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# RESEARCH IN HIGH-ENERGY OXIDIZERS

## Final Report

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Group 4
Downgraded at 3-Year Intervals
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Air Force Rocket Propulsion Laboratory
Edwards, California 93523
Air Force Systems Command
United States Air Force

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## FOREWORD

(U) The work reported herein was performed under Contract F04611-67-C-0007 and covers the period 15 February 1968 through 15 February 1969. The program was monitored by Lt. Charles Stone, Lt. Ray Foscante and Dr. F. Dewey, AFRPL, Edwards Air Force Base, California.

(U) The program manager for this contract is Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The Project Scientist for the Program is Dr. D. Pilipovich, Principal Scientist of Oxidizer and Fluorine Chemistry. Contributing to this research effort were Mr. M. G. Warner, Dr. K. O. Christe, Dr. S. Evans and Mr. R. D. Wilson. Dr. R. Keller also served as a consultant and Mr. S. Cohz performed the mass spectrometric analyses.

(U) This report contains no classified information extracted from other classified documents.

(U) This report has been assigned the Rocketdyne number R-7790.

(U) This technical report has been reviewed and is approved.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

## ABSTRACT

(C) The principal objective of this program was the preparation of new alkyl $ONF_2$ compounds. The free radical coupling reactions of difluoramino and alkoxy radicals were studied by electrochemical techniques. Compatibility problems wereuncovered when difluoramino-difluoromethoxide ($F_2NCF_2O^-$) was cooxidized with methoxide, t-butoxide or the tetramethoxy borohydride in aprotic systems. Difluoramine was found to be an efficient $\cdot NF_2$ radical source when complexed with pyridine or tetrahydrofuran at low temperatures in an acetonitrile system.

(C) Anodic cooxidation of $(CH_2)_4O:HNF_2$ and $(CH_3)_3COH$ gave $(CH_3)_3CF$. With $CH_3OH$, the products of anodic oxidation in the presence of $(CH_2)_4O:HNF_2$ were $CH_3OCH_2NF_2$, $CH_3OCH_2NF_2$, $CH_3OCH(NF_2)OCH_3$, and $CH_3OCHO$. The electrolysis of $C_5H_5N:HNF_2$ and $B(OCH_3)_4^-$ on graphite gave a mixture of $CH_3ONO$ and $N_2F_4$. The methyl nitrite is believed to be a decomposition product of the desired $CH_3ONF_2$.

(U) A brief study of the picrate/$HNF_2$ system gave no indication of a coupled product. The anodic oxidation of the derivatives of 2,2,2-trifluoro ethanol on platinum in acetonitrile gave $CF_3CH_2OCF_3$ and $(CF_3CH_2O)_2$. A cogeneration of $CF_3CH_2O^\cdot$ and $\cdot NF_2$ radicals was not achieved.

(C) Nonelectrochemical coupling reactions between the t-butoxy and the $NF_2$ radical were studied under varying conditions. Perfluoroformamide and its alkali metal salts, $N_2F_4$, and $HNF_2$ with t-butyl hypochlorite and t-butyl peroxide as $(CH_3)_3CO$ gave no direct evidence for the formation of $(CH_3)_3CONF_2$. Attempts to prepare $CH_3ONF_2$ by direct fluorination of $CH_3ONH_2$ in $H_2O$ or $CH_3CN$ solution were unsuccessful.

(U) The chemistry of bis-(fluoroformyl) peroxide, BFFP, was briefly studied toward the synthesis of intermediates. A new compound was formed from BFFP and KF and was isomeric with BFFP. Mass spectral data and $F^{19}$ nmr confirmed the structure as the ozonide of difluoroketene (2,3,5-trioxa-4,4-difluorocyclopentanone). Cesium fluoride and BFFP gave good yields of $(CF_3OO)_2C{=}O$ and $CF_3OOC(O)F$.

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# SECTION I

## INTRODUCTION

(C) The high potential of alkyl $ONF_2$ compounds as monopropellants (for example $CH_3ONF_2$ has a theoretical $I_s$ of 312 seconds) or oxidizers (for example $(F_2NO)_3C-CH_2-C(ONF_2)_3$ when combined with $B_5H_9$ has a theoretical $I_s$ of 333 sec) makes this novel class of compounds potentially important. Further, alkyl $ONF_2$ compounds of low volatility have a high theoretical performance potential in solid formulations. Thus, compounds such as $((F_2NO)_3C)_2-CH_2$, while an excellent oxidizer, could also be considered as a candidate plasticizer in a suitable formulation. The purpose of the present study was to determine if an alkyl $ONF_2$ compound could be prepared and characterized. Our approaches were divided into two general classifications; one involving a major electrochemical synthetic study and a minor, more conventional synthesis task. We planned during this program on exploiting free radical coupling reactions between an alkoxy and an $NF_2$ radical because the existence of these two radicals is well established. The selection of the electrochemical method of generating these radicals was predicated on the projected stabilization of the alkoxy radical through an absorption process at the point of generation; i.e., the anode surface. This report then will be primarily devoted to the description of the electrochemical evaluation of a variety of systems, each of which was considered capable of producting the desired radicals.

## SECTION II

## SUMMARY AND CONCLUSIONS

(C) Reactions were sought in attempting to synthesize difluoroaminoxyalkanes, $RONF_2$. In essence, the coupling of the radicals RO· and $NF_2$ was anticipated to yield the desired $RONF_2$ species. Two general methods for the generation of suitable radicals were pursued with an electrochemical approach receiving the major emphasis. The more "classical" chemical approaches were limited to the reaction of hypochlorites, peroxides, and alkoxyamines.

(U) The electrochemical studies carried out were confined to nonaqueous media and utilized complete instrumentation for electrode characterization and anodic process evaluation as a function of solvent, additive, and electrode. Using reliable reference electrodes, cyclic voltammetric data served as a model for macroscale electrolyses in the synthesis studies. Important observations in the electrochemical synthesis study include:

(U) 1. Perfluoroformamide, $NF_2CFO$, is not a suitable reagent for $NF_2$ radicals in basic media. While readily yielding $N_2F_4$, in an anodic process its marginal compatibility with coreactants precluded its use in a practical electrochemical system. Most bases from which an alkoxide radical was desired are reactive with $NF_2CF_2O^-$. Further, the complete degradation of either $F_2NCFO$ or its salt, $NF_2CF_2OK$, was noted with trace amounts of $H_2O$.

(U) 2. Polarization data in methanolic systems showed $CH_3OH$ to be easily oxidized. In neutral or acid media, the oxidation was confirmed to occur on carbon; i.e., the formation of the hydroxy methyl radical, $CH_2OH$, was observed. In basic media, product analysis in coreactant systems pointed to the generation and fixation of the desired methoxy radical, $CH_3O\cdot$.

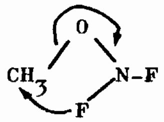
(C) 3. Sodium tetramethoxyborohydride, $NaB(OCH_3)_4$, was found to be a ready source of $CH_3O\cdot$ in an anodic process. Further, its cooxidation with $HNF_2$ complexed with an amine base, was achieved with the formation of $CH_3ONO$. The electroreactions occurring were the oxidation of $3(CH_3O)_4^-$ to $CH_3O\cdot$ and of the $HNF_2$ to $\cdot NF_2$. The desired coupling to $CH_3ONF_2$ was inferred inasmuch as a current balance was established for the products found, $CH_3ONO$ and $N_2F_4$.

(C) The formation of $CH_3ONO$ could be rationalized through the following sequence of reactions:

$$B(OCH_3)_4^- \longrightarrow CH_3O\cdot + e + (CH_3O)_3B$$

$$HNF_2 \longrightarrow \cdot NF_2 + H^+ + e$$

$$CH_3O\cdot + \cdot NF_2 \longrightarrow$$



$$\longrightarrow CH_3F + FNO$$

$$FNO + CH_3OH \longrightarrow CH_3ONO + HF$$

$$CH_3F + ROH \xrightarrow{\text{Base}} CH_3OR$$

(C) The equivalence of current and $CH_3ONO$ must point to the intermediacy of another material. Further, the electrode processes for each starting reagent preclude the direct formation of the nitrite by an anodic process. The known chemistry of the rearranged products are also consistent with the observations. Thus, it was apparent that an internal rearrangement $(S_Ni)$ occurred with $CH_3ONO$ being formed in an amount equivalent to $CH_3ONF_2$.

(U) 4. Direct evidence was obtained for the generation of the trifluoroethoxy radical, $\cdot OCH_2CF_3$. Anodic oxidation of the salt $CF_3CH_2ONa$ gave $(CF_3CH_2O)_2$ and $CF_3CH_2OCF_3$. However, a cooxidation with $HNF_2$ was not effected.

(C) 5. The salt of picric acid was electrooxidized, presumably to the radical $\cdot OC_6H_2(NO_2)_3$. A cooxidation with an $NF_2$ source was also achieved; however, the aromatic ring presumably acted as an electron sink for the odd electron and no coupling to $RONF_2$ occurred.

(U) 6. Cathodic processes involving the plating out of a metal, such as Na or K, were detrimental in prolonged electrolyses. The problem was obviated by using a rapidly stirred mercury cathode. The formation of an amalgam led to a fast cathodic process at reasonably low cell potentials.

(U) 7. The complex fluorides $KPF_6$, $NaPF_6$, $NaBF_4$, and $LiBF_4$ were for the most part satisfactory as supporting electrolytes in the solvents $CH_3CN$, $CH_3CON(CH_3)_2$, and methanol. Sufficiently high oxidation potentials of these materials permitted a broad range of anode potentials to be used in the electrochemical study. Magnesium perchlorate, $MgClO_4$, gave a fast, acceptable cathodic process but the anodic reaction led to explosive compositions, presumably through the formation of chlorine oxides.

(C) 8. Tertiary butyl alcohol and $HNF_2$ were cooxidized in $CH_3CN$ using $KPF_6$ as the supporting electrolyte. The products consisted mainly of t-BuF and $N_2F_4$. Again, as in the case of $CH_3OH$, the apparent primary product t-$BuONF_2$ may have rearranged to a more stable species.

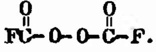
(C) 9. Although no $RONF_2$ compounds were isolated from the electrochemical reactions, several complex compounds were synthesized which illustrate the potential of the technique. These include $CH_3OCH_2NF_2$, $(F_2NCH_2)_2O$, $(CH_3O)_2CHNF_2$, $CH_3OC(O)NF_2$, $(CF_3CH_2O)_2$, and $CF_3CH_2OCF_3$. The latter two are new materials.

(C) The chemical approaches carried out toward the synthesis of $RONF_2$ gave results entirely consistent with those found in the electrochemical area. Again, strong evidence was obtained for the intermediacy of $RONF_2$. Some of the more significant findings include:

(C)

1. Alkyl hypochlorites and $KOCF_2NF_2$ did not give $RONF_2$ but gave instead $ClNF_2$. Uncomplexed $NF_2C(O)F$ and t-BuOCl gave t-$BuNF_2$, $NF_2Cl$, and t-BuOC(O)F.
2. The photolysis of t-BuOCl and $N_2F_4$ gave t-BuF and acetone. The t-BuF was thought to arise from the $S_Ni$ reaction of t-$BuONF_2$. With $HNF_2$, t-BuOCl gave excellent yields of $ClNF_2$ and no indication of $RONF_2$.
3. The products from the photolysis of t-butyl peroxide and $N_2F_4$ were consistent with the primary formation of t-$BuONF_2$.
4. In aqueous media, the fluorination of $CH_3ONH_2$ gave $CH_3ONO$, $CH_3ONO_2$ and $CH_3ON{=}NOCH_3$ most of which no doubt arose through oxygenation from peroxides formed. In nonaqueous solvent, the fluorination of $CH_3ONH_2$ gave $CH_3ONO$ and $CH_3F$. Again, the intermediacy of $CH_3ONF_2$ is probable.

Several routes to novel chemical intermediates were established through the interaction of alkali fluorides on bis- (fluoroformyl) peroxide. It was found, for example, that high yields of novel compounds could be realized in a simple, one step reaction. Prior to this study, these were obtained only with great difficulty:

1. The new compound, difluoroketene ozonide, (2,5,5 trioxa-4,4, difluorocyclopentanone) was prepared by the treatment of $C_2F_2O_4$ with activated potassium fluoride. It is present in equilibrium and is isomeric with  $F\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-F$. The mass pattern and $F^{19}$ nmr were unambiguous in its identification.
2. The action of activated CsF on $C_2F_2O_4$ gave principally $CF_3OOC(O)F$ and $(CF_3OO)_2C{=}O$.

## SECTION III

## DISCUSSION

### ELECTROCHEMICAL SYNTHESIS

(C) The single objective of this task was the synthesis of new energetic alkyl $ONF_2$ compounds for propellant applications requiring stable solid propellant or monopropellant ingredients. The synthetic approach we have taken was based on the concept that a free radical coupling reaction of difluoramino and alkoxy radicals would lead to the desired products, as represented by the general equation,

$$RO\cdot + \cdot NF_2 \longrightarrow RONF_2 \qquad (1)$$

where R is an alkyl or aryl hydrocarbon structure which may possess fluoro, nitro, or difluoramino substituents.

#### General Considerations

(U) As seen in Eq. 1 , the synthetic scheme requires the simultaneous generation of two different radical species each of which must have a sufficient life span and a favorable electron distribution on the appropriate atom to permit the desired bond formation to occur. The course of an interaction between such radicals will depend on many factors, some of which may be largely uncontrollable. However, we can make some general distinctions between the radicals formed by means of thermal or photoinitiation and those formed by means of an electrochemical process.

(U) Thermal or photoinitiation requires the rupture of a chemical bond and usually results in an environment of electronically activated radicals which are highly reactive and relatively short lived. Molecules formed as a result of radical combination under these conditions may also be activated and thus require "quenching" before a stable configuration can be obtained. In contrast, an electrochemical process such as the anodic oxidation of an anion neither requires bond rupture nor necessarily results in an electronically activated species. The anion is oxidized on the electrode at a site which has a high enough potential to establish the equilibrium,

$$X^- \rightleftharpoons X\cdot + e^- \qquad (2)$$

and which provides an environment for desolvation, orientation and adsorption on the surface. The resulting radicals may be highly stabilized in the environment of the electrode surface and the immediate surrounding anolyte layer. The increased stability and life span of the radicals might make possible increased local concentrations of these species on the electrode surface and enhance the probability of the desired coupling reaction.

(U) A factor of prime importance in considering an electrochemical system is the compatibility of the reagents with a supporting medium which has the requisite conductivity. The solvent of choice must have a high enough dielectric constant (12 is about the lower limit) to support the ionization of an inert salt (supporting electrolyte) and also have the wide liquid range and low volatility appropriate for the study. Thus, the choice of a solvent becomes extremely limited when the strict requirement of chemical compatibility is also imposed.

