dicyanoethylene-1,2-dithiolato)-metal(III) Chelates.—The oxidized forms of the nickel, palladium, and platinum chelates were prepared by iodine oxidation of

the reduced forms essentially according to the directions previously described.³

Acknowledgments.—We wish to thank Drs. D. R. Eaton, C. J. Fritchie, Jr., M. Thomas Jones, and R. G. Kepler for helpful discussions.

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The Electrochemistry of Inorganic Difluoramino Compounds. I. The Mechanism of the Electrochemical Oxidation of Difluoramine and the Use of this Reaction in the Synthesis of Alkyl Difluoramines

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The mechanism of the anodic oxidation of difluoramine on platinum electrodes has been studied using the techniques of cyclic voltammetry, coulometry, and chronopotentiometry. The reaction has been shown to be pH dependent, irreversible, kinetically controlled, and strongly dependent on the oxidation state of the electrode. The primary product of the electron transfer, which involves the loss of one electron per difluoramine molecule, is the difluoramino radical, $\cdot NF_2$. If no other radicals are present at the electrode surface, the difluoramino radicals rapidly combine to form tetrafluorohydrazine. In the presence of simultaneously generated alkyl radicals, however, the difluoramino radicals have been shown to react to form alkyl difluoramines according to the reaction $R\cdot + \cdot NF_2 \rightarrow RNF_2$. In this manner, CH_3NF_2 , $CH_3CH_2NF_2$, and CD_3NF_2 have been prepared.

The chemistry of the $-NF_2$ group is of considerable current interest, and several comprehensive reviews of the chemistry of difluoramino compounds have recently appeared.¹⁻³ To date, however, no investigation of the electrochemistry of these compounds has been reported.

As part of an integrated study of the electronic configuration and behavior of the difluoramino group,⁴ we are currently investigating the electrochemical reactions of the inorganic difluoramino compounds. The present paper describes a study of the anodic oxidation of difluoramine and the use of this reaction in the synthesis of alkyl difluoramino compounds.

Results and Discussion

Mechanism of the Anodic Oxidation of Difluoramine.

—The anodic cyclic voltammetry of HNF_2 was studied over the pH range 0.7 to 10.3 in aqueous buffer systems, using a planar platinum electrode. In acidic systems ($pH \leq 6.85$), HNF_2 was found to undergo an irreversible oxidation which takes place at a potential dependent on the pH of the system. In basic systems the HNF_2 was converted to N_2F_2 , and no oxidation waves were observed over the voltage range 0 to ± 1.2 v. vs. s.c.e.

Typical cyclic voltammetric scans are shown in Fig. 1 and 2 for the oxidation of HNF_2 in 0.2 M $HClO_4$ and a 1.0 M acetic acid–sodium acetate buffer of pH 4.8, respectively. Accurate measurement of the peak potential of the wave (E_p) is not possible owing to the shape of the current–voltage curve for these irreversible oxidations. The variation of the half-peak potential ($E_{p/2}$), however, which may be more accurately estimated, clearly shows the position of the waves on the voltage axis to be pH dependent. In addition, although $E_{p/2}$ varies from +0.61 v. in the $HClO_4$ system (pH 0.7) to 0.37 v. in the acetic acid system, the height

of the diffusion current wave (i_p) is the same in both cases, within experimental error, suggesting that there is no change in the number of electrons involved in the oxidation, or in the electroactive species, over this pH range. The variation of i_p with the square root of the voltage scan rate ($V^{1/2}$) and the concentration of HNF_2 (C_{HNF_2}) in the bulk of the electrolysis solution was studied in both systems and, as shown in Fig. 3 and 4, plots of i_p vs. $V^{1/2}$ and i_p vs. C_{HNF_2} were found to be linear over the limited range studied. Thus the oxidation appears to be diffusion controlled under these conditions.

The over-all irreversibility of the oxidation is suggested by several observations. First, the current–voltage curve of the anodic scan in cyclic voltammetry has a drawn-out shape rather than the sharp peak normally exhibited by a reversible electrode reaction. Second, in a reversible oxidation, the product of the electrode reaction should give a cathodic reduction peak on the reverse sweep of the cyclic scan, at a potential near that at which the oxidation takes place. For a completely reversible process, the difference between the anodic and cathodic peak potentials should be $0.056/n$ v., in which n is the number of electrons involved in the oxidation. For irreversible processes, the difference between cathodic and anodic peaks is larger. Since no cathodic peak is observed for HNF_2 , at least within 0.5 v. of the oxidation peak, the over-all reaction at the electrode surface appears to be irreversible. Finally, in current reversal chronopotentiometric studies of the reaction, no transition time for reduction of the product of the oxidation of HNF_2 was observed when the polarity of the current was reversed at the transition time for the oxidation process. This over-all irreversibility, however, may be due to an irreversible chemical reaction in which the product of the primary electrolysis reaction is rapidly converted to a nonelectroactive species, as well as to an irreversible electrode reaction.

Controlled potential microcoulometric determinations showed that one electron per HNF_2 molecule is involved in the electrode reaction.

(1) C. J. Hoffman and R. G. Neville, *Chem. Rev.*, **62**, 1 (1962).

(2) A. V. Pankratov, *Usp. Khim.*, **32**, 336 (1963).

(3) C. B. Colburn in "Advances in Fluorine Chemistry," Vol. 3, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworths, Washington, D. C., 1962.

(4) Hercules Powder Company, Quarterly Reports No. 1–3, June 15, 1963, Sept. 15, 1963, and Dec. 15, 1963; A.R.P.A. Contract No. DA-31-124-ARO(D)-62.

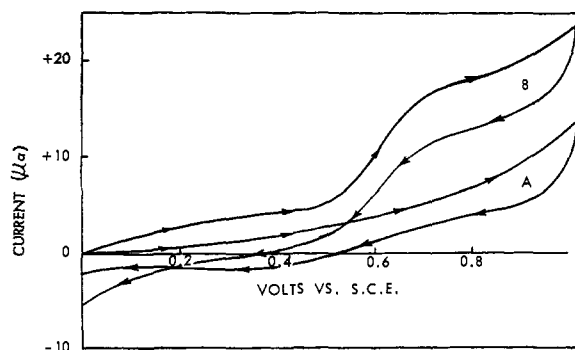


Fig. 1.—Oxidation of HNF_2 in 0.2 M HClO_4 : curve A = blank; curve B = 0.0063 M HNF_2 (arrows indicate direction of potential scan); scan rate = 100 mv./sec.

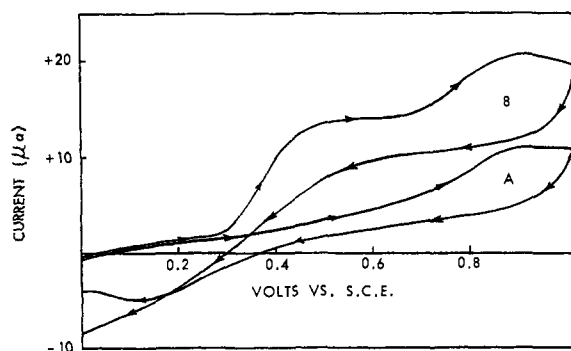


Fig. 2.—Oxidation of HNF_2 in $1.0\text{ M acetic acid} + 1.0\text{ M sodium acetate}$: curve A = blank; curve B = 0.0063 M HNF_2 (arrows indicate direction of potential scan); scan rate = 100 mv./sec.

A macroscale electrolysis of HNF_2 was run using a smooth platinum electrode as the anode. The anode products were continuously swept from the anode compartment, trapped, and analyzed. The principal anodic product was N_2F_4 .

To extend the study of the mechanism of the electrochemical oxidation of HNF_2 , the chronopotentiometry of HNF_2 in acidic aqueous systems was studied and, in the course of this work, the oxidation reaction was observed to be affected by the condition of the surface of the platinum electrode at which the oxidation is carried out. For easier interpretation of these results, it may be profitable to consider first the structure of the platinum electrode surface.

The exact chemical nature of the surface of a platinum electrode has a significant effect on the reversibility of many electrode reactions⁵ and has been studied by numerous authors whose work has recently been reviewed⁶ by Young. By means of a thorough chemical and electrochemical study of platinum electrode surfaces, Feldberg and co-workers⁵ have established the existence of three discrete states of the electrode: (a) the oxidized state, designated by the symbol $\text{Pt}(\text{O})_x$; (b) a half-reduced state, represented by $\text{Pt}(\text{OH})_x$; and (c) the reduced or "clean" state, represented by Pt. The $\text{Pt}(\text{O})_x$ state, in which x is not necessarily an integer and (O) refers merely to chemisorbed oxygen atoms on the electrode surface, may be produced by strong chemical or electrochemical oxidation of the electrode. The Pt state is produced by thorough reduction—chemical or electrochemical—

(5) S. W. Feldberg, C. G. Enke, and C. E. Bricker, *J. Electrochem. Soc.*, **110**, 826 (1963), and references therein.

(6) L. Young, "Anodic Oxide Films," Academic Press, London, 1961.

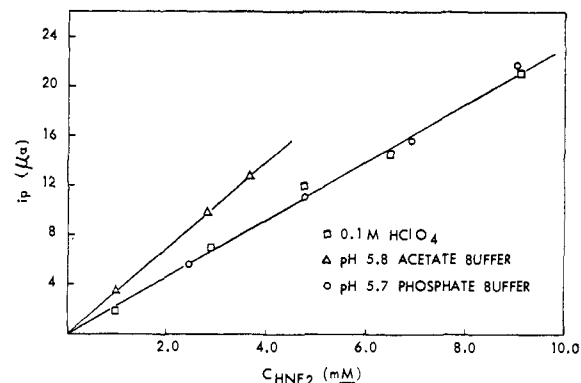


Fig. 3.—Variation of peak current (i_p) with HNF_2 concentration (C_{HNF_2}) (slope variation due to use of different electrode areas).

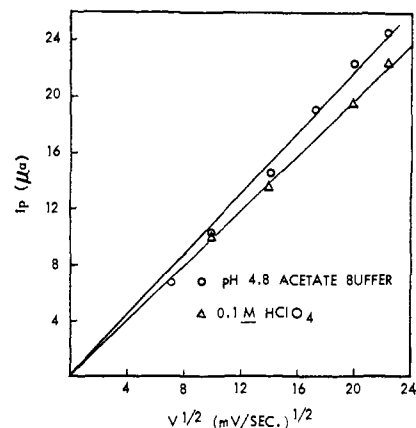


Fig. 4.—Variation of peak current (i_p) with voltage scan rate (V).

of all the surface oxides on a platinum electrode. The $\text{Pt}(\text{OH})_x$ state, in which OH represents chemisorbed hydroxyl groups rather than a discrete platinum hydroxide species, is produced by strong oxidation and subsequent reduction of the electrode. It may be formed, for example, by repeated cycling of the electrode potential in a strong acid (1 N HClO_4 or H_2SO_4) from a potential at which the $\text{Pt}(\text{O})_x$ state is formed to one at which it is reduced. The half-reduced state is often referred to as an "active" state since several authors have shown that it increases the rate of electron transfer in some oxidation-reduction reactions. Examples are the reduction of IO_3^- ,⁷ O_2 ,⁸ and vanadium.⁹

One effect of the nature of the platinum electrode surface on the oxidation of HNF_2 in an electrolyte system of 0.1 M NaClO_4 and 0.02 M HClO_4 in water is shown in Fig. 5. Curve 1 in this figure was obtained prior to the addition of HNF_2 to the solution and shows no oxidation waves in the potential region in which HNF_2 is oxidized. Curve 2 was obtained after the solution was made 0.0038 M in HNF_2 . The quarter-wave potential ($E_{1/4}$) observed for HNF_2 in this run ($+0.64\text{ v. vs. s.c.e.}$) agrees well with the value expected from the results of cyclic voltammetric studies of HNF_2 in similar systems ($E_{p/2} = +0.61\text{ v. in } 0.2\text{ M HClO}_4$).