(C) Originally our concept of an electrochemical synthesis of an $ONF_2$ compound involved the various difluoramine methoxides (Ref. 1 and 2) $F_2NCF_2O^-$, $(F_2N)_2CFO^-$, and $(F_2N)_3CO^-$ which had been prepared by the reactions of $F_2NCFO$ with KF in anhydrous acetonitrile. We visualized the oxidation of a methoxide to the methoxy radical,

$$F_2NCF_2O^- \longrightarrow F_2NCF_2O\cdot + e^- \qquad (3)$$

followed by a reaction with $NF_2$ radicals supplied by the introduction of $N_2F_4$

$$F_2NCF_2O\cdot + \cdot NF_2 \longrightarrow F_2NCF_2ONF_2 \qquad (4)$$

(C) Because acetonitrile is an excellent solvent for electrochemical work and its compatibility with the difluoramino methoxides was well established, the addition of $KPF_6$ as the supporting electrolyte completed the requirements for an electrochemical solvent system in which to study the oxidation. The preliminary experiments, however, demonstrated that the electro oxidation of $F_2NCF_2O^-$ on platinum at -35 C gave a quantitative yield of $N_2F_4$; a result which apparently precluded the possibility of fixing the difluoramino-difluoromethoxy radical as postulated in Eq. 3 and 4.

(C) The early results that we obtained did suggest a new method of synthesizing an $ONF_2$ compound. Because the oxidation of $F_2NCF_2O^-$ had evidently resulted in the generation of $NF_2$ radicals on the anode, their capture by alkoxy radicals generated simultaneously could lead to the desired $RONF_2$ structure.

(C) With the synthesis of an alkyl $ONF_2$ compound as the main objective, we were forced to consider what effect the addition of a strongly basic alkoxide such as $CH_3O^-$ or $(CH_3)_3CO^-$ might have on the electrochemical system. Although there was a possibility that the two types of alkoxide anions would be compatible (e.g., $CH_3O^-$ and $F_2NCF_2O^-$), we were aware that acetonitrile would not tolerate the strong bases. The alternate electrochemical $NF_2$ radical source was $HNF_2$, but its decomposition by strong bases was well known.

(U) The initial steps in the investigations concerned the selection of an electrochemical solvent medium which would be compatible with the strong bases and an assessment of the mutual compatibility of the two types of alkoxides. The results of these preliminary studies led eventually to an evaluation of alternate, less basic alkoxy radical sources such as the anions $B(OCH_3)_4^-$, $CH_3OCO_2^-$, $CF_3CH_2O^-$, and $CF_3CH_2OC(CF_3)_2CO^-$.

(C) We also investigated the use of $HNF_2$ as an $NF_2$ radical source in protic or aprotic systems confined to acidic or very weakly basic alkoxy radical sources.

(U) To establish the conditions most propitious to the end synthetic goal, electrochemical techniques were employed to characterize the electrode reactions of the individual radical source reagents and to study the voltammetric behavior of the systems prior to macro-scale electrolysis. Using a three-electrode system and a divided cell, polarization curves were determined by voltammetry at linearly varying anode potentials (e.g., using an electronic potentiastat, the anode potential was varied linearly with respect to the reference electrode while the cell current response was being recorded). By means of polarization data we were able to examine several important features of the electrochemical system before an actual electrolysis was attempted. These features are summarized as:

1. The useful anodic potential range of the solvent systems (solvent and supporting electrolyte above) on a given electrode.
2. The existence of an electro-oxidation process involving the test reagent under study.
3. Half-wave potentials for the process and the relationship between anode diffusion current density and the concentrations of the reagent.
4. The activity of different electrode materials.
5. The effect of temperature on the rate of the oxidation process.
6. Coulombic or potential dependent passivation phenomena.
7. The effect on the voltammetric characteristic of a given system caused by the addition of other reagents.

(U) We were specifically interested in establishing the conditions for the simultaneous oxidation of two species; however, the voltammetric data on the two together told us only the total oxidation rate at a given potential and gave little indication of the relative rates of the two processes involved. Thus, one of the most important phases of the diagnostic work is the macroscale electrolysis and product analysis.

(U) By means of electrolyses at preselected anode potentials, it was possible to explore the various regimes of the polarization curves and to deduce from product analyses the rates of the electrode processes as a function of potential. Identification and quantitative analysis of the anolyte products made possible an assessment of the Faradaic efficiency of the electrode processes and enable us in some cases to differentiate between the electrochemical and the chemical steps involved. Thus, product analyses which were combinations of volume measurements and infrared, mass, and $F^{19}$ nmr spectra, helped to ascertain success or failure of an attempted electrochemical synthesis.

(U) Because the supporting electrolyte plays an important role in the electrochemical system, care was taken to select materials which possessed the following properties:

1. Solubility within the range 0.2 M to 1.0 M.
2. Solution specific conductivity of at least $4.0 \times 10^{-3}$ $ohm^{-1}$ $cm^{-1}$ at -30 C.
3. Resistance to anodic oxidation over a wide potential range.
4. Compatibility with the reagents and products.

(U) For systems based on the anhydrous solvents acetonitrile, N,N-dimethylacetamide and methanol the salts, $KPF_6$, $NaPF_6$, $NaBF_4$ and $LiBF_4$ met all the above requirements.

(U) The problem of severe cathodic polarizations led us to consider the use of a tetraalkyl ammonium saltsas a supporting electrolyte which would undergo cathodic reduction without fouling the platinum surface. However, none of the salts tested ($n\text{-}Bu_4NF$, $Me_4NBF_4$, and $Me_4NF$) were sufficiently soluble nor resisted oxidation over a wide enough anodic potential range. The cathodic polarization problem was finally solved by the use of a rapidly stirred mercury cathode for the reduction of alkali metal cations. The formation of an analgam made possible a fast cathodic process at relatively low cell potentials. Magnesium perchlorate provided a fast cathodic process even on platinum; however, the perchlorate ion became involved in the anodic oxidation on Pt in $CH_3CN$ at 3.0 v vs $Ag/Ag^+$ and produced an explosive product mixture containing $ClO_2$ (Table 1, electrolysis No. 7). In a methanolic system, an extreme cathodic polarization was precluded by the facile reduction of methanol itself as shown in the equation:

$$CH_3OH + e^- \longrightarrow CH_3O^- + 1/2\ H_2 \qquad (5)$$

Electrochemical Generation of the Alkoxy Radical

(C) In attempting to synthesize an alkyl difluoraminoxy compound such as $CH_3ONF_2$ or $(CH_3)_3CONF_2$, we sought to achieve the coupling of the two component radicals RO· and ·$NF_2$ generated simultaneously by the electrochemical oxidation of two suitable radical sources. The difluoramino radical can be readily generated by either of two anodic oxidation processes. One of them is through the oxidation of $F_2NCF_2O^-$ in neutral or basic aprotic media as in the equation,

$$F_2NCF_2O^- \longrightarrow \cdot NF_2 + CF_2O + e^- \qquad (6)$$

(C) In this case, the anion was formed <u>in situ</u> by the low temperature reaction of $F_2NCFO$ and KF in the solvent followed by electrochemical decomposition. The other process involves the oxidation of $HNF_2$ in an acidic or very weakly basic protic or aprotic system as shown in the equation,

$$HNF_2 \longrightarrow \cdot NF_2 + H^+ + e^- \qquad (7)$$

The limitations set by these systems were carefully observed in the selection of possible alkoxy radical sources.

(U) The alkoxy radical in theory may be generated electrochemically from, the alcohol (ROH), the alkoxide anion ($RO^-$), or a complex anion such as $B(OR)_4^-$.

## TABLE 1

### THE ELECTROLYSIS OF $CH_3OH$ AND $HNF_2$ IN 1.0 M $Mg(ClO_4)_4$ ACETONITRILE SOLUTION

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode | | | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Material and Area | Potential (V) vs Ag/AgCl | Current Density, $ma/cm^2$ | | |
| 7 | 1.0 M $Mg(ClO_4)_2$ in $CH_3CN$ | 0.24 M $HNF_2$<br>0.24 M THF<br>$CH_3OH$ added at 2.61 mmoles/hr | -44 | Pt<br>0.5 $cm^2$ | 3.0 ±0.2v vs $Ag/Ag^+$ | 200 to 500 | | Ni cathode, cell potential ranged 32 to 45v. Products: $N_2F_4$, $ClNF_2$, $ClO_2$; -142 C. Product trap exploded upon warming. |

Of these sources, the anions are more likely to yield a high concentration of alkoxy radicals on an anode surface according to the equations,

$$RO^- \longrightarrow RO\cdot + e^- \qquad (8)$$

$$B(OR)_4^- \longrightarrow RO\cdot + B(OR)_3 + e^- \qquad (9)$$

The reaction in Eq. 8 is consistent with a strongly basic solution, while Eq. 9 involves only a weakly basic system. The use of an alcohol as the alkoxy radical source may be complicated by the necessity of an O-H dissociation prior to oxidation.

(U) In the case of methanol, anodic discharge in a basic solution takes place at potentials approximately 0.5 v lower than in a neutral or acidic solution. Under the latter conditions, the major mode of oxidation involves the homolytic cleavage of a C-H bond (90 kcal/mole) as in the equation,

$$CH_3OH \longrightarrow \cdot CH_2OH + H^+ + e^- \qquad (10)$$

whereas methoxy radical formation necessitates the cleavage of an O-H bond (108 kcal/mole) and probably takes place to a much smaller extent as in

$$CH_3OH \xrightarrow{\text{acidic}} CH_3O\cdot_{(ads)} + H^+ + e^- \qquad (11)$$

On the subject of electrochemical methoxylation reactions, the existing literature (Ref. 3 ) affords little evidence to support the existence of methoxy radicals as intermediates except under basic conditions. The anodic methoxylation of substituted furans in acidic methanol evidently involves the formation of a cation radical which reacts with the solvent followed by reoxidation and solvolysis to a final, methoxylated product.

Similarly, the α-methoxylation of alkylbenzenes in neutral and basic methanol (Ref. 4 and 5) may involve both aromatic radical and carbonium ion intermediates in the following manner;

$$RH \longrightarrow R\cdot + H^{+} + e^{-} \qquad (12)$$

$$R\cdot \longrightarrow R^{+} + e^{-} \qquad (13)$$

and subsequent reaction with methoxy radical or methanol,

$$R\cdot + CH_3O\cdot\ (ads) \longrightarrow ROCH_3 \qquad (14)$$

### (C) Investigation of the $CH_3O^-/F_2NCF_2O^-$ System

Initially, our objective was to establish a suitable aprotic solvent system which would be compatible with both $CH_3O^-$ and $F_2NCF_2O^-$, and would provide adequate conductivity with a supporting electrolyte. A solvent mixture consisting of 70-percent N,N-dimethyl acetamide (DMA) and 30-percent tetrahydrofuran (THF) did give, with a supporting electrolyte, low but tolerable values of specific conductivity.

(C) The mixed DMA/THF solvent was found to be completely compatible with the insoluble alkoxides t-BuOK and $CH_3ONa$. The preparation of tetramethyl ammonium methoxide was then undertaken to have a starting material with the required solubility. The compound was prepared by the reaction,

$$(CH_3)_4NF + NaOCH_3 \longrightarrow (CH_3)_4NOCH_3 + NaF \qquad (15)$$

in anhydrous methanol. Removal of the methanol under high vacuum at ambient temperatures proved to be extremely difficult and higher temperatures were avoided because of the suspected low thermal stability of the compound. In fact, a recent study of its thermal decompositions was reported by W. Kenneth Musker* (Ref. 6).

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*In a telephone conversation with the author, he disclosed that his efforts to obtain the methoxide free of methanol were also unsuccessful. His analyses confirmed the retention of one mole of methanol in the final solid product, e.g., $(CH_3)_4NOCH_3\cdot HOCH_3$.

We concluded that the methoxide would not be useful in this form because we had demonstrated that methanol, even in low concentrations, would react with $F_2NCF_2O^-$ in acetonitrile at low temperatures to give $HNF_2$ and $N_2F_2$.

(U) The difficulties encountered in attempting to prepare a DMA soluble methoxide free of protic impurities appeared to be insurmountable and we redirected our efforts toward the preparation of some less basic methoxy sources which could be employed either in a DMA or an acetonitrile solvent system.

A monocarbonic ester salt of the type, $CH_3O\overset{O}{\overset{\|}{C}}O^- \ M^+$ was expected to undergo anodic oxidation according to the equation,

$$CH_3OCO_2^- \longrightarrow CH_3O\cdot + CO_2 + e^- \qquad (16)$$

(C) Tetramethylammonium methyl carbonate was prepared by treating the methoxide with $CO_2$ in N,N-dimethylacetamide at room temperature. The precipitation of the methyl carbonate from the DMA solution strongly indicated its insufficient solubility for use in a DMA or acetonitrile-based electrochemical system. Unlike the sodium methyl carbonate, which was also insoluble in those solvents, the tetramethylammonium methyl carbonate was found to be soluble in methanol and thus was regarded as a candidate reagent for later use in a protic system involving $HNF_2$.

(U) The nonbasic complex borohydride, $B(OCH_3)_4^-$, was also considered as a possible methoxy radical source. Anodic oxidation of the anion was envisioned as follows,

$$B(OCH_3)_4^- \longrightarrow CH_3O\cdot + B(OCH_3)_3 + e^- \qquad (17)$$

H. C. Brown and E. Mead (Ref. 7 ) reported the preparation and some properties of the sodium salt. Its ease of preparation, good thermal stability, and nonbasicity made it an attractive reagent.

A sample of $NaB(OCH_3)_4$ was prepared by the reaction of trimethyl borate with sodium methoxide in methanol,

$$B(OCH_3)_3 + NaOCH_3 \xrightarrow[20^\circ]{CH_3OH} NaB(OCH_3)_4 \qquad (19)$$

Anodic polarization curves are shown in Fig. 1.

(C) Two critical sets of conclusions were derived and formed the basis for an important turning point in the synthetic effort. They were:

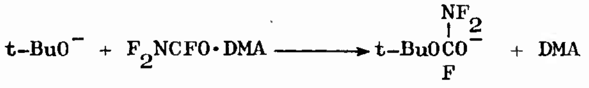
1. Compatibility tests revealed that $NaB(OCH_3)_4$ would react with $F_2NCFO$ in the absence of a solvent at temperatures as low as -80 C to give $CH_3O\overset{O}{C}\text{-}NF_2$ and $NaFB(OCH_3)_3$ quantitatively.

   Unexpectedly, the anions $B(OCH_3)_4^-$ and $F_2NCF_2O^-$ were also incompatible and reacted in acetonitrile at -40 C to give the observed volatile products $N_2F_2$ and $CO_2$

   These observations made it impossible to consider the use of complex borohydride in a system involving $F_2NCF_2O^-$ as the coreagent.

2. By carrying out reactions in anhydrous tetrahydrofuran at -30 C we found that $F_2NCFO$ forms a 1:1 complex with N,N-dimethyl acetamide, and because of this reaction the KF complex salt of $F_2NCFO$ could not be formed in DMA solvent.