When the potential of the platinum electrode reached $+1.25\text{ v.}$ in run 2, the applied current was shut off,

(7) F. C. Anson, *J. Am. Chem. Soc.*, **81**, 1557 (1959).

(8) J. J. Lingane, *J. Electroanal. Chem.*, **2**, 296 (1961).

(9) C. W. Oatley, *Proc. Phys. Soc. (London)*, **51**, 318 (1939).

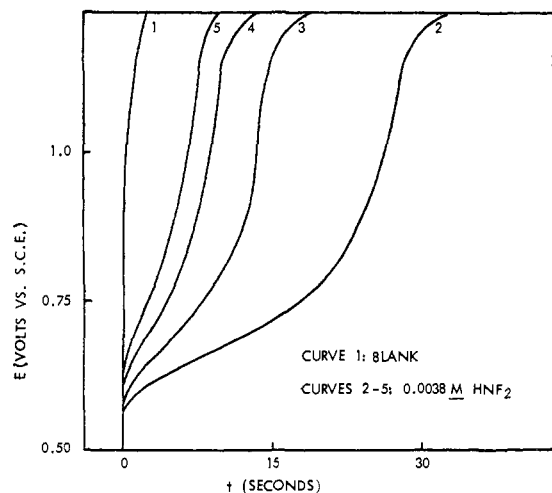


Fig. 5.—Chronopotentiometry of HNF_2 : electrolyte, $0.1 M \text{NaClO}_4 + 0.02 M \text{HClO}_4$; electrode, platinum, 2.07 cm^2 ; applied current, 0.2 ma .

and the electrode was left on open circuit while the solution was stirred for 60 sec. After being stirred, the solution was allowed to stand at rest for 60 sec., and curve 3 was run. This procedure was repeated for curves 4 and 5. The transition time for HNF_2 obtained in this manner decreased in each succeeding run. In addition, although the potential of the electrode on open circuit drifted slowly to a more cathodic value, the start potential for each run became progressively more anodic. As additional runs were made, the transition time decreased until eventually no HNF_2 oxidation was observed at all.

If the solution was allowed to stand for 90 min. between runs, the potential of the electrode on open circuit drifted to the initial value for run 2, and the original potential-time curve (curve 2, Fig. 5) was reproduced exactly. When the current polarity was reversed at the end of each anodic chronopotentiogram, and a reducing current was passed through the electrode until the electrode potential was returned momentarily to $0.0 \text{ v. vs. s.c.e.}$, the anodic chronopotentiograms were accurately reproduced.

These data show that the oxidation of HNF_2 on platinum electrodes is inhibited by the presence of an oxide film on the platinum surface. In a series of anodic chronopotentiograms such as shown in Fig. 5, the oxide layer gradually builds up and increases the inhibition of the HNF_2 oxidation, if the electrode is not re-reduced between runs. When the electrode is re-reduced momentarily to a potential of $0.0 \text{ v. vs. s.c.e.}$ after each run, the oxide film is reduced, and an active platinum surface is available for the next chronopotentiogram. No HNF_2 wave is observed when an active platinum electrode, produced by reduction to 0.0 v. , is preanodized for 60 sec. with a 1.2-ma. current before an HNF_2 chronopotentiogram is run under the conditions used in curve 2, Fig. 5.

The inhibition of an electrode reaction by oxidation of the electrode appears to be a common phenomenon and has been observed for the electrooxidation of oxalic acid,¹⁰ iodine,¹¹ hydrogen peroxide,¹² arsenic(III),¹³ thiocyanate,¹⁰ nitrite,¹⁰ (ethylenedinitrilo)-

(10) F. C. Anson and F. A. Schultz, *Anal. Chem.*, **35**, 1114 (1963).

(11) F. C. Anson and J. J. Lingane, *J. Am. Chem. Soc.*, **79**, 1015 (1957).

(12) J. Giner, *Z. Elektrochem.*, **64**, 491 (1960).

(13) D. Davis, *Talanta*, **3**, 335 (1960).

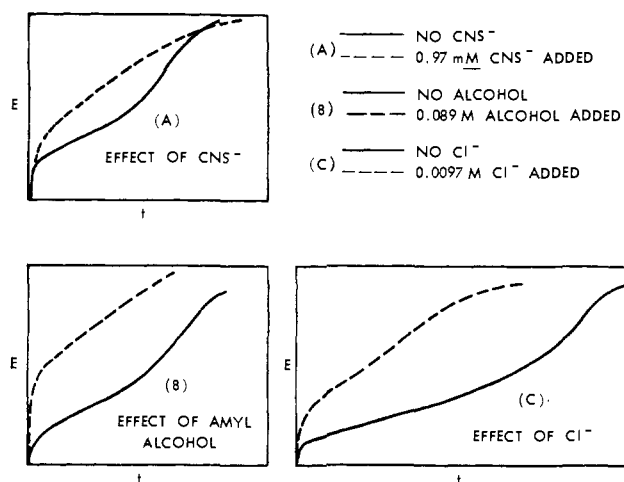


Fig. 6.—Effect of surface-active substances on the chronopotentiometry of HNF_2 (all solutions contain $0.1 N \text{NaClO}_4 + 0.02 N \text{HClO}_4 + 2.16 \text{ mM} \text{HNF}_2$).

tetraacetocobalt(II),¹⁴ and methanol.¹⁵ For oxalic acid, the electrode reaction consists of two steps—adsorption of the oxalic acid on the platinum surface, followed by the electron-transfer step. The presence of an oxidized layer on the electrode apparently interferes with the adsorption step, causing the observed inhibition. Strongly adsorbed species such as Cl^- , CNS^- , and amyl alcohol, when added to the electrolysis solution, inhibit the HNF_2 reaction even on an active electrode. This is shown in Fig. 6 in which chronopotentiometric waves for HNF_2 are shown, before and after adding Cl^- , CNS^- , and amyl alcohol to the solutions. This effect appears to be due to blocking of the active surface by adsorbed species.

In addition, we have found that the HNF_2 oxidation is also inhibited by the clean (Pt) state. When the active surface on a platinum electrode is removed by HClO_4 , or by prolonged electrochemical reduction of the electrode, the same effect is observed as caused by a Pt(O)_x surface; that is, τ becomes shorter, and the wave is displaced toward more anodic potentials, as shown by the data in Fig. 7 and 8.

Figure 7 shows the effect of gradual removal of the active layer on the HNF_2 wave. Curve 1, Fig. 7, is a chronopotentiometric wave which was recorded after repeated cycling of the electrode potential between $+1.4$ and $0.0 \text{ v. vs. s.c.e.}$ in $0.05 M \text{HClO}_4 + 0.15 M \text{NaClO}_4$. After this run, the electrode was removed from the cell, rinsed in warm, concentrated HClO_4 for 30 sec., rinsed with distilled water, dried, and replaced in the electrolysis cell. Another wave, curve 2, was recorded, and the procedure was repeated for waves 3, 4, and 5. These data show that as the active layer is gradually removed by the HClO_4 , the HNF_2 oxidation is inhibited.

In Fig. 8, the effect of building up the active state on an originally clean electrode is shown. Curve 1 was run as a blank, with no HNF_2 present, on a clean platinum electrode. Curves 4 to 43 were run after the addition of HNF_2 to the solution, and the curve number corresponds to the number of anodic-cathodic cycles to which the electrode was subjected before the curve was recorded. In this experiment, a complete anodic-

(14) F. C. Anson, *J. Electrochem. Soc.*, **110**, 436 (1963).

(15) S. Gilman and M. W. Breiter, *ibid.*, **109**, 1099 (1962).

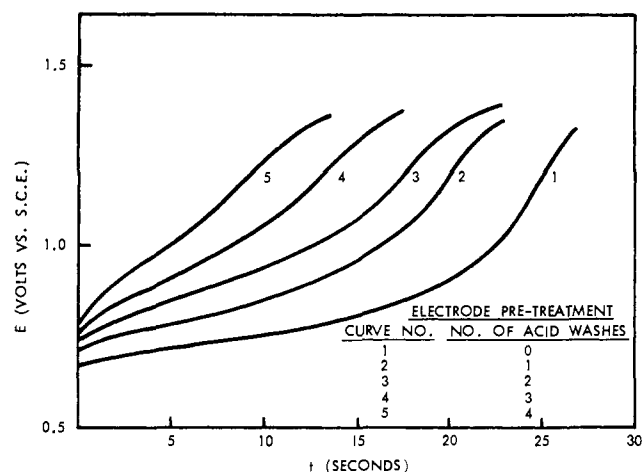


Fig. 7.—Effect of acid pretreatment of the electrode on the oxidation of HNF_2 : electrode, Pt, 1.53 cm^2 ; electrolyte, $0.05 \text{ M HClO}_4 + 0.150 \text{ M NaClO}_4 + 0.0044 \text{ M HNF}_2$ in H_2O ; applied current, 0.5 ma .

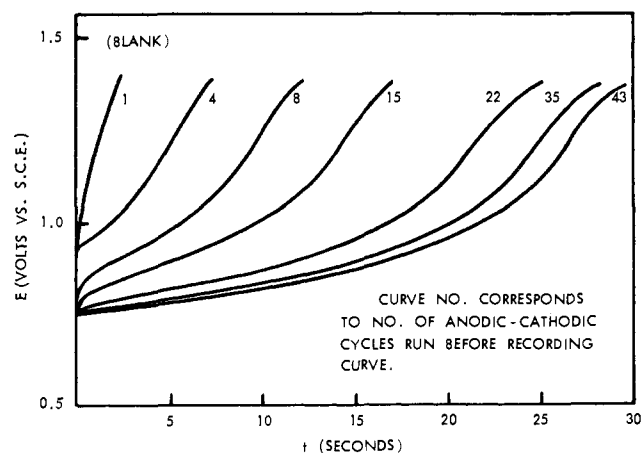


Fig. 8.—Effect of electrode activation on HNF_2 oxidation waves: electrode, Pt, 1.53 cm^2 ; electrolyte, $0.2 \text{ M HClO}_4 + 0.0044 \text{ M HNF}_2$; applied current, 0.5 ma .

cathodic cycle refers to a procedure in which an anodic current of 0.5 ma . was passed through the electrode in an unstirred solution (0.2 M HClO_4) until the potential of the electrode reached $+1.4 \text{ v. vs. s.c.e.}$ The current polarity was then reversed until the electrode potential momentarily reached $0.0 \text{ v. vs. s.c.e.}$ Finally, the current was shut off and the solution was stirred for 30 sec. and allowed to come to rest for 60 sec. before a chronopotentiometric run was made. These data show that as the active layer builds up, τ increases, the wave shifts to a less anodic potential, and the potential break becomes better defined.

In Fig. 9, the product of the current density (i_0) and the square root of the transition time is plotted as a function of N , the number of anodic-cathodic cycles which were used in pretreating the electrode in the experiment in which the curves in Fig. 8 were obtained. According to the well-known Sand equation,¹⁶ relating i_0 and τ to the concentration of electroactive species (C), number of electrons involved in the reaction (n), the Faraday constant (F), and the diffusion coefficient of the electroactive species (D), the product $i_0\tau^{1/2}$ should be a constant at constant C , as shown in eq. 1.

$$i_0\tau^{1/2} = \frac{nFD^{1/2}\pi^{1/2}C}{2} \quad (1)$$

(16) H. J. S. Sand, *Phil. Mag.*, **1**, 45 (1901).