   Polarization data (Fig. 2 ) showed conclusively that the $F_2NCFO$/DMA complex could not be oxidized on a platinum electrode within the anodic range of the DMA solvent system. Polarization data indicated that the addition of a strong base, t-BuOK, (itself insoluble in DMA) gave rise to an oxidizable anion, possibly through the displacement of DMA from the complex as shown in the equation,



$$t\text{-}BuO^- + F_2NCFO\cdot DMA \longrightarrow t\text{-}BuO\underset{F}{\overset{NF_2}{C}}O^- + DMA \qquad (20)$$

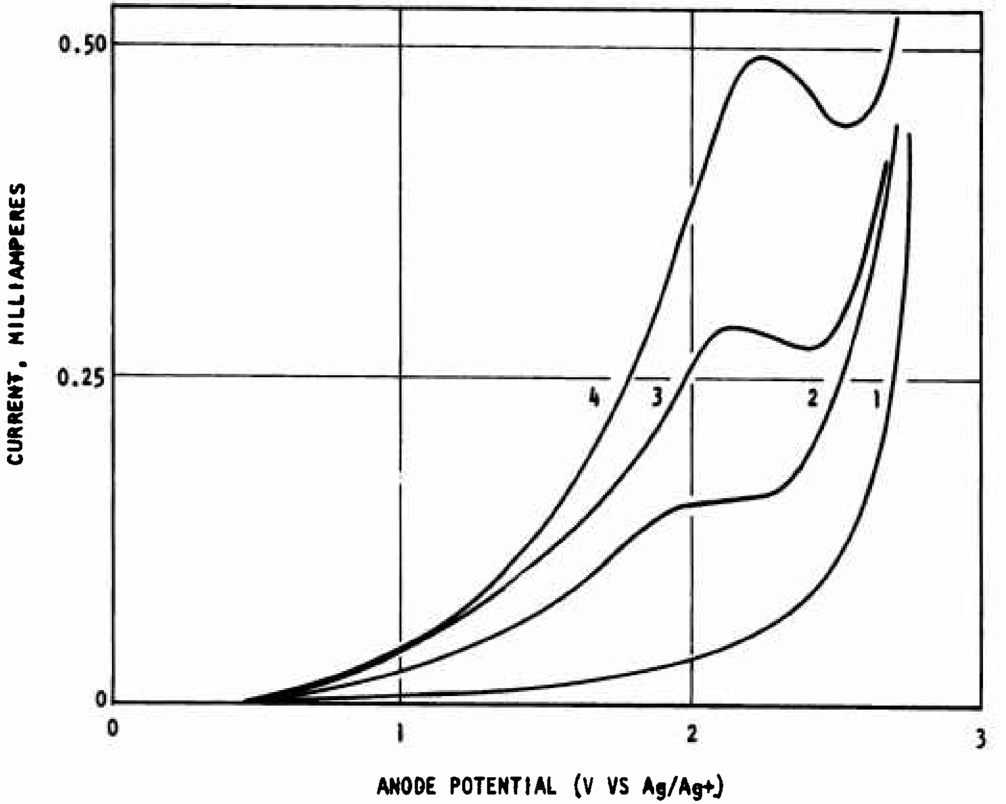


Figure 1. Anodic Polarization Curves on Pt/Pt (0.01 cm$^2$) in 0.5 M $KPF_6$ Solution in Acetonitrile/Tetrahydrofuran (90/10) at 0 C, Scan Rate 167 mv/min

1. Solvent System, Followed by Addition of,
2. $NaB(OCH_3)_4$ (2.0 mmoles)
3. $NaB(OCH_3)_4$ (4.0 mmoles)
4. $NaB(OCH_3)_4$ (5.0 mmoles)

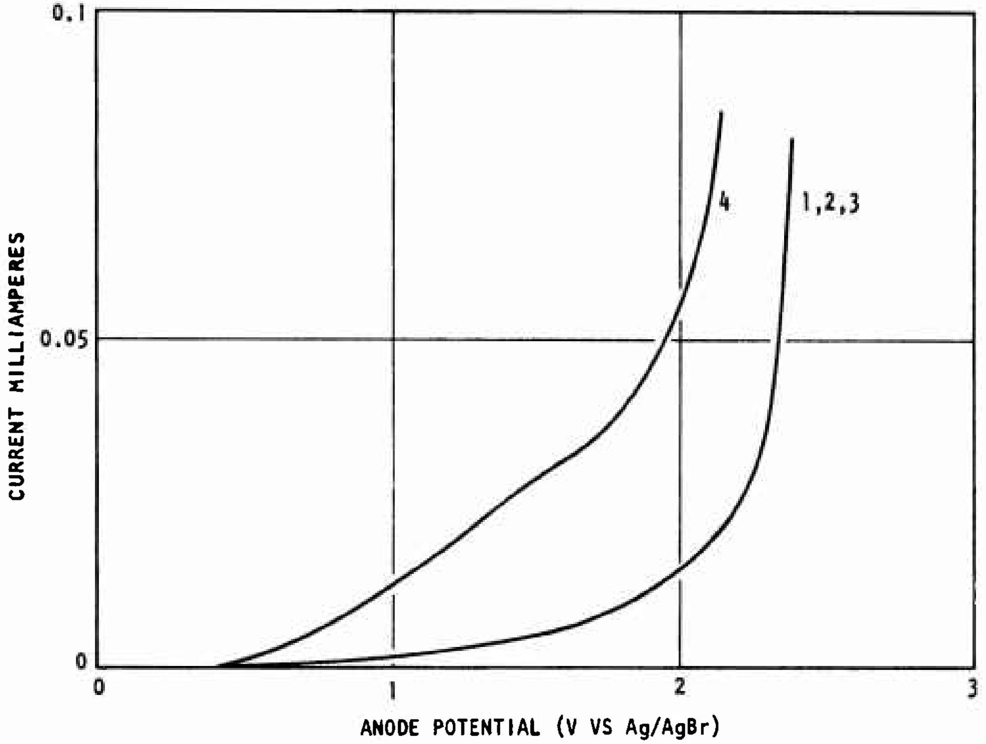


Figure 2. Anodic Polarization Curves on Pt/Pt (0.01 $cm^2$) in 0.5 M $KPF_6$ Solution in N,N-dimethylacetamide/Tetrahydrofuran (70/30) at -40 C, Scan Rate 167 mv/min

1. Solvent System, Followed by the Addition of;
2. 0.04 M $F_2NCFO$
3. Saturated $(CH_3)_4NF$
4. Slurry 0.04 M $(CH_3)_3COK$

(C) However, electrolysis (Table 2, No. 1 and 2) of the resulting solution on platinum at 1.5 + 0.1 v vs Ag/AgBr gave $CO_2$ as the only volatile product detected. Because no $N_2F_4$ was found, any $NF_2$ radicals generated were evidently captured immediately by t-butoxy radicals or by some other component of the system. Thus, we had discovered that the one solvent compatible with the strongly basic alkoxides complexed or solvated $F_2NCFO$ in such a way that prevented the formation of the anion, $F_2NCF_2O^-$, which was to be the $\cdot NF_2$ radical source.

Thus, it was necessary to discontinue work on the perfluoroformamide systems until a compatible alkoxy radical source could be found for studies in a suitable solvent.

## Anodic Oxidation of $HNF_2$ and an Alcohol

(C) Our efforts were directed toward a study of the anodic oxidation of $HNF_2$.

$$HNF_2 \xrightarrow{\text{anode}} \cdot NF_2 + H^+ + e^- \qquad (21)$$

Ward and Wright (Ref. 8 ) studied $HNF_2$ oxidation in aqueous buffer systems over the range pH ≤ 6.85. In basic systems, $HNF_2$ decomposed too rapidly to be studied (Ref. 9 ). The pH dependence of the oxidation half wave potential was explained in terms of a pre electron-transfer dissociation step,

$$HNF_2 \rightleftharpoons H^+ + {}^-NF_2 \qquad (22)$$

followed by oxidation of $NF_2^-$,

$$NF_2^- \longrightarrow \cdot NF_2 + e^-. \qquad (23)$$

(C) Starting with an aprotic solution of 0.5M $KPF_6$ in acetonitrile, we introduced $HNF_2$ and THF to form the stable 1:1 complex $(CH_2)_4\,O{:}HNF_2$ and studied its cyclic voltammetric behavior at -37 C using the micro black

## TABLE 2

### THE ELECTROLYSES OF $F_2NCFO$ IN N,N-DIMETHYLACETAMIDE-TETRAHYDROFURAN WITH $(CH_3)_3COK$

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode | | | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Material and Area | Potential (V) vs Ag/AgCl | Current Density, ma/$cm^2$ | | |
| 1 | 0.5 M $KPF_6$ in DMA/THF (70/30) | 0.04 M $F_2NCFO$ t-BuOK (4 mmoles) | -40 | Pt/Pt (13.5 $cm^2$) Rotating Cylinder | 1.5 ±0.1v vs Ag/AgBr | 0.15 | 0.52 | Volatile product, $CO_2$ (22 cc) |
| 2 | 0.5 M $KPF_6$ in DMA/THF (70/30) | 0.06 M $F_2NCFO$ t-BuOK (4 mmoles) | -40 | Same | 1.6 ±0.5v vs Ag/AgBr | 0.15 | 0.52 | Volatile product, $CO_2$ (12 cc) |

platinum anode against an $Ag/Ag^+$ reference electrode. Using a scan rate of 833 mv/min hour, an anodic oxidation wave was observed with a half-wave potential at 2.55 v and peak current response of 0.5 ma at 2.82 v. A three-fold increase in the concentration of the complex gave a peak current of 0.8 ma.

(C) For the initial coupling attempt, t-butanol was chosen as the alkoxy radical source,

$$(CH_3)_3COH \xrightarrow{anode} (CH_3)_3CO\cdot + H^+ + e^- \qquad (24)$$

The addition of an equimolar amount of $(CH_3)_3OH$ to the cell containing $(CH_2)_4O\cdot HNF_2$ (3.0 mmoles) in 50 ml of anolyte produced a sharp rise in current response giving a maximum of 6.5 ma at 2.76 v with the cell temperature at -30 C.

(C) A constant current electrolysis (Table 3 , No. 3) was carried out starting with 0.1 M $(CH_2)_4O\cdot HNF_2$ and 0.06 M$(CH_3)_3COH$ reagent concentrations. Volatile products were swept continuously from the cell during the 3-hour electrolysis at 60 ma with 6.72 mF of current being passed. The potential of the spinning cylindrical black platinum electrode gradually increased from 2.31 v to 2.58 v vs $Ag/Ag^+$ while the cell temperature was kept in the range -30 to -35 C. The volatile product swept out of the cell was identified as $N_2F_4$ (19.5 cc; 0.87 mmole), and fractionation of the anolyte yielded $(CH_3)_3CF$ (108 cc; 4.82 mmoles).

(C) The high yield of the alkyl fluoride (~75 percent of the current) is at first puzzling considering the reactant system. Its formation by chemical reaction in the ROH-$HNF_2$ system is remote and its direct formation from radical coupling is precluded. Further, the high yield in a dilute solution implies that it is a product of rearrangement rather than by substitution on the tertiary carbon. The only intermediate consistent with this is the desired $(CH_3)_3CONF_2$. If this compound decomposed, it would yield $(CH_3)_3CF$ and FNO in analogy to the decomposition of $FSO_3NF_2$

## TABLE 3

## THE ELECTROLYSIS OF $(CH_3)_3COH$ AND $HNF_2$ IN ACETONITRILE

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode |  |  | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Material and Area | Potential (V) vs Ag/AgCl | Current Density, ma/$cm^2$ |  |  |
| 3 | 0.5 M $KPF_6$ in $CH_3CN$ | 0.1 M $HNF_2$<br>0.1 M THF<br>0.06 M $(CH_3)_3COH$ | -37 | Pt/Pt (13.5 $cm^2$) Rotating Cylinder | 2.45 ±0.13v vs $Ag/Ag^+$ | 4.44 | 6.72 | Volatile Products: $N_2F_4$ (19.5 cc, 0.87 mmole) and $(CH_3)_3CF$ (108 cc, 4.82 mmoles) |

which gives $SO_2F_2$ and FNO. No FNO was detected in the anode products, and it is likely that it would be most reactive in the protic system used. For example, its reaction with $HNF_2$ would give $N_2F_4$ and NO with the latter being undetected in the scale of our reaction.

(U) One of the significant observations in the electrolysis is that no acetone was formed. This fact strongly suggests that the radical $(CH_3)_3CO\cdot$ is being retained on the anode surface sufficiently long in order for its capture to occur. This was most encouraging inasmuch as the stabilization of the akoxy radical through anodic oxidation was one of the key premises leading to our approach and augured well for fixing more reactive species such as the $CH_3O\cdot$ radical.

(C) In the above electrolysis, a total of 6.72 mF of current was passed. If one assumes that the $N_2F_4$ arises from $NF_2$ radicals formed anodically, a balance of 4.98 mF remains. Within experimental error, this value is equivalent to the 4.82 mm of $(CH_3)_3CF$ found. This result is somewhat puzzling inasmuch as it tends to preclude a two electron process such as as

$$ROH + HNF_2 \longrightarrow RONF_2 + 2H^+ + 2e. \qquad (25)$$

(C) The above two electron reaction (assuming $N_2F_4$ arose at the anode) would require a total of 11.38 mF of current and at the very least 9.74 mF with $N_2F_2$ arising from chemical attack. The primary electrode reaction during the electrolysis may have been the oxidation of the t-butyl alcohol with a subsequent alkoxy radical reaction with $HNF_2$. It was noted that the electrolysis was conducted at a potential below that giving the peak current for the $HNF_2$ oxidation, and the resulting rate of $HNF_2$ oxidation at the anode could be small.

(C) The electrolysis of $HNF_2$-$(CH_3)_3COH$ gave us a strong indication that the t-butoxy radical could be fixed by reaction with $HNF_2$. However, the fact that only $(CH_3)_3CF$, presumably arising from $(CH_3)_3CONF_2$, was found pointed out a difficulty in its isolation from the anolyte. At the same electrolysis temperature, a more volatile primary product would be less susceptible to subsequent rearrangement or side reaction through its continuous removal.

(C) The methanol/$HNF_2$-THF system was then chosen for exploratory studies inasmuch as the high volatility expected for $CH_3ONF_2$ should enable it to be swept out of the anolyte during a low temperature electrolysis and thus avoid possible reaction with $H^+$ and other species in the cell. The advantage of higher product volatility, however, may be sacrificed to the probable greater difficulty in coupling $\cdot NF_2$ with the highly-reactive methoxy radical before hydrogen abstraction or decomposition take place. An extensive study of alkoxy radical stability in the gas phase at 195 C by Rust _et al_. (Ref. 10) shows the high rate of hydrogen abstraction by methoxy radicals compared to the less reactive t-butoxy radicals which probably have a longer radical life but prefer decomposition through C-C bond rupture over hydrogen abstraction. Liquid phase studies of t-butylperoxide decomposition at 100 C and 17 C show a high proportion of hydrogen abstractions by $(CH_3)_3CO\cdot$ radicals and suggest that the conditions used by Rust _et al_. exaggerate the difference between methoxy and t-butoxy reactivities. These differences would be minimized on the surface of an anode at low temperature.

(C) Cyclic voltammetric data showed a well-defined anodic oxidation wave for 0.02 M $CH_3OH$ in 0.5 M $MPF_6/CH_3CN$ at 24 C with E 1/2 at 2.5 v using 833 mv/min scan rate. The high activation over-potential required for the oxidation reflects the fact that C-H and/or O-H bond cleavage must occur. The addition of water (0.02 M) to the solution does not cause any appreciable depolarization but simply adds to the magnitude of the alcohol wave over which it is superimposed. The role of THF in the $HNF_2$ oxidation process was determined in a semiquantitative manner using the following procedure:

1. To 0.5 M $KPF_6/CH_3CN$ (60 ml) anolyte at -38 C was added $HNF_2$ (1.0 mmole) in the $He/N_2$ carrier gas streams (Fig. 3 , curve 2) The anodic oxidation wave exhibited a peak current of 0.028 ma

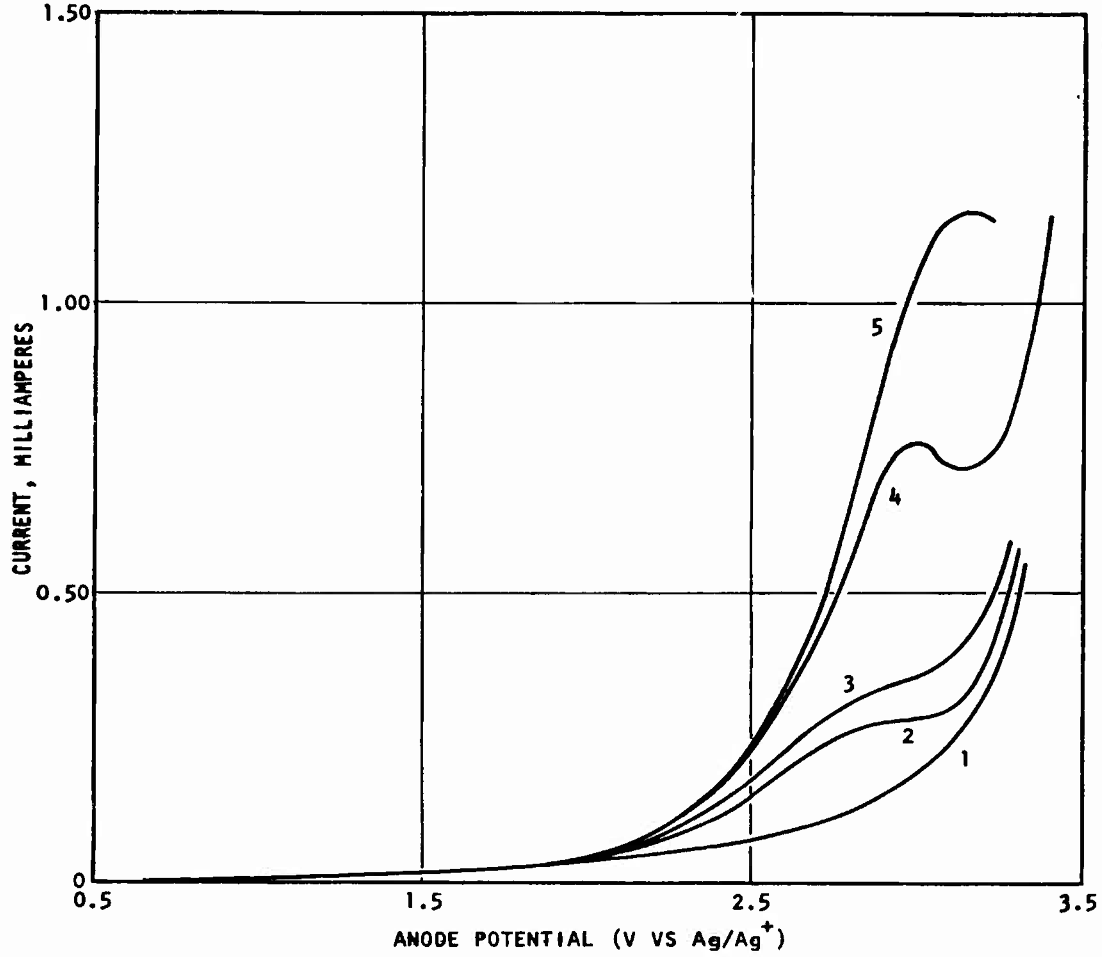


Figure 3. Anodic Polarization Curves on Pt/Pt (0.01 cm$^2$) in 0.5 M $KPF_6$ Acetonitrile at -38 C, Scan Rate 167 mv/min

1. Solvent System, Followed by the Addition of
2. $HNF_2$ (1.0 mmole)
3. $HNF_2$ (1.0 mmole)
4. $(CH_2)_4O$ (0.2 ml)
5. $HNF_2$ (1.0 mmole)

at 2.63 v using 167 mv/min scan. The addition of a second aliquot of $HNF_2$ (1.0 mmole) brough the peak current response to 0.035 ma at the same potential (curve 3). A small amount of $HNF_2$ may have been swept out of the cell during the short time interval required to make the additions and measurements. After standing 1.25 hours, the peak current had declined to about 0.025 ma, presumably because of the loss of $HNF_2$.

2. Tetrahydrofuran (0.2 ml) was added to the anolyte and the anodic oxidation wave exhibited a peak current of 5.75 ma at 2.72 v using 167 mv/min scan rate (curve 4). Finally, a third addition of $HNF_2$ (1.0 mmole) gave the response shown in curve 5.

(C) The oxidation waves obtained with $HNF_2$ alone (1 above) indicate that the process is controlled by the extent of $HNF_2$ ionization,

$$HNF_2 \rightleftharpoons H^+ + NF_2^- \qquad (26)$$

which determines the concentration of $NF_2^-$ and thus the rate of the oxidation

$$NF_2^- \longrightarrow \cdot NF_2 + e^- \qquad (27)$$

The addition of THF evidently increases the concentration of $NF_2^-$ through complex formation and dissociation,

$$HNF_2 + (CH_2)_4O \longrightarrow (CH_2)_4O{:}HNF_2 \rightleftharpoons (CH_2)_4OH^+ + NF_2^- \qquad (28)$$

and is responsible for the observed increase in peak current.

Table 4 electrolyses No. 4, 5, 6, and 8 summarize the experimental data for three attempted anodic coupling reactions involving the $CH_3OH$-$HNF_2/(CH_2)_4O$ system in 0.5 M $KPF_6/CH_3CN$ solutions. In the first experiment, severe cathodic polarization became the current limiting

## TABLE 4

## THE ELECTROLYSES OF $CH_3OH$ AND $HNF_2$ IN ACETONITRILE

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode |  |  | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Material and Area | Potential (V) vs Ag/AgCl | Current Density, ma/cm$^2$ |  |  |
| 4. | 0.5 M $KPF_6$ in $CH_3CN$ | 0.2 M $HNF_2$<br>0.2 M THF<br>0.1 M $CH_3OH$ | -35 | Pt/Pt (13.5 cm$^2$) Rotating Cylinder | 2.4v vs $Ag/Ag^+$ | 7.4 | 9.5 | Most of $HNF_2$ was recovered. Found small amount of $N_2F_4$ and $SiF_4$ but no C-H products. |
| 5 | 0.5 M $KPF_6$ in $CH_3CN$ | 0.1 M $HNF_2$<br>0.2 M THF<br>0.1 M $CH_3OH$ | -35 | Pt/Pt (6.7 cm$^2$) Rotating Cylinder | 3.1v vs $Ag/Ag^+$ | 17.8 | 6.5 | Products: $N_2F_4$ (10 cc) $CH_3OCHO$ (10 cc), some $SiF_4$, HCN and compound identified by mass spectrometer as $CH_3OCH_2NF_2$ |
| 6 | 0.5 M $KPF_6$ in $CH_3CN$ | 0.67 M $HNF_2$<br>1.0 M THF<br>2.0 M $CH_3OH$ | 0 | Pt (0.10 cm$^2$) | 2.8v vs $Ag/Ag^+$ | 300 | 10 | Product: $N_2F_4$ (12 cc) |
| 8 | 0.4 M $KPF_6$ in $CH_3CN$ | 0.48 M $HNF_2$<br>0.48 M THF<br>CH OH added at 2.61 mmoles/hr | -30 | Pt (0.5 cm$^2$) | 4.3 to 5.1v vs | 200 |  | Hg cathode, cell potential ranged 23 to 40v. Product: $N_2F_4$ |

factor and the maximum anode potential obtainable was 2.4 v using the 13.5-$cm^2$ black platinum rotating cylinder. Most of the $HNF_2$ was recovered, but the oxidation products derived from $CH_3OH$ could not be found by vacuum line fractionation and infrared analysis.

(C) The cathodic polarization problem was overcome by the addition of 1 or 2 ml of methanol to the cathode compartment so that the cathode reaction would be

$$CH_3OH + e^- \longrightarrow 1/2\ H_2 + CH_3O^- \qquad (29)$$

instead of the deposition of potassium metal. For the second experiment (No. 5), the surface area of the anode was reduced by 50 percent making possible the higher anode potential (3.1 v) and current density (17.8 ma/$cm^2$) operating with a constant current of 120 ma. Under these conditions, the simultaneous oxidation of $HNF_2$ and $CH_3OH$ was obtained and product analysis revealed significant amounts of $N_2F_4$, $CH_3OCHO$, and an unidentified $NF_2$-CHO compound. Unreacted $HNF_2$, $CH_3OH$, and THF were also found in addition to small amounts of HCN and $SiF_4$.

(C) The third electrolysis (No. 6) was carried out in a standard H-cell using a bright platinum wire anode (area about 0.10 $cm^2$) in an effort to work with a considerably higher current density and higher $HNF_2$ concentrations. The only product swept out of the cell was $N_2F_4$ and complete work-up of the solution was not attempted because of accidental mixing of anolyte and catholyte. High current densities at the anode could also be maintained through the use of a rapidly stirred mercury cathode (electrolysis No. 8), but extensive solvent discharge occurred at the high anode potentials that resulted during the constant current electrolysis.

(U) The idea of working with high concentrations and high current densities at low temperatures stems from the known electrolytic preparation (Ref. 11) of alkali metal peroxyidicarbonates from saturated aqueous $M_2CO_3$ at about -15 C. A minimum current density of 500 to 1500 ma/$cm^2$ is required to affect the anodic coupling of $CO_3^-$ and going to current densities of that magnitude promised to be beneficial in the present work.

(C) The product analyses reported for electrolysis No. 5 included an unidentified compound containing C, H, O, N, and F. Subsequent mass spectrometric analysis of the -95 C anolyte fraction from that electrolysis identified $CH_3OCH_3NF_2$ as one of the major constituents along with methyl formate, a small amount of methly acetate, HCN, $SiF_4$, $CH_2O$, and starting materials. The mass and infrared spectra of the difluoraminomethyl methyl ether was consistent with those reported by Rohm and Haas (Ref. 12).

(C) After clearing the mass spectrum of all the known N-F constituents, substantial residuals were noted for m/e 52 ($NF_2^+$) and 33 ($NF^+$). Because no $N_2F_4$ was found in the infrared spectrum of the fraction containing the ether, the residual peaks indicate the presence of at least one additional NF compound. (The mass spectra of $CHNF_2$ compounds such as $CH_3OCH_2NF_2$, $F_2NCH_2OCH_2NF_2$, and $CH_3OC(O)NF_2$ exhibit very weak m/e 52 peaks (0.5 to 2.3 percent) in relation to their $CH_3^+$ peak, m/e 15 (100 percent).)

(C) An electrolysis similar to electrolysis No. 5 was run on a somewhat larger scale in an effort to accumulate a larger quantity of anode products. The same cell and $Ag/Ag^+$ reference electrode were used in both cases. Although the electrolysis was conducted at a 10 C higher temperature and used a higher flowrate of carrier gas, only a small amount of product mixture other than $N_2F_4$ (22.7 cc) and solvent was swept out of the cell during the electrolysis. Mass spectrometric analysis indicated that the gaseous products, in addition to $N_2F_4$, consisted of $CH_3OCH_2NF_2$, $CH_3OCH(NF_2)OCH_3$, $CH_3OCH_2OCH_3$, and $HCO_2CH_3$ making a total volume of about 5 cc. No residual 52 or 33 m/e peaks were observed. Fractionation and analysis of the anolyte components revealed large amounts of unreacted $CH_3OH$, THF, and $HNF_2$ along with a small amount of $CH_3OCH_2OCH_3$ (8.7 cc).

(C) The nature and distribution of the products did not give a quantitative correlation with the amount of current passed; however, they do indicate that the oxidation of methanol is the major, if not the sole, anodic process taking place. Formation of the observed products can be explained in terms of a primary oxidation of methanol to a radical and a proton, followed by decomposition with other secondary chemical reactions occurring as follows:

$$CH_3OH \longrightarrow \cdot CH_2OH + H^+ + e^- \tag{30}$$

$$\cdot CH_2OH \longrightarrow CH_2O + 1/2\ H_2 \tag{31}$$

$$CH_3OH + CH_2O + H^+ \xrightarrow{H^+} CH_3OCH_2O^+H_2 \tag{32}$$

$$\left[CH_3OCH_2O^+H_2\right] \longrightarrow \left[CH_3OCH^+{}_2\right] + H_2O \tag{33}$$

$$\left[CH_3OCH^+{}_2\right] \begin{array}{l} \xrightarrow{HNF_2} H^+ + CH_3OCH_2NF_2 \\ \xrightarrow[CH_3OH]{} H^+ + CH_3OCH_2OCH_3 \end{array} \tag{34}$$

$$\left[CH_3OCH^+{}_2\right] \longrightarrow H^+ + CH_3OCHO \tag{35}$$

Other mechanisms certainly may be proposed, but further speculation is not warranted at this time. The important conclusion is that all $NF_2$ compounds identified are not formed through an oxidation coupling but by reactions of $CH_3OCH_2{}^+$ with $HNF_2$ and other species.

(C) Under the experimental conditions we had been using, the anodic oxidation of methanol proceeded at a higher rate and at a lower potential than did the oxidation of difluoramine. The only remedy already metntioned would be to maintain a high ratio of $HNF_2$ to $CH_3OH$, even to the extent of adding methanol incrementally to the anolyte during an oxidation of difluoramine. An alternate remedy rested on the possibility of lowering the oxidation potential of $HNF_2$ by using a complexing agent of stronger basicity than THF.