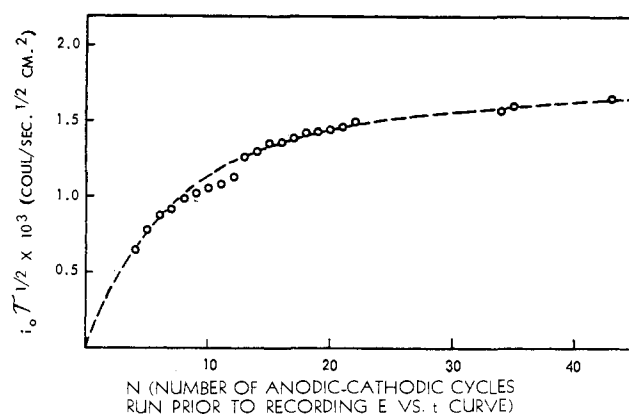
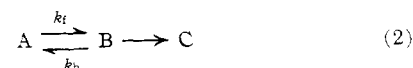


Fig. 9.—Effect of increasing electrode activation on the oxidation of HNF_2 : electrode, Pt, 1.53 cm^2 ; electrolyte, $0.2 \text{ M HClO}_4 + 0.0044 \text{ M HNF}_2$ in H_2O ; applied current, 0.5 ma .

The data in Fig. 9, however, show that $i_0\tau^{1/2}$ increases as the active surface is formed on the platinum electrode. The data in Fig. 5 to 9 strongly suggest that the active surface which catalyzes the HNF_2 oxidation corresponds to the $\text{Pt}(\text{OH})_2$ state defined by Feldberg and co-workers.⁵

To study the HNF_2 oxidation mechanism in more detail, the variation of the chronopotentiometric constant with the applied current and HNF_2 concentration was investigated on electrodes which had previously been activated by cycling between $+1.4$ and 0.0 v. in 0.2 M HClO_4 . On such electrodes, reproducible potential time curves could be obtained if the electrode was reduced to 0.0 v. after each chronopotentiometric run, which was carried to $+1.4 \text{ v.}$

According to eq. 1, the product $i_0\tau^{1/2}$ should remain constant as i_0 is varied, if C remains constant, for a diffusion-controlled electrode reaction. When the variation of $i_0\tau^{1/2}$ with i_0 was studied for HNF_2 under various conditions, however, $i_0\tau^{1/2}$ was found to decrease significantly as i_0 was increased. This result shows that adsorption of HNF_2 on the electrode surface prior to the electron-transfer reaction is obviously not a factor, or at least that any contribution from adsorption is smaller than effects which cause a decrease in $i_0\tau^{1/2}$.^{17,18} The data obtained under various conditions are shown in Fig. 10. This behavior corresponds to that expected for an electrode reaction in which the electron-transfer step is preceded by a chemical reaction, such as



in which A is a species which is not electroactive. The boundary value problem for this mechanism has been solved by Delahay and Berzins,¹⁹ and the resulting chronopotentiometric equation was

$$i_0\tau^{1/2} = \frac{\pi^{1/2}nFCD^{1/2}}{2} - \left(\frac{\pi^{1/2}}{2K(k_f + k_b)^{1/2}} \right) i_0 \quad (3)$$

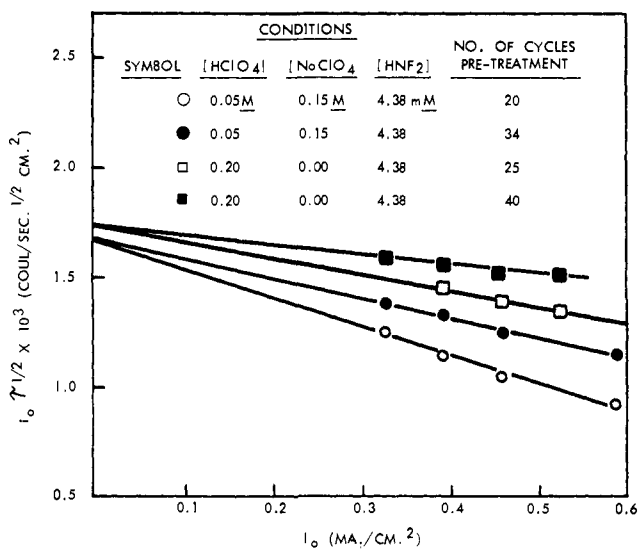
where $K = k_f/k_b$

The data in Fig. 10 are compatible with eq. 3, within the experimental error, and several general observations may be made from them. First, from the intercept of the plots at $i_0 = 0$ the value of D for HNF_2 in aqueous solutions may be estimated using eq. 3. As-

(17) H. A. Laitinen and L. M. Chambers, *Anal. Chem.*, **36**, 5 (1964).

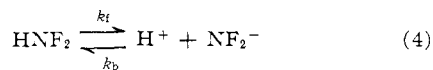
(18) A. J. Bard, *ibid.*, **35**, 340 (1963).

(19) P. Delahay and T. Berzins, *J. Am. Chem. Soc.*, **75**, 2486 (1953).