A cyclic voltammetric study of the $HNF_2$-pyridine complex in 0.5 M $KPF_6$/ acetonitrile at -20 C showed a distinct oxidation with peak current at 1.8 v vs $Ag/Ag^+$, approximately 1.0 v lower than the HNF·THF oxidation. Consideration was given to the possible detrimental effect of the increasing $H^+$ concentration during the electrolyses. The use of bases such as pyridine could serve a dual role; i.e., aid in the ionization of $HNF_2$ and remove the $H^+$ from the reaction medium.

(C) Representative polarization curves determined in acetonitrile solvent ($KPF_6$ added as the supporting electrolyte) are shown in Fig. 4 . The oxidation of acetonitrile (curve 1) occurred at approximately 3.2 v. The polarization curve determined in the presence of $HNF_2$ (curve 2) shows an oxidation wave at about 2.2 v. In the presence of the pyridine-$HNF_2$ complex (curve 3), an oxidation wave was obtained with a half-wave potential of approximately 1.45 v vs Ag/AgCl. Polarization curves determined at lower and lower scan rates resulted in curves similar in shape to curve 3. Note that even under steady-state conditions there was a marked fall-off in current at about 2.0 v indicating that there was no limiting diffusion current in the conventional sense. Extended electrolysis conducted in the region before the peak (e.g., between 1.7 and 2.0 volts) resulted in the quantitative production of $N_2F_4$ (Table 5 No. 9). Thus, $HNF_2$ was being oxidized at potentials well below the decomposition of solvent and, in fact, about 0.7 volt lower than the oxidation of $HNF_2$ in the absence of pyridine. Under these conditions, the anodic reaction can be represented by:

$$C_5H_5N{:}HNF_2 \longrightarrow C_5H_5NH^+ + 1/2\ N_2F_4 + e^- \qquad (36)$$

(C) A typical polarization curve determined on a smooth platinum microelectrode (Fig. 5 ) showed that the methanol oxidation in acetonitrile (curve 1) was shifted to higher potentials in the presence of pyridine (curve 2). The oxidation curve for the Py: $HNF_2$ complex in the presence of $CH_3OH$ (curve 3) is similar in shape to curve 3, Fig. 4 except that the fall-off in current at potentials greater than 2.0 v was not as severe. Extended electrolysis

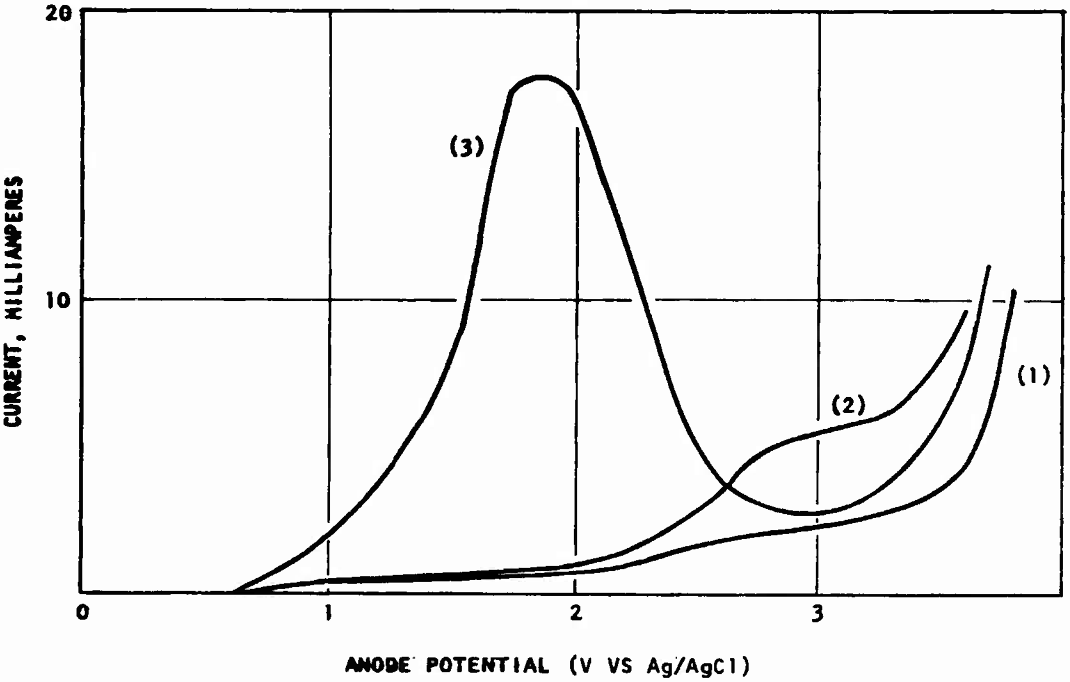


**Figure 4.** Potentiostatic Polarization Curves on Plantinized Platinum Anode (2.38 $cm^2$) vs Ag/AgCl Reference Electrode in 0.4 M $KPF_6/CH_3CN$ at -30 C Contain:

1. 0.2 M $C_5H_5N$ scanned at 50 V/hr
2. 0.1 M $HNF_2$ scanned at 15 V/hr
3. 0.1 M $C_5H_5N:HNF_2$ and 0.1 M $C_5H_5N$ scanned at 1.5 and 5.0 V/hr

## TABLE 5

### THE ELECTROLYSES OF $C_5H_5N:HNF_2$ ALONE AND WITH $CH_3OH$ IN ACETONITRILE

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode | | | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Material and Area | Potential (V) vs Ag/AgCl | Current Density, ma/$cm^2$ | | |
| 9 | 0.4 M $KPF_6$ in $CH_3CN$ | 0.1 M $HNF_2$<br>0.2 M $C_5H_5N$ | -22 | Pt/Pt (2.38 $cm^2$) | 1.7 to 2.0v vs Ag/AgCl | 2.5 | | Product: $N_2F_4$ (100 percent yield) |
| 10 | 0.4 M $KPF_6$ in $CH_3CN$ | 0.1 M $HNF_2$<br>0.2 M $C_5H_5N$<br>0.5 M $CH_3OH$ | -35 | Same | 3.2v vs Ag/AgCl | 4.2 | 1.5 | Products: $N_2F_4$ (1.6 cc) $CH_3ONO$ (0.1 cc) |

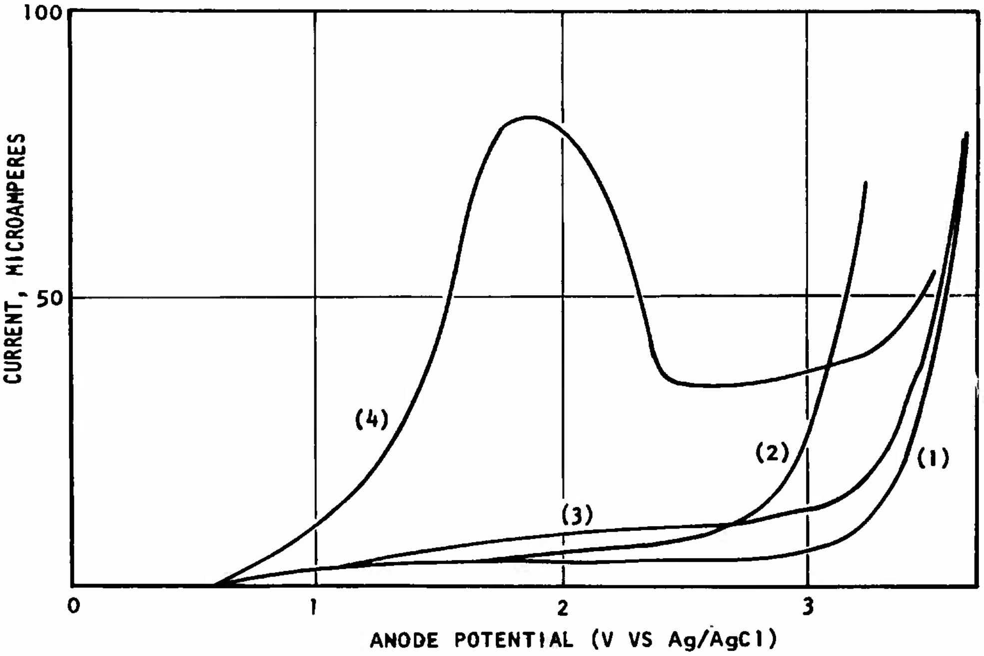


Figure 5. Potentiostatic Polarization Curves on a Smooth Platinum Anode (0 11 $cm^2$) vs Ag/AgCl Reference Electrode in 0.4 M $KPF_6/CH_3CN$ at -32 C Without Stirring, Scan Rate 833 mv/min

1. Solvent System Alone
2. 0.13 M $CH_3OH$
3. 0.13 M $CH_3OH$ and 0.14 M $C_5H_5N$
4. 0.50 M $CH_3OH$, 0.11 M $C_5H_5N$ and 0.03 M $C_5H_5N{:}HNF_2$

(macroscale) conducted at 3.2 v vs Ag/AgCl (curve 3) resulted in the formation of only a small quantity of $N_2F_4$ (Table 5 , No. 10). This low yield of $N_2F_4$ indicates the onset of passivity at potentials between 2.5 and 3.2 v. This is in agreement with the analysis of polarization curves determined at varying scan rates. Our data indicate that the passivity only occurs in a specific potential range and that the electrode completely returns to normal between consecutive scans. The fact that curve 3 reaches a low level diffusion current between 2.5 and 3.2 v may indicate the onset of cooxidation; however, the passivity of the electrode to the Py:$HNF_2$ oxidation severely limits the utility of these conditions. It appears, then that pyridine adhering to the electrode surface cannot complex $HNF_2$ inasmuch as we would have an electrode which presumably would be very rich in difluoramino radicals at relatively low potentials.

(C) The effect of pyridine on the anodic oxidation of methanol in 0.25 M $NaBF_4/CH_3OH$ solution was studied by means of potentiostatic polarization data as shown in Fig. 6 . The oxidation of the "neutral" methanolic solvent system took place at potentials below 1.9 v vs Ag/AgCl, curve (1). The addition of 0.2 M $C_5H_5N$ created a different electrode surface on which the overpotential for $CH_3OH$ oxidation was increased by approximately 0.7 v, curve (2). The final solution containing 0.2 M $C_5H_5N$ and 0.1 M $C_5H_5H:HNF_2$ exhibited a well-formed oxidation wave for the Py:HNF complex with approximately the same half-wave potential as obtained in acetonitrile and propiontrile solutions.

(C) Extended electrolysis of methanolic solution of Py:$HNF_2$ in the potential region of 1.5 to 2.5 v on curve 3, Fig. 6 gave approximately an 80 percent yield of $N_2F_4$ (Table 6 , No. 11). This result dramatically demonstrated the effective inhibition of the methanol oxidation at potentials below 2.5 v in methanol and further suggests that a region of cooxidation may exist at potentials greater than 2.0 v vs Ag/AgCl.

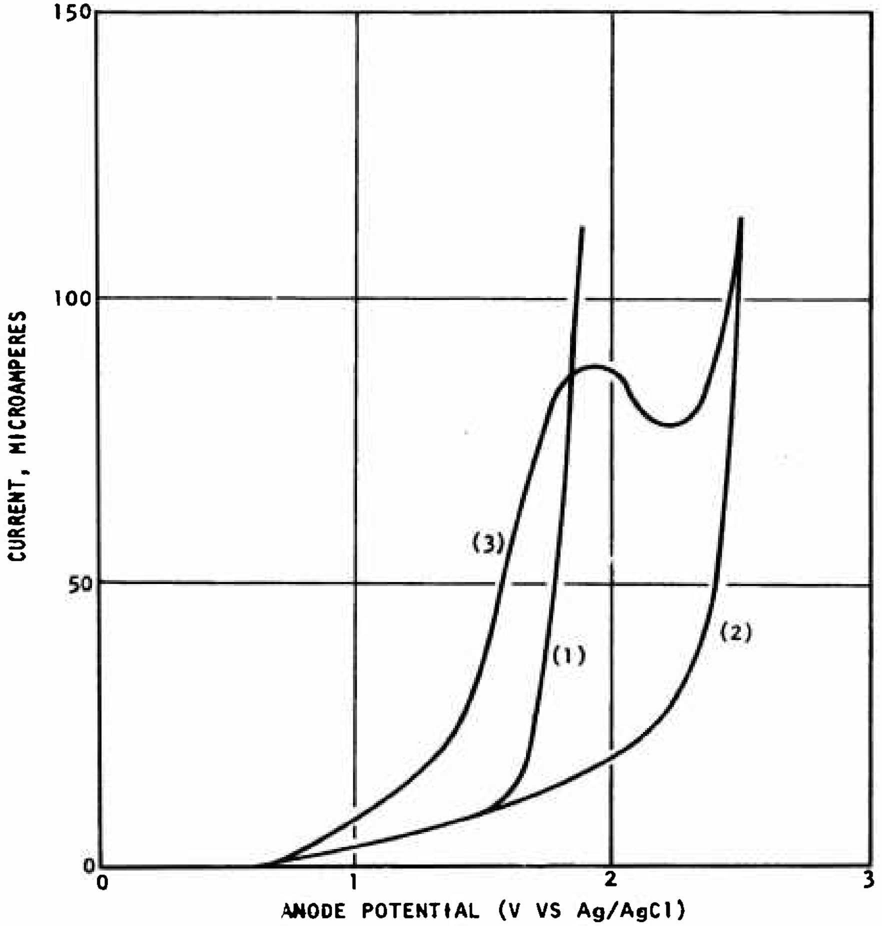


Figure 6. Potentiostatic Polarization Curves on a Smooth Platinum Anode (0.11 $cm^2$) vs Ag/AgCl Reference Electrode in 0.25 M $NaBF_4/CH_3OH$ at -28 C Without Stirring, Scan Rate 833 mv/min

1. Solvent System Along
2. 0.2 M $C_5H_5N$
3. 0.2 M $C_5H_5N$ and 0.1 M $C_5H_5N:HNF_2$

TABLE 6

THE ELECTROLYSES OF $C_5H_5N\ HNF_2$ ON PLATINUM IN METHANOL ALONE AND IN METHANOL CONTAINING $NaB(OCH_3)_4$

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode |  |  | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Material and Area | Potential (V) vs Ag/AgCl | Current Density, $ma/cm^2$ |  |  |
| 11 | 0.25 M $NaBF_4$ in $CH_3OH$ | 0.1 M $HNF_2$<br>0.4 M $C_5H_5N$<br>$CH_3OH$ M Solvent | -37 | Same | Cycled 1.5 to 2.5v vs | 1.7 av | 0.6 | Products: $N_2F_4$ (5.5 cc) $CH_3ONO$ (0.1 cc), traces of $N_2O$ and $CO_2$ |
| 13 | 0.25 M $KPF_6$ in $CH_3OH$ | 0.1 M $HNF_2$<br>0.2 M $C_5H_5N$ | -20 | Pt/Pt (2.38 $cm^2$) | 2.2 to 3.7v vs Ag/AgCl | 3.3 | 0.77 | Products: $N_2F_4$ (~0.05 mmole), $CH_3ONO$ (~0.1 mmole) |
| 14 | 1.0 M $LiClO_4$ in $CH_3OH$ | 0.2 M $HNF_2$<br>0.2 M $C_5H_5N$ | -16 | Same | 2.0 ±0.2 v vs Ag/AgCl | 1.26 | 0.57 | Products: $N_2F_4$ (~0.05 mmole), no $CH_3ONO$ or any evidence of perchlorate precipitation |
| 15 | Sat. $NaBF_4$ in $CH_3OH$ | 0.2 M $HNF_2$<br>0.2 M $C_5H_5N$<br>0.9 M $NaB(OCH_3)_4$ | -20 | Same | 1.4 to 2.2v vs Ag/AgCl 2.0v av | 1.0 av | 0.48 | Products: $N_2F_4$ (0.25 mmole, 100 percent), traces of $CH_3ONO$ and $N_2F_4$ |

The methanolic solution of Py:$HNF_2$ appeared to create the conditions for the success of the desired coupling reaction. If we assumed that the methoxylation of pyridine did not occur or played only a minor role in the electrode process, we could readily vary the relative rates of oxidation of $CH_3OH$ and Py:$HNF_2$ and thereby control the amounts of their respective oxidation products adsorbed on the electrode surface.