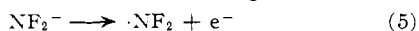
Fig. 10.—Variation of $i_0\tau^{1/2}$ with i_0 .

suming the geometrical area of the electrodes to be the true area, the value obtained was 2.1×10^{-6} cm.²/sec., with a standard deviation of 0.11×10^{-6} cm.²/sec. for a number of measurements under different conditions. The assumption that the geometrical area is equal to the true area may not be exactly correct for our electrodes which correspond to lightly platinized electrodes whose true surface area is larger than the geometrical area. Probably only a very small error is introduced into our calculations, however, because the effective "diffusional area" of an electrode does not increase with platinization as long as the surface roughness remains small compared with the diffusion layer thickness. Experimentally, Osteryoung, Lauer, and Anson²⁰ found the diffusional area of a platinum electrode to increase by only 17% in going from a clean surface to one so highly platinized that it appeared "quite black." In our work, no physical change of the electrode was detectable to the naked eye, so that the area increase can be expected to be quite small. Secondly, the quantity $K(k_f + k_b)^{1/2}$ appears to increase significantly, and thus the slope of the $i_0\tau^{1/2}$ vs. i_0 plot decreases as the acidity of the supporting electrolyte and the extent of activation increase. This phenomenon may account for our failure to observe a kinetic effect in cyclic voltammetric work, in which the electrode was inadvertently always maintained in a highly activated state.

On the basis of the experimental data presented above, a likely pre-electron-transfer step which could be postulated would be dissociation of the HNF₂ according to the equation



followed by oxidation of NF₂⁻ according to



and formation of N₂F₄ as in



This reaction scheme accounts for the observed pH dependence of the reaction, kinetic behavior, and products.

(20) R. A. Osteryoung, G. Lauer, and F. C. Anson, *J. Electrochem. Soc.*, **110**, 926 (1963).

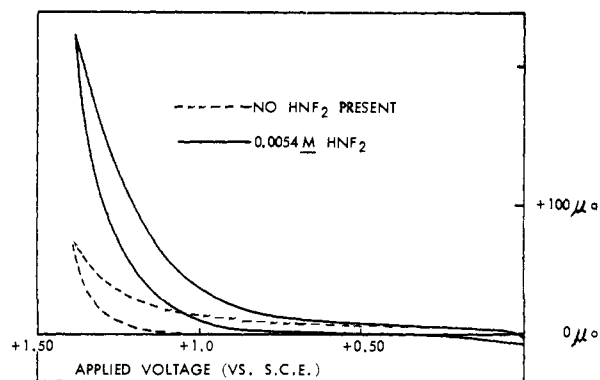


Fig. 11.—Cyclic voltammetry of HNF₂ in H₂O: supporting electrolyte, 0.1 M acetic acid + 0.1 M sodium acetate; electrode, graphite; area = 0.316 cm.².

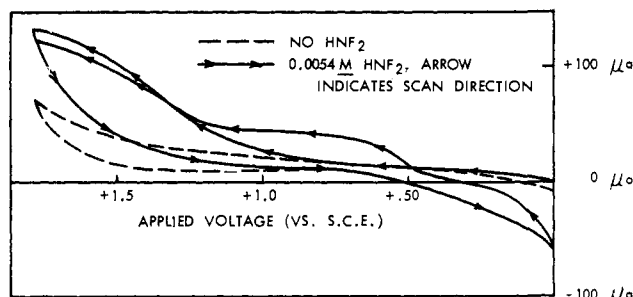


Fig. 12.—Cyclic voltammetry of HNF₂ in glacial acetic acid: supporting electrolyte, 0.5 M sodium acetate; electrode, platinum; area = 0.129 cm.².

Cyclic Voltammetry of HNF₂ in Nonaqueous Systems.

—In studying the cyclic voltammetry of HNF₂ in nonaqueous systems, both platinum and paraffin-treated, spectroscopic grade, graphite anodes were used. The latter are especially advantageous for electrochemical studies in nonaqueous solvents because of their low residual currents and convenient geometry.

In the present work, the electrodes were first compared in an aqueous acetate buffer containing HNF₂.

Typical current-voltage curves for this system are shown in Fig. 2 and 11. On the platinum electrode, a well-defined oxidation wave for HNF₂ is observed at $E_{p/2} = +0.37$ v. vs. s.c.e. On the graphite electrode, however, the oxidation of HNF₂ takes place at a much more anodic potential and no distinct wave is observed owing to the rise of the background current at the same potential as the HNF₂ wave. This potential shift again shows the important effect of the electrode surface on the characteristics of the electrode reaction in HNF₂ oxidations.

In glacial acetic acid, an interesting phenomenon is observed in the oxidation of HNF₂ on platinum, as shown in Fig. 12. In the first anodic scan on a clean electrode in a freshly stirred solution, the only oxidation wave observed, due to HNF₂, occurs at $E_{p/2}$ of about +1.30 v. On the second and succeeding scans, a wave is observed at $E_{p/2} = +0.53$ v. As the number of scans increases, the height of the wave increases until, after four or five scans, it reaches a height approximately one-third more than that on the second scan and does not increase in size on succeeding scans. If the electrode is returned to an applied potential of 0.0 v. and allowed to stand before another anodic scan is made, or if a series of successive cyclic scans

are run between 0.0 and +1.0 v., the +0.53-v. wave decreases in size. If the electrode potential is held at +1.8 v. and then returned to 0.0 v. and an anodic scan run immediately, the wave increases in size proportionately to the time the electrode was held at +1.8 v. Thus, it appears that this wave is due to the oxidation of some species formed as a result of the oxidation of HNF_2 at a more positive potential on the first scan. It is unlikely that the original electrolysis product (HNF_2^+ or $\cdot\text{NF}_2$) would be further oxidized at a more cathodic potential on succeeding scans. The wave at +0.5 v. is probably due to the oxidation of the product of a chemical reaction of the primary electrolysis product with the solvent, or with some other species produced during the electrolysis.

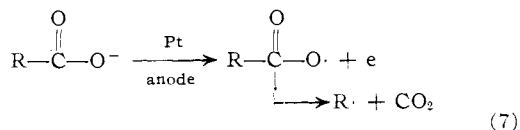
Results obtained with the graphite electrode in glacial acetic acid were similar to those obtained in water. No distinct wave was observed, but an increased current at potentials greater than +1.0 v. vs. s.c.e. indicates the presence of an oxidation reaction.