(C) Thus, the next step was to confirm through macroscale electrolyses the oxidation of $HNF_2$ and $CH_3OH$ in the presence of pyridine at anode poetntials corresponding to characteristic regions of the steady-state polarization curves already obtained. The experimental details of the macroscale electrolyses are presented in Table 6.

(C) Previously we had observed small amounts of $CH_3ONO$ in the electrolysis products from both $CH_3CN$ and $CH_3OH$ solvent systems and postulated that it may represent the capture of $CH_3O\cdot$ radicals by NO rather than the decomposition of $CH_3ONF_2$. The objective of electrolysis No. 12 was to determine whether nitric oxide itself would resist oxidation under the conditions where it was thought to act as a methoxy radical scavenger. If NO were readily oxidized to $NO^+$, one would expect a subsequent reaction with methanol (rather than $CH_3O\cdot$) to produce $CH_3ONO$, as in the equation,

$$NO^+ + CH_3OH \longrightarrow CH_3ONO + H^+ \qquad (37)$$

In this case, the formation of $CH_3ONO$ could not serve as evidence for methoxy radical generation.

(C) Electrolysis No. 12 (Table 7 ) consisted of potentiostatic polarization scan from 0.7 to 2.7 v vs Ag/AgCl and back at 250 mv/min on an acetonitrile solution saturated with nitric oxide at -35 C. A well-defined oxidation wave was obtained with a half-wave potential at 1.35 v. The anolyte became a dark blue solution suggesting the presence of a nitroso compound such as $CH_3NO$ or $ONCH_2CN$. The products swept out of the cell after the

TABLE 7

THE ELECTROLYSIS OF NITROGEN OXIDE (NO) IN ACETONITRILE

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode | | | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
| | | | | Material and Area | Potential (V) vs Ag/AgCl | Current Density, ma/cm2 | | |
| 12 | 0.4 M $KPF_6$ in $CH_3CN$ | Saturated with NO | -35 | Pt/Pt 2.38 $cm^2$ | Linear Scan from 0.7 to 2.7v vs Ag/AgCl and back | 11.4 maximum | | Products: $N_2O$ and $CH_3ONO$ found. Blue color indicated a nitroso compound. Scan rate 250 mv/min. Electrolysis time 16 minutes. |

16-minute scan were identified as $CH_3ONO$ and $N_2O$ in quantities indicative of a chain reaction mechanism.

(C) Therefore, the formation of $CH_3ONO$ during an oxidation of $HNF_2$:Py in either methanol or acetonitrile perhaps needed further clarification. We had concluded that the formation of methyl nitrite must have come from the decomposition of the desired $CH_3ONF_2$. In light of the above, NO, derived from undetermined impurities, may account for some of the $CH_3ONO$ observed.

(C) We had already made some progress towards distinguishing between these two possibilities. If nitric oxide were indeed present during an oxidation of $HNF_2$:Py, it would have to arise from a chemical reaction of $\cdot NF_2$ radicals with $O_2$ or some oxygen source adsorbed on the electrode. Assuming no quantity limit on the oxygen source, the rate of NO formation would be related to rate of $HNF_2$ oxidation regardless of anode potential, and $CH_3ONO$ would be produced along with $N_2F_4$ even in the low potential regimes where the discharge of $CH_3OH$ or $B(OCH_3)_4-$ does not occur. On the other hand, if $CH_3ONO$ actually represented the decomposition of $CH_3ONF_2$, it would only be found in an electrolysis at potentials high enough for cooxidation.

(C) Refering again to Table 6 , a comparison of the product yields in electrolysis No. 13, 14, and 15 indicated that the higher potentials favor $CH_3ONO$ formation on a platinum anode and tended to support the $CH_3ONF_2$ decomposition theory.

(C) The electrolysis of $HNF_2$-pyridine on graphite in methanol containing $NaB(OCH_3)_4$ gave a material/current balance in terms of the two major volatile products, $N_2F_4$ and $CH_3ONO$ (Table 8 , electrolysis No. 16), and we again postulated that the methyl nitrite was a decompsotion product of the desired $CH_3ONF_2$.

(C) Five macroscale electrolyses in methanolic systems are represented graphically in Fig. 7 to show the general relationship of $N_2F_4$ yield with anode potential range. On platinum, the drop off in $N_2F_4$ yield with

## TABLE 8

### THE ELECTROLYSES OF $(CH_3)_2C_5H_3N{:}HNF_2$ ON GRAPHITE IN METHANOL ALONE AND IN METHANOL CONTAINING $NaB(OCH_3)_4$

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode |  |  | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Material and Area | Potential (V) vs Ag/AgCl | Current Density, ma/cm$^2$ |  |  |
| 16 | Sat. $NaBF_4$ in $CH_3OH$ | 0.1 M $HNF_2$<br>0.2 M 2,6-lutidine,<br>0.9 M NaB $(OCH_3)_4$ | -20 | Pyrolytic Graphite (G.E.) (5.0 cm$^2$) | 2.2 ±0.2v vs Ag/AgCl | 1.0 to 4.0 | 1.7 | Products: $N_2F_4$ (0.25 mmole, 29 percent), $CH_3ONO$ (0.56 mmole, 65 percent). Pulsed current |
| 17 | 1.0 M $LiClO_4$ in $CH_3OH$ | 0.1 M $HNF_2$<br>0.2 M 2,6-lutidine | -27 | Pyrolytic Graphite 1.44 cm$^2$ | 1.4v vs Ag/AgCl | 8.7 | 1.86 | Products: $N_2F_4$ (18.2 cc, 0.81 mmole, 89.3 percent), trace of $CH_3ONO$. |
| 18 | 1.0 M $LiClO_4$ in $CH_3OH$ | 0.2 M $HNF_2$<br>0.2 M 2,6-lutidine | -24 | Same | 1.9v vs Ag/AgCl | 69.5 | 6.5 | Products: $N_2F_4$ (39 cc, 1.74 mmoles, 54 percent), traces of $CH_3ONO$ and a carbonyl compound |

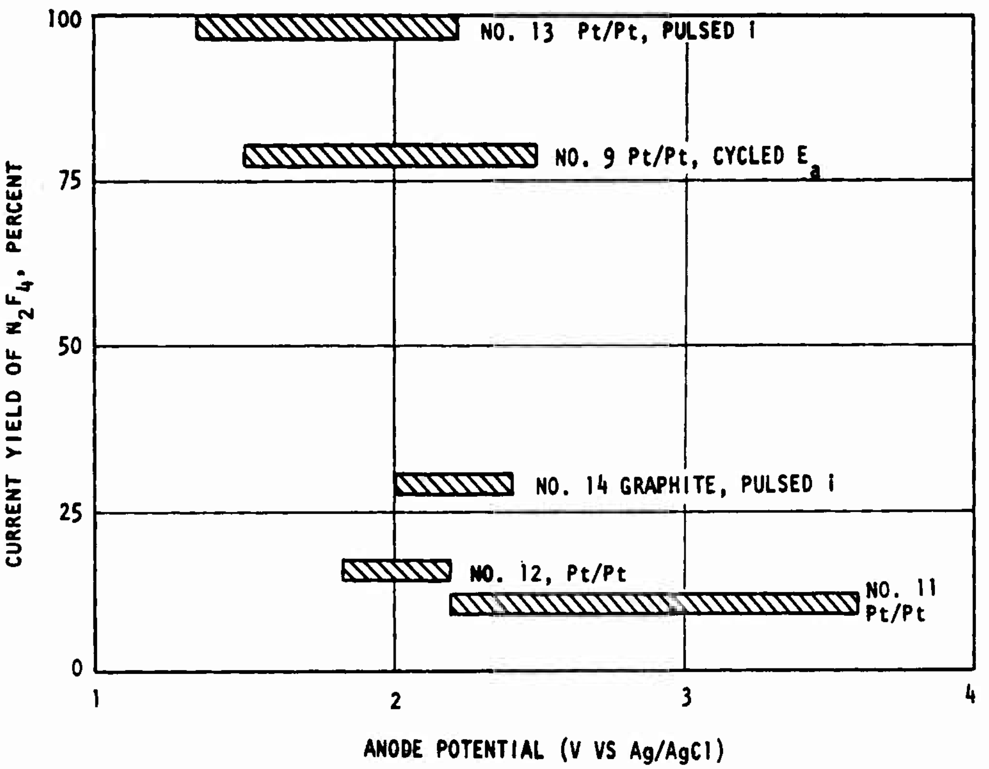


Figure 7. General Relationship of the Yield of $N_2F_4$ With the Anode Potential Range in Various Methanolic Systems

increasing potential is accompanied by extremely poor overall material balance. This probably represents the onset of passivity towards the $HNF_2$:Py oxidation and the oxidation of solvent becoming the major anodic process. The yield of $N_2F_4$ on graphite appears to fit the pattern well; however, the high yield of $CH_3ONO$ may indicate the onset of cooxidation without an accompanying passivation of the $HNF_2$:Py oxidation.

(C) An oxidation at low potential (Table 8 , No. 17) of $HNF_2$:2,6-lutidine on graphite in methanol gave a high yield of $N_2F_4$ and only a trace of $CH_3ONO$. This result demonstrated that $CH_3ONO$ formation on graphite was not due to the chemical conversion of $\cdot NF_2$ to NO or $NO^+$ in the presence of various possible oxygen sources on the anode surface, such as $O_2$, $HO\cdot$ or [CHO], followed by a reaction of NO or $NO^+$ with the solvent. Thus, the fact that $CH_3ONO$ was only formed at anode potentials high enough for cooxidation again substantiated the thesis that it resulted from the decomposition of $CH_3ONF_2$.

(C) Macroscale electrolysis No. 18 represents a cooxidation of $HNF_2$:2,6-lutidine and $CH_3OH$ in the absence of $B(OCH_3)_4^-$. The production of $N_2F_4$ (54 percent) and only a trace of $CH_3ONO$ indicated that little or none of the desired $CH_3ONF_2$ was formed and strongly suggested that the $B(OCH_3)_4^-$ anion was the methoxy radical source in electrolysis No. 16. Evidently the oxidation of methanol under neutral or weakly basic conditions resulted almost exclusively in C-H bond cleavage and the products are esters and ethers which cannot be readily separated from the solvent.

(C) We concluded that the mildly basic $B(OCH_3)_4^-$ anion was an efficient reagent for the anodic generation of methoxy radicals, as in the equation,

$$B(OCH_3)_4^- \longrightarrow B(OCH_3)_3 + CH_3O\cdot + e^- \qquad (38)$$

and that the cooxidation of $HNF_2$:base and $B(OCH_3)_4^-$ resulted in the formation of $CH_3ONF_2$ which completely decomposed giving $CH_3ONO$ in the electrochemical system. Of course, the anolyte environment may not be consistent with good compatibility with $RONF_2$ species.

(C) The apparent non-passivation of the base-$HNF_2$ oxidation on graphite was believed to be the key difference between the behavior of the two electrode materials. The polarization curves (Fig. 8 ) clearly showed that the anodic oxidation characteristics of a graphite electrode (spectro grade, Ultra Carbon Corp.) are significantly different from those of a platinum electrode involving the same electro active species. Notice in curve 1 that gross decomposition of the solvent occurred around 2.0 v vs Ag/AgCl making the apparent useful anodic range of the acetonitrile system approximately 1 volt narrower than the range observed with a platinum electrode. Curves 2 and 3 revealed that $HNF_2$ alone or 2,6-lutidine alone contributed only a minor oxidation current. Curve 4 represents the oxidation of the $HNF_2$:2,6-lutidine complex. The half-wave potential is approximately 1.40 v vs Ag/AgCl. In curve 4, the ascending and descending scans at 120 mv/min traced almost the same path indicating that the wave represents very nearly the steady-state reversible rate values for the reaction within the potential range shown. The oxidation on graphite apparently took place with a very low activation overpotential. In contrast, the pseudo half-wave potential of 1.45 v for the same reaction on platinum was probably observed too low due to the onset of passivation at potentials above 2.0 v vs Ag/AgCl.

(C) Because of the low overpotentials required on graphite, its narrow anodic range in acetonitrile is probably no less useful than the wider range of platinum in acetonitrile. In fact, if the low potential electrolysis (No. 15, Table 6 ) had been run on graphite, it is very likely that co-oxidation of $HNF_2$:base and $B(OCH_3)_4^-$ would have occurred.