In a solvent system of 0.1 *M* acetic acid and 0.1 *M* sodium acetate in absolute methanol, no HNF_2 waves were observed on either platinum or graphite electrodes. On platinum, methanol gave a very large oxidation wave beginning at $\approx +0.1$ v. Small increases in the current at +1.0 v. were observed on the addition of HNF_2 . These increases appeared to be proportional to the HNF_2 concentration, but the large methanol current made further study of this system impracticable.

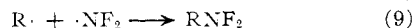
In ethanol containing 0.1 *M* acetic acid and 0.1 *M* sodium acetate, the oxidation of HNF_2 appears to be very similar to the aqueous system. On platinum, a well-defined HNF_2 wave is observed with $E_{p/2}$ at +0.30 v. On graphite no distinct wave is observed. However, the base current in the presence of HNF_2 , at potentials greater than +0.90 v., increases proportionately to the HNF_2 concentrations. Similar results are also obtained in acetonitrile.

Electrochemical Synthesis.—In the previous section, the proposed mechanism for the oxidation of HNF_2 at a platinum anode involved an intermediate difluoramino radical.

If this mechanism is correct, it should be possible to react the intermediate difluoramino radical with other compounds or radicals at or near the anode surface. The best known anodically generated free radical is the alkyl radical generated as an intermediate in the Kolbe reaction.



If the difluoramino radical and the alkyl radical were generated simultaneously, then reaction 6 as well as reactions 8 and 9 would be expected to occur. The



alkyl radical is formed at a more positive potential than is the $\cdot\text{NF}_2$ radical. As a result, the amounts of the products formed would be expected to vary with current density (or electrode potential) and concentration of HNF_2 and alkanoate ion. More N_2F_4 would be formed at low current densities and high HNF_2 concentrations.

To confirm that the electrolytically generated difluoramino radical could be used in synthesis, the reaction between methyl radical and difluoramino radical was carried out.

In a typical run, an aqueous solution 1 *M* in NaOAc , 1 *M* in HOAc , and 0.1 *M* in HNF_2 was electrolyzed at a smooth platinum anode at a current density of 0.2 amp./cm.². The gaseous electrolysis products were continuously swept from the cell during electrolysis, condensed in a liquid nitrogen trap, fractionated, and analyzed. Of the HNF_2 initially present, 60% was converted to CH_3NF_2 , 26% was converted to N_2F_4 , and 11% was recovered as HNF_2 . A large amount of ethane was also produced. During the electrolysis the potential of the anode remained between 2.7 and 2.9 v. vs. s.c.e.

The same reaction also occurred in glacial acetic acid. A glacial acetic acid solution 0.1 *M* in HNF_2 and 1 *M* in sodium acetate was electrolyzed at a current density of 0.03 amp./cm.². The gaseous product contained N_2F_4 , CH_3NF_2 , and ethane.

During these electrolyses, an appreciable amount of HNF_2 was swept from the cell before it could be oxidized. Electrolyses attempted in a closed system to minimize this difficulty resulted in explosions in the gaseous phase over the anode solution, so this approach was abandoned.

The reaction between the electrolytically generated alkyl and difluoramino radicals was investigated under a variety of conditions and the results are given in Table I. The yield and the amount of HNF_2 converted

TABLE I
ELECTROLYSIS RESULTS UNDER VARIOUS CONDITIONS^a

Run	Composition of electrolysis soln. (50 ml.)	Current, amp. (time, min.)	Conversion of HNF_2 to CH_3NF_2 , %	Yield, %
1	1 <i>M</i> NaOAc 1 <i>M</i> HOAc 0.1 <i>M</i> HNF_2	0.5 (120)	24	38
2	Same	1 (60)	36	45
3	Same	2 (30)	60	68
4	Same	2 (10)	40	67
5	1 <i>M</i> NaOAc 1 <i>M</i> HOAc 0.2 <i>M</i> HNF_2	1 (2 hr.)	28	37

^a The anode was smooth Pt, 10 cm.² (one side).

to CH_3NF_2 are shown to increase with current density. The best results obtained were in run 3 in which 60% of the HNF_2 present was converted to CH_3NF_2 . In this run, the current efficiency was about 10%, the remainder of the current being used to form a large amount of ethane and a small amount of N_2F_4 . The reason that the yield is significantly higher than the conversion is that some of the HNF_2 is swept from the cell before it can react. The side reaction responsible for the yield loss is the formation of N_2F_4 . The lower the current, the more N_2F_4 formed. In all of these runs, more than 97% of the HNF_2 used was accounted for as HNF_2 , CH_3NF_2 , or N_2F_4 . Currents higher than 2 amp. were impractical with the cell used because of heating problems.

The electrolytic preparation of CH_3NF_2 is a completely satisfactory laboratory synthesis, and numerous preparations have been made. In addition, analogous

reactions have been used to prepare $\text{CH}_3\text{CH}_2\text{NF}_2$ from propionic acid and CD_3NF_2 from CD_3COOD . Since the main objective of the synthetic work was to support the mechanism studies, no attempt has been made to define optimum conditions for the preparative electrolysis completely.

Experimental

Apparatus.—The instrument used in all experiments involving cyclic voltammetry, coulometry, or chronopotentiometry was a modular instrument based on operational amplifier circuitry as described by DeFord.²¹

For the recording of cyclic voltammetric current waves, a Moseley Autograf x - y recorder was used at voltage scan rates of 200 mv./sec. and less. At faster scan rates a Tektronix Model 502 oscilloscope was used.

In chronopotentiometric and coulometric experiments in which a time-base recorder was required, a Sargent-Multi-Range recorder, catalog No. S-72150, was used.

All voltammetric work was carried out in a water-jacketed electrolysis cell maintained at $25.0 \pm 0.1^\circ$.