### (C) The Anodic Oxidation of $HNF_2$ and Picrates

Because the theoretical stability of various target $RONF_2$ compounds may directly related to the relative electronegativity of the R group, we extended our anodic polarization studies to carbinols having highly electronegative alkyl and aryl structures. The polarization curves obtained in acetonitrile containing three carbinols in the presence of

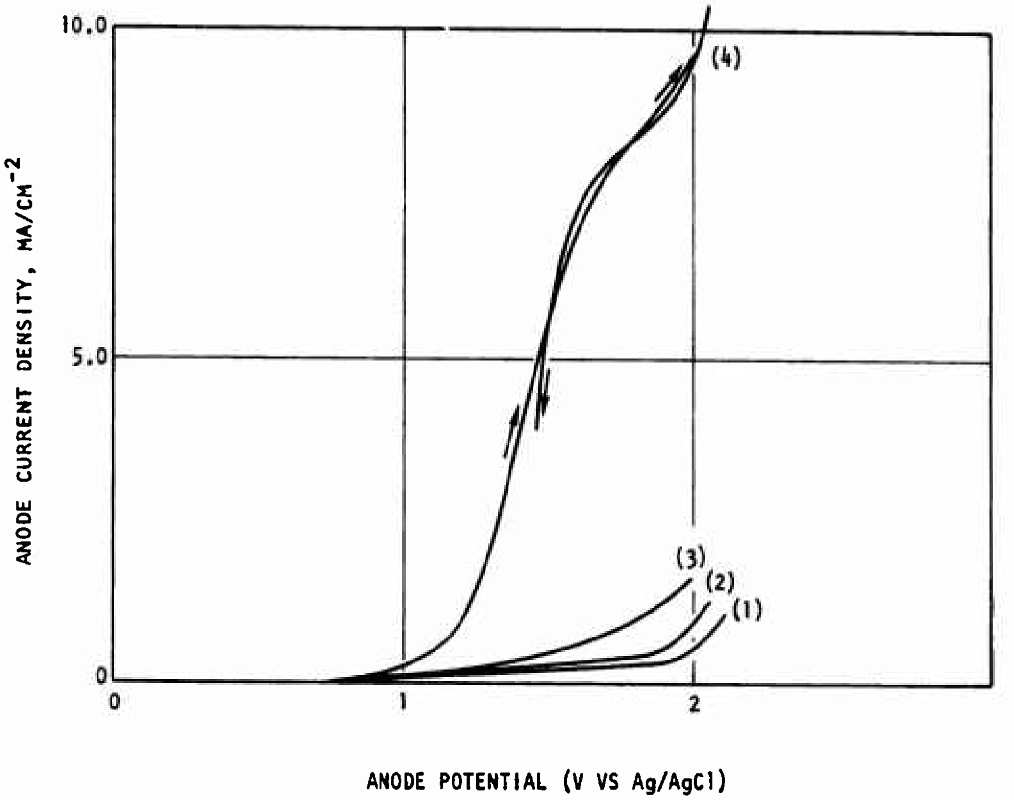


Figure 8. Potentiostatic Anodic Polarization Curves on Graphite (0.14 cm$^2$), Scan Rate 120 mv/min, Temperature -28 C

1. Solvent System, 0.84 M $LiBF_4/CH_3CN$
2. 0.1 M $HNF_2$ in Solvent System
3. 0.2 M 2,6-Lutidine in Solvent System
4. 0.1 M $HNF_2$ and 0.2 M 2,6-Lutidine in Solvent System

2,6-lutidine are presented in Fig. 9 . Curve 1 represents the anodic polarization of graphite in a 0.84 M $LiBF_4/CH_3CN$ solution. Curves 2, 3, and 4 were obtained after the successive additions of 2,6-lutidine, $CF_3CH_2OH$ and $C_2F_5CH(OH)_2$. Only a low-level oxidation of lutidine took place at potentials under 2.0 v vs Ag/AgCl. There seemed to be very little interaction between lutidine and the weakly acidic fluorocarbinols. The addition of the very strong acid, picric acid, undoubtedly resulted in the formation of 2,6-lutidinium picrate. The oxidation of the picrate anion is represented by curve 5. Thus, picric acid appeared useful in anodic oxidative coupling with $HNF_2$ using the graphite/acetonitrile system and the complexing agent, 2,6-lutidine. The possibility of using a different basic catalyst (1,4-diazabicyclo [2,2,2] octane), to activate trifluoroethanol for anodic oxidation was tested. Again polarization data indicated that there was no oxidation of the alcohol on a graphite anode. The absence of an oxidation with free alcohols demonstrated that an anionic derivative was required for the anodic oxidation of an electronegatively substituted carbinol.

(C) In undertaking the study of a picric acid derivative we had been immediately confronted by some familiar obstacles. The high half-wave potential, 1.76 v vs Ag/AgCl, and the low solubility of lutidinium picrate in acetonitrile both indicated that a cooxidation with an $HNF_2$ complex and graphite would be difficult to obtain. Electrolysis No. 19 in Table 9 presents the data on an experiment which was carried through in spite of the initial precipitation of lutidinium picrate or potassium picrate from the anolyte solution. The polarization curves taken just prior to the electrolysis are presented in Fig. 10 where an oxidation wave (curve 2) presumably represents the discharge of the picrate ion in solution. The subsequent addition of $HNF_2$ gave the broad wave (curve 3) indicating a high rate of $HNF_2$ oxidation relative to that of the sparingly soluble picrate. The product found after the passage of 2.46 mF was $N_2F_4$ in a 93 percent yield based on current. This result confirmed that little if any cooxidation had been realized.

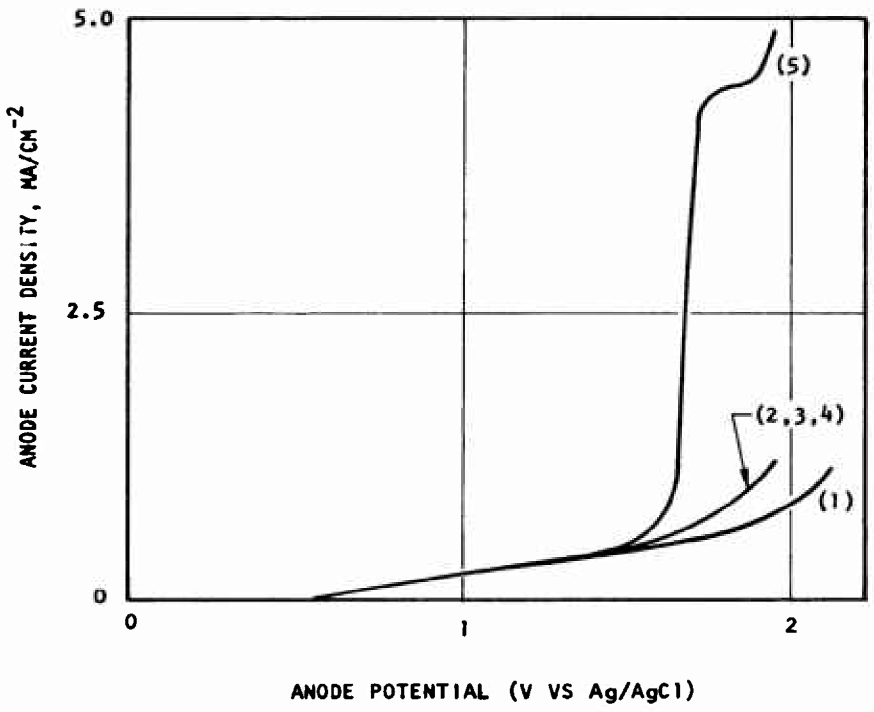


Figure 9. Potentiostatic Anodic Polarization Curves on Graphite ($0.14$ cm$^2$), Scan Rate 120 mv/min, Temperature -28 C

1. Solvent System, 0.84 M $LiBF_4/CH_3CN$ Followed by Successive Additions of:
2. 2,6-Lutidine
3. $CF_3CH_2OH$
4. $C_2F_5CH(OH)_2$
5. Picric Acid

TABLE 9

THE ELECTROLYSES OF PICRATES WITH $HNF_2$ IN ACETONITRILE

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode |  |  | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Material and Area | Potential (V) vs Ag/AgCl | Current Density, ma/cm$^2$ |  |  |
| 19 | 0.4 M $KPF_6$ in $CH_3CN$ | 0.08 M $HNF_2$<br>0.2 M 2,6-Lutidine<br>Picric Acid (10 mmole) | -25 | Graphite 1.8 cm$^2$ | 1.92 | 6 ±1 | 2.46 | Total $HNF_2$ (4.7 mmoles) added in three equal portions during 6-hour electrolysis. Precipitate of picrate formed with the addition of 2,6-lutidine. Product: $N_2F_4$ (1.15 mmole) 93 percent. |
| 20 | 0.8 M $LiBF_4$ in $CH_3CN$ and THF (5:1) | 0.03 M $HNF_2$<br>0.25 M Na-<br>0.1 M Pyrid. | -25 | G.E. Pyrolytic Graphite 2.25 cm$^2$ | 2.00 | 3.5 ±0.5 | 1.04 | Total $HNF_2$ (1.2 mmoles) added. Products: $N_2F_4$ (0.38 mmole), 73 percent; trace of $CH_3ONO$. Some picrate precipitation occurred when cooling cell. |
| 21 | 0.25 M $NaPF_6$ in $CH_3CN$ and THF (3:1) | 0.08 M $HNF_2$<br>0.25 M Na- | +15 | Pt/Pt 2.38 cm$^2$ | 2.23 | 17 ±18 | 2.07 | Products: $N_2F_4$ (0.19 mmole) 18 percent; trace of $CH_3ONO$. nmr and ir analyses were negative for $RONF_2$, $RNF_2$ and RF products. |

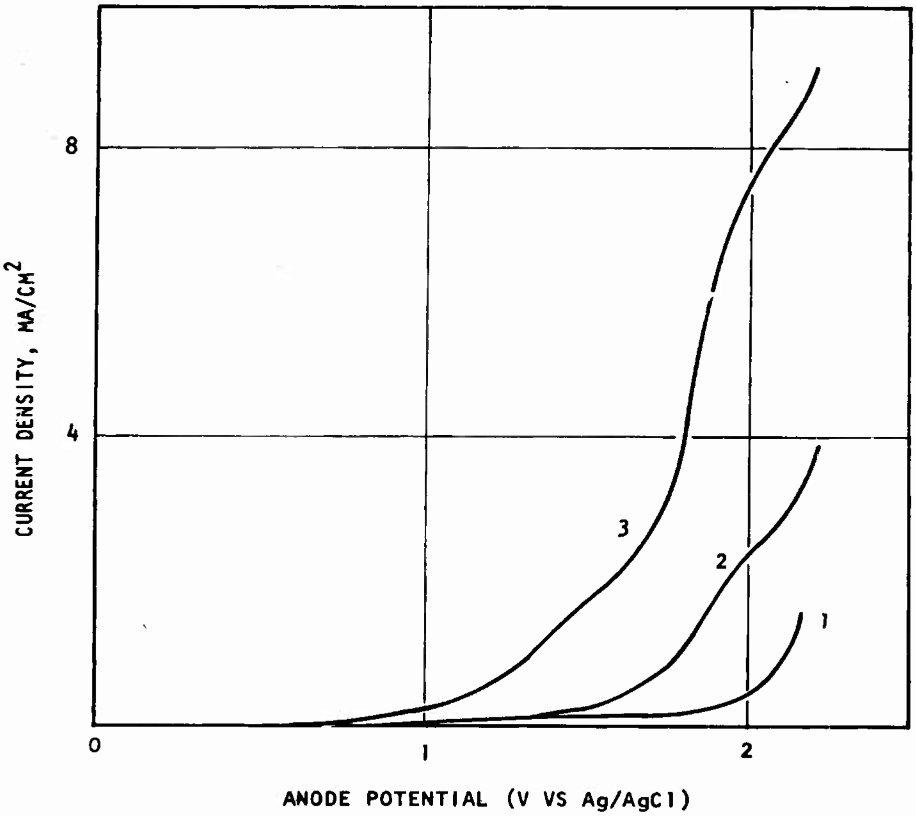


Figure 10. Anodic Polarization Curves on Spectro-Grade Graphite ($1.8\ cm^2$), Scan Rate 120 mv/min, Temperature -25 C

1. 0.5 M Picric Acid/0.4 M $KPF_6$ in $CH_3CN$ Anolyte (20 ml) Followed by Successive Additions of:
2. 2,6-Lutidine (4.0 ml) (Picrate Precipitate Formed)
3. $HNF_2$ (35 cc); the Point on Curve No. 3 at 192 V vs Ag/AgCl Represents the Initial Conditions of Electrolysis No. 19

(U) A small amount of anhydrous sodium picrate was prepared to determine its solubility and oxidation characteristics in acetonitrile. This salt was found to be only slightly soluble in a $LiBF_4/CH_3CN$ solution; however, during the subsequent investigation, tetrahydrofuran was found to be an effective solubilizing additive. Preliminary compatibility tests indicated that pyridine, but not 2,6-lutidine, was compatible with sodium picrate. Also, anodic polarization in a sodium picrate solution caused the rapid disintegration of an Ultra Carbon Corporation (spectro grade) graphite anode. General Electric's pyrolytic graphite proved to be structurally stable under the same conditions.

(U) Figure 11 represents a series of potentiostatic polarization curves on a pyrolytic graphite anode in acetonitrile with increasing concentration of sodium picrate. Curves 2, 3, and 4 clearly show the increasing height of the diffusion current plateau with increasing picrate concentration. Curve 5 demonstrates that the limited solubility of the picrate in acetonitrile can be overcome by the addition of THF. Because THF is not a particularly good ionizing solvent, we suspected the formation of solvated ion pairs which, if true, apparently offered no inhibition of the picrate oxidation, as can be seen by the final level of the diffusion plateau. A lowering of the viscosity of the solution by THF may result in an increased mobility of the ions present. THF itself undergoes oxidation on graphite at potentials very close to that of solvent decomposition as shown in Fig. 12 , curve 2.