Electrodes.—In all voltammetric work, a three-electrode system was used in order to eliminate any voltage drop caused by resistance between the indicator and reference electrodes.

The reference electrode was a Beckman No. 1170 fiber-type, saturated calomel reference electrode; the auxiliary electrode was a 1.0-cm.² platinum foil welded to a platinum contact wire sealed in glass.

Two types of indicator electrodes were used, a 2.07-cm.² platinum foil similar to the auxiliary electrode and a cylindrical platinum wire sealed in glass and coated with Apiezon wax everywhere except on the end, which was ground flat and polished. This electrode had a planar area of 0.049 cm.².

Chemicals.— HNF_2 was prepared by hydrolysis of trityldifluoramine, and stock solutions were prepared by dissolving sufficient HNF_2 in deaerated distilled water to prepare a 0.1 M solution. This stock solution was stored in glass under nitrogen and standardized immediately prior to use in all experiments by treating an aliquot with excess KI in 0.1 M H_2SO_4 and titrating the liberated iodine with standard sodium thiosulfate solution.

All other chemicals were reagent grade materials used without further purification.

Microcoulometric Determination of n .—The electrolysis cell used in microcoulometric experiments consisted of a polarographic H-cell in which the anode and cathode compartments were separated by a porous glass frit. The anode was a platinum foil, 1×8 cm., which was placed in one compartment of the cell, while the reference and auxiliary electrodes were placed in the other compartment. The anode solution was stirred with a glass-coated magnetic stirring bar in the anode compartment. The procedure used in a determination of n was as follows.

The cell, stirrer, and electrodes were assembled with the cell mounted in a constant-temperature water bath maintained at 25.0° . An aqueous solution (5 ml.) containing 0.1 M acetic acid and 0.1 M sodium acetate was placed in each side of the cell, the anode potential was set at $+0.8$ v. *vs.* s.c.e., and the cell current was recorded as a function of time until it decayed to a constant value (less than 1.0 $\mu\text{a.}$). Then an aliquot of an aqueous solution containing 0.1 M HNF_2 (2 or 3 drops) was added to the anode compartment and the anode current recorded as a function of time (Sargent recorder, 0.5 in./min. chart speed). The amount of the previously standardized HNF_2 solution used was determined by withdrawing the aliquot from the storage bottle in a hypodermic syringe, weighing the syringe and the solution to the nearest 0.1 mg., adding the sample to the cell, and reweighing the syringe.

When the cell current had decreased to approximately half its initial value, the experiment was stopped. The amount of HNF_2 consumed was calculated from the amount originally

added to the cell multiplied by the ratio of the final cell current to the original cell current. The quantity of electricity used was determined by measuring the area under the recorded current-time curve, and n was calculated from these values using the expression

$$n = \frac{(\text{coulombs of electricity used})}{(\text{moles of HNF}_2 \text{ consumed}) \times F} \quad (10)$$

where F is the faraday (96,484 coulombs).

Determination of Reaction Products.—The electrolysis cell used in this work consisted of a 300-ml. titration flask as the anode compartment and a medium porosity, flat-bottomed alundum cup (30-ml. capacity) inserted in the flask as the cathode compartment. The pores of the alundum cup, above the liquid level, were sealed with polyethylene resin. The anode consisted of a piece of platinum foil 10 cm.² in area (one side) formed into a cylinder around the cathode compartment. The cathode was a cylinder of silver gauze. The anode compartment was sealed from the atmosphere by a snug-fitting Teflon cap. The cap was fitted with an inlet and an outlet for sweeping out the gaseous electrolysis products and an electrical connection to the anode.

Electrolysis was carried out as follows. A solution was prepared approximately 0.1 M in HNF_2 and 0.5 M in NaClO_4 . A small amount of HClO_4 was added (final pH 2.3) to ensure that the solution was acid. Fifty milliliters of this solution was added to the anode compartment of the electrolysis cell. A few milliliters of 0.5% HClO_4 was added to the cathode compartment and the cell placed in an ice bath. A current of 0.6 amp. was passed through the cell for 2 hr. During this time, the anode compartment was continuously swept with a slow stream of nitrogen. The nitrogen stream was then passed through four liquid nitrogen traps where the electrolysis products were condensed. This condensate was fractionated by low-temperature vacuum distillation and the products identified and analyzed by infrared and mass spectrometry.

The yield of N_2F_4 obtained was about 70%. Small amounts of NO and N_2O were found, probably from hydrolysis of HNF_2 or N_2F_4 .

Electrochemical Synthesis Procedure.—The electrolysis cell consisted of a 300-ml. titration flask fitted with a Teflon cap. The cathode was a cylinder of platinum gauze and the anode was a concentric cylinder of smooth platinum foil, 10 cm.² in area (one side). No diaphragm was used to separate the anode and the cathode. The cap was fitted with an inlet and an outlet for sweeping out the gaseous electrolysis products and electrical connections to the anode and cathode.

A typical electrolysis was run as follows. An aqueous solution (50 ml.) approximately 0.1 M in HNF_2 , 1.0 M in acetic acid, and 1.0 M in sodium acetate was placed in the electrolysis cell. The cell was immersed in an ice bath. A current of 1 amp. was passed for 1 hr. During this time a slow stream of nitrogen was passed over the solution. The nitrogen was then passed through three liquid nitrogen traps where the electrolysis products were condensed. The products were combined in one trap and fractionated by low-temperature vacuum distillation. Three fractions were taken: -78° , -126° , and -196° . These fractions were then analyzed by mass and infrared spectrometry. The major components of the -196° trap were ethane, carbon dioxide, and N_2F_4 . The -126° trap contained methyl difluoramine as a major component and a smaller amount of HNF_2 . The -78° trap was essentially empty. The HNF_2 was removed from the methyl difluoramine by passing the mixture in the -126° trap through a column packed with KOH pellets. The methyl difluoramine thus obtained was better than 99% pure.

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