(C) The next objective was to establish the conditions most favorable to a cooxidation of the picrate and an $HNF_2$ complex. The obvious first choice was the $THF:HNF_2$ complex because earlier work with platinum anodes showed that its oxidation would occur only at relatively high potentials. However, anodic polarization curve 3 in Fig. 12 shows that no oxidation of the $THF:HNF_2$ complex will occur on G.E. pyrolytic graphite within the anodic range of the solvent systems. This unexpected result made necessary the use of the $pyridine:HNF_2$ complex in attempting to "engineer" a cooxidation on graphite. The rate of the highly efficient $Py:HNF_2$ oxidation

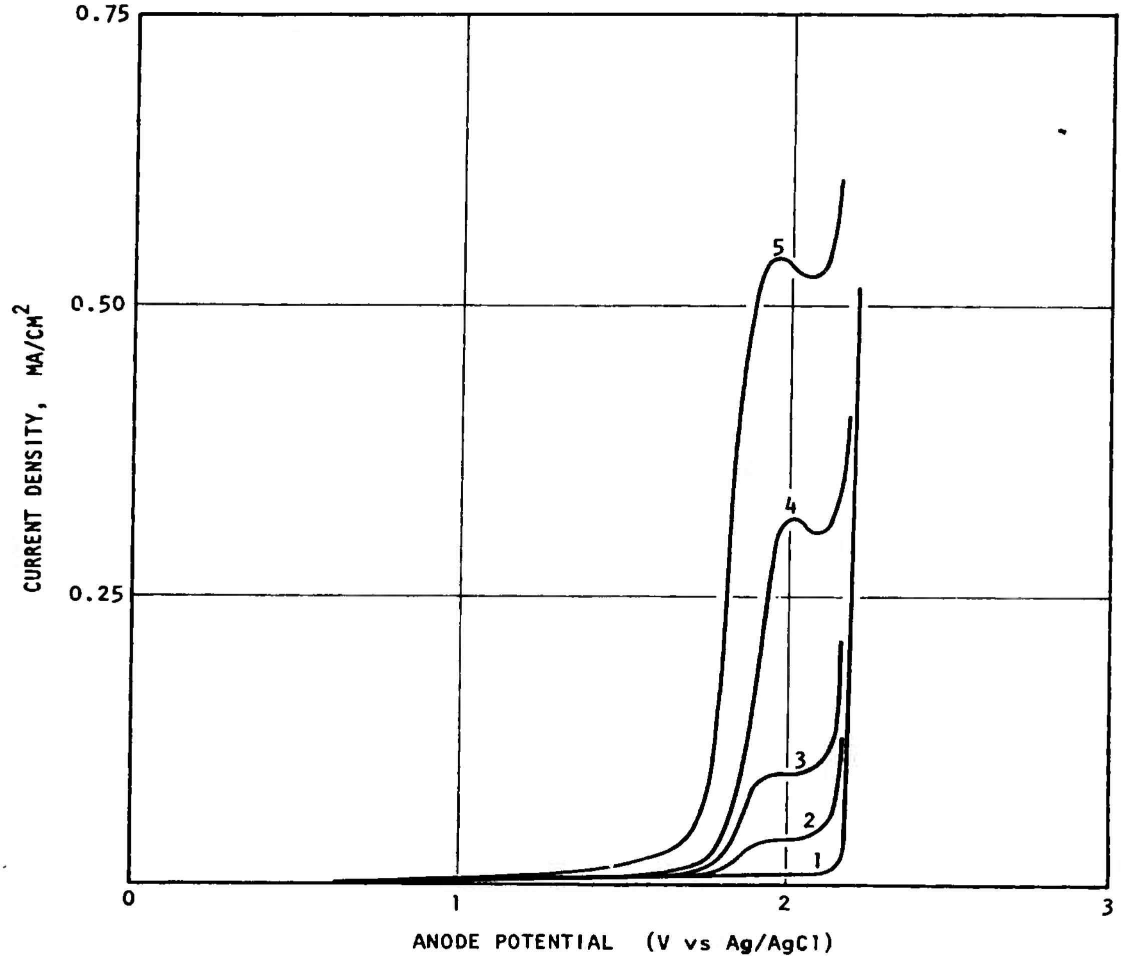


Figure 11. Anodic Polarization Curves on G.E. Pyrolytic Graphite ($2.25 \text{ cm}^2$), Scan Rate 120 mv/min, Temperature ~25 C

1. 0.84 M $LiBF_4$ in $CH_3CN$ Anolyte (20 ml) Followed by the Successive Additions of:
2. Saturated Sodium Picrate in $CH_3CN$ (0.25 ml)
3. Saturated Sodium Picrate in $CH_3CN$ (0.50 ml)
4. Excess Solid Sodium Picrate
5. $(CH_2)_4O$ (5.0 ml) Making a Homogeneous Anolyte Solution

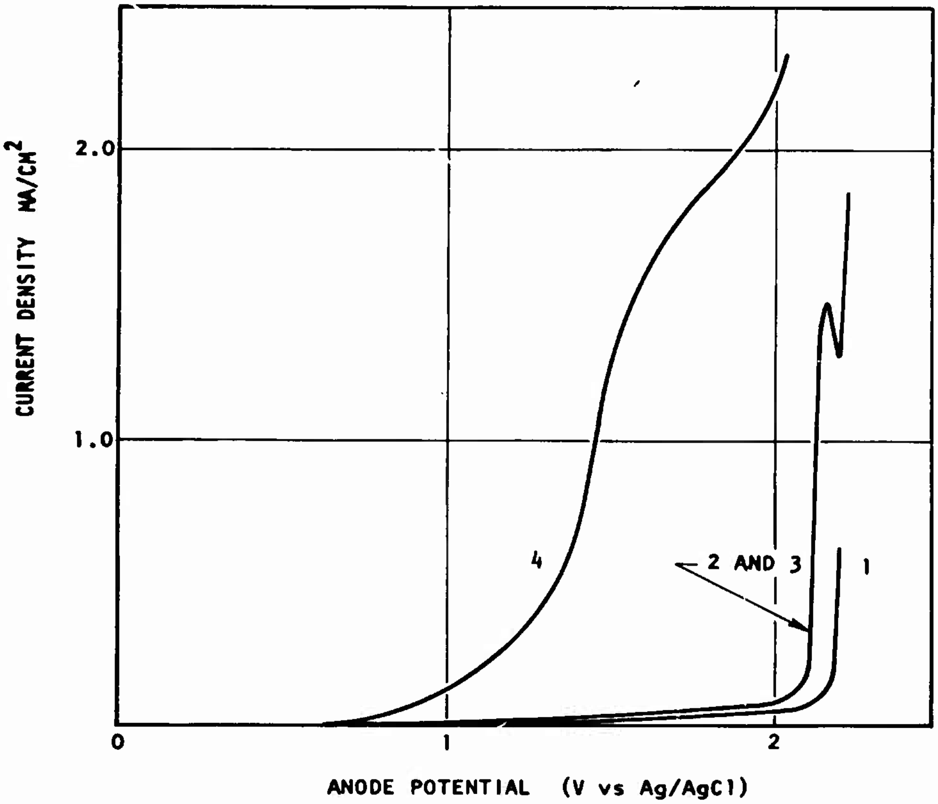


Figure 12. Anodic Polarization Curves on G.E. Pyrolytic Graphite ($2.25\ cm^2$), Scan Rate 120 mv/min, Temperature -25 C

1. 0.84 M $LiBF_4$ in $CH_3CN$ Anolyte (20 ml) Followed by Successive Additions of:
2. $(CH_2)_4O$ (5.0 ml)
3. $HNF_2$ (35 cc)
4. Pyridine (1.0 ml)

would have to be controlled by limiting the reagent concentrations. Curves 4 in Fig. 12 shows that the oxidation of Py:$HNF_2$ on G.E. pyrolytic graphite can achieve appreciable rates at relatively low potentials.

(C) In Fig. 13 , the two curves depict the approximate oxidation rate relationship of picrate and Py:$HNF_2$ at various potentials when the molar ratio of picrate to $HNF_2$ was 10:1 and excess pyridine was present. The point on curve 2 at 2.0 v vs Ag/AgCl represents the initial conditions of electrolysis 20 in Table 9 . The 73 percent yield of $N_2F_4$ based on current indicated only moderate success in the effort to hold back the rate of $HNF_2$ oxidation relative to that of picrate. Except for a trace of methyl nitrite, no other product was found in the volatile fractions of the anolyte. A diethyl ether extract of the solid residue was analyzed by $F^{19}$ nmr using a Freon 11 internal standard. There was no indication in the spectrum of an $RONF_2$, $RNF_2$ or RF type of product.

(C) Because the electrolyses with sodium picrate and $HNF_2$ gave no indication of a coupling, we could only conclude from this short study that the picrate structure was probably unsuitable for a radical coupling type of reaction. No further work was done on the picrate systems.

## (C) Anodic Oxidation of $HNF_2$ and Trifluoroethoxide

The effort to prepare a hydrocarbon-$ONF_2$ derivative was extended to a study of a fluoroalkoxide as a possible coreactant in an anodic coupling reaction with $HNF_2$. Three anionic derivatives of 2,2,2,-trifluoroethanol were prepared, these being $CF_3CH_2ONa$, $NaB(OCH_2CF_3)_4$ and the mixed borohydride, $NaB(OCH_3)_3OCH_2CF_3$. The latter two compounds were not found in the literature and were prepared by the following reactions:

$$CF_3CH_2OH + NaBH_4 \longrightarrow NaB(OCH_2CF_3)_4 + 4H_2 \qquad (39)$$

$$CF_3CH_2ONa + B(OCH_3)_3 \longrightarrow NaB(OCH_3)_3OCH_2CH_3 \qquad (40)$$

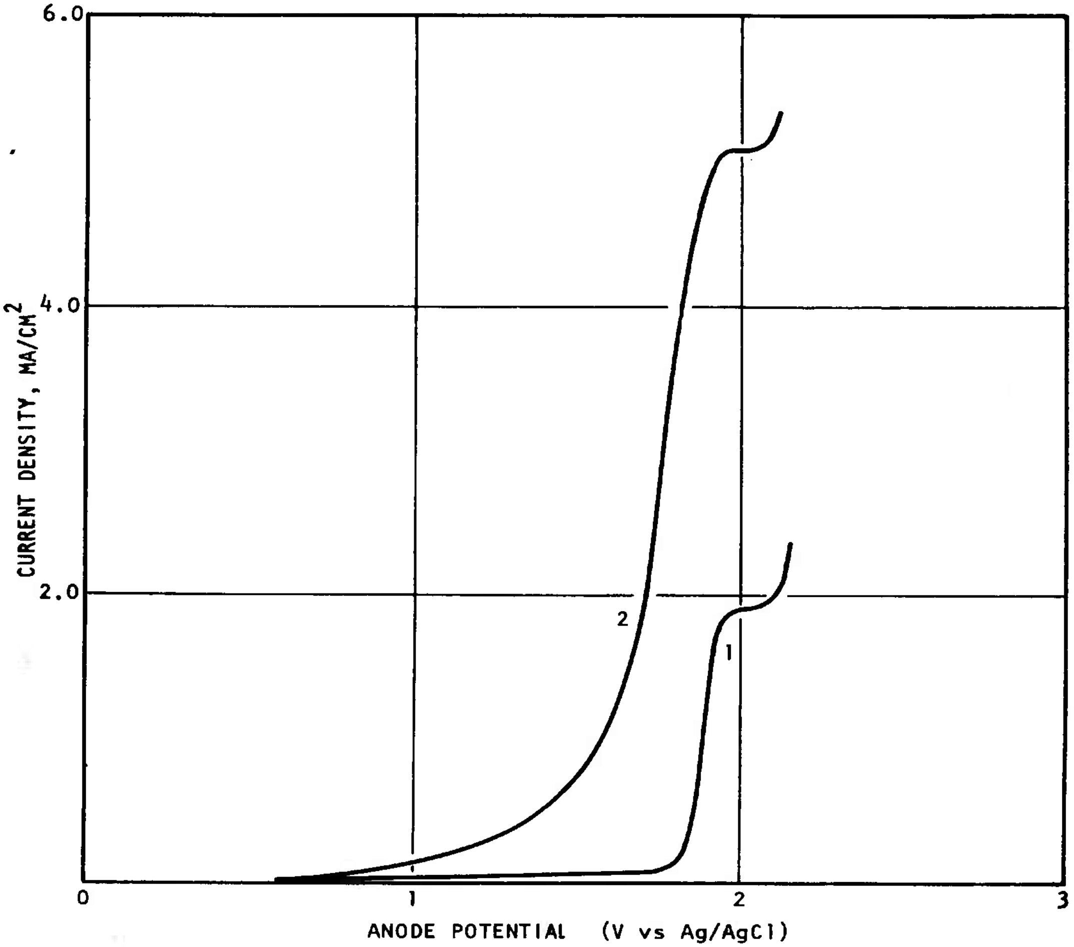


Figure 13. Anodic Polarization Curves on G.E. Pyrolytic Graphite ($2.25\ cm^2$), Scan Rate 120 mv/min, Temperature -25 C

1. 0.25 M NaPicrate/0.8 M $LiBF_4$ in $CH_3CN/(CH_2)_4O$ (5:1) Anolyte (20 ml) Followed by the Addition of:
2. $HNF_2$ (12.5 cc) and Pyridine (0.5 ml); the Point on Curve No. 2 at 2.0 V vs Ag/AgCl Represents the Initial Conditions of Electrolysis No. 20

Preliminary tests indicated that only $NaB(OCH_2CF_3)_4$ was readily soluble in $CH_3CN$ with the other two being slightly soluble. A slurry of the trifluoro ethoxide in $CH_3CN$ at -35 C did not decompose $HNF_2$, and we anticipated no $HNF_2$ incompatibility with the other compounds.

(C) Polarization data were obtained on each of the compounds in acetonitrile to determine its electrochemical characteristics under oxidizing conditions on graphite and on platinum. Again, these data were necessary to select the conditions for an anodic cooxidation with an $HNF_2$ complex.

(U) The polarization curves obtained for solutions of $NaB(OCH_2CF_3)_4$ in $CH_3CN$ containing $LiBF_4$ as the supporting electrolyte indicated that no oxidation could be obtained at potentials within the useful anodic range of the solvent systems on either graphite or platinum. This is shown in Fig. 14 and in Fig. 15 , curves 1, 2, and 3.

(U) The polarization curves for $NaOCH_2CF_3$ on Pt suffered from a lack of reproducibility which may have been related to the initial conditions of the electrode surface or the manner in which the solutions were prepared. In Fig. 16 , the curves obtained for $NaOCH_2CF_3$ in acetonitrile on graphite showed a low level oxidation which lacked any region of diffusion current control.

(U) The test solution in this case had been aged overnight and some visible changes were noticed prior to running the voltammetric experiments. The original suspension had turned into a clear but slightly colored solution. Using the same aged test solution on platinum, the curves in Fig. 17 displayed a somewhat similar form to those obtained on graphite except for the mild inflection in curve 2. In contrast, a well-defined oxidation wave was obtained on platinum with the introduction of a freshly prepared slurry of $NaOCH_2CF_3$ in 0.42 M $LiBF_4/CH_3CN$ as shown in Fig. 18 , curves 1 and 2. Curve 2 was not reproducible, since subsequent repetition of the experiment gave very little oxidation current above the base curve. It was apparent from the above data that a slow interaction of the alkoxide

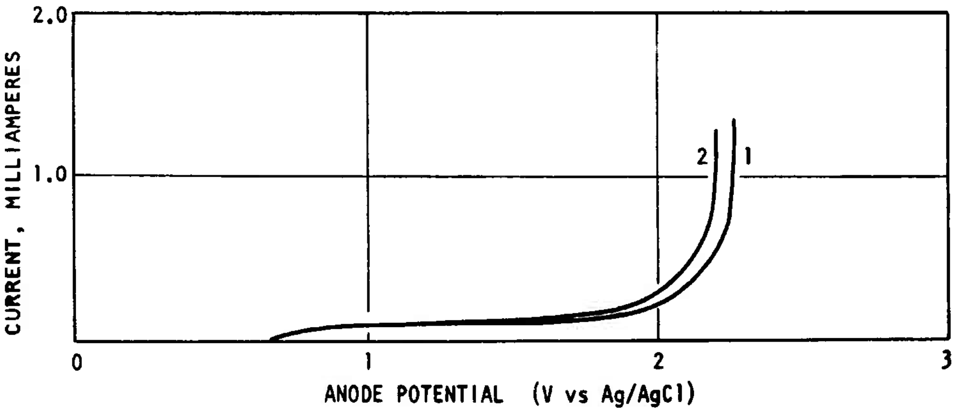


Figure 14. Anodic Polarization Curves for $NaB(OCH_2CF_3)_4$ on G.E. Pyrolytic Graphite at -5 C, Scan Rate 120 mv/min

1. 0.42 M $LiBF_4/CH_3CN$ (20 ml) Followed by the Addition of;
2. 0.5 M $NaB(OCH_2CF_3)_4/CH_3CN$ (2.0 ml)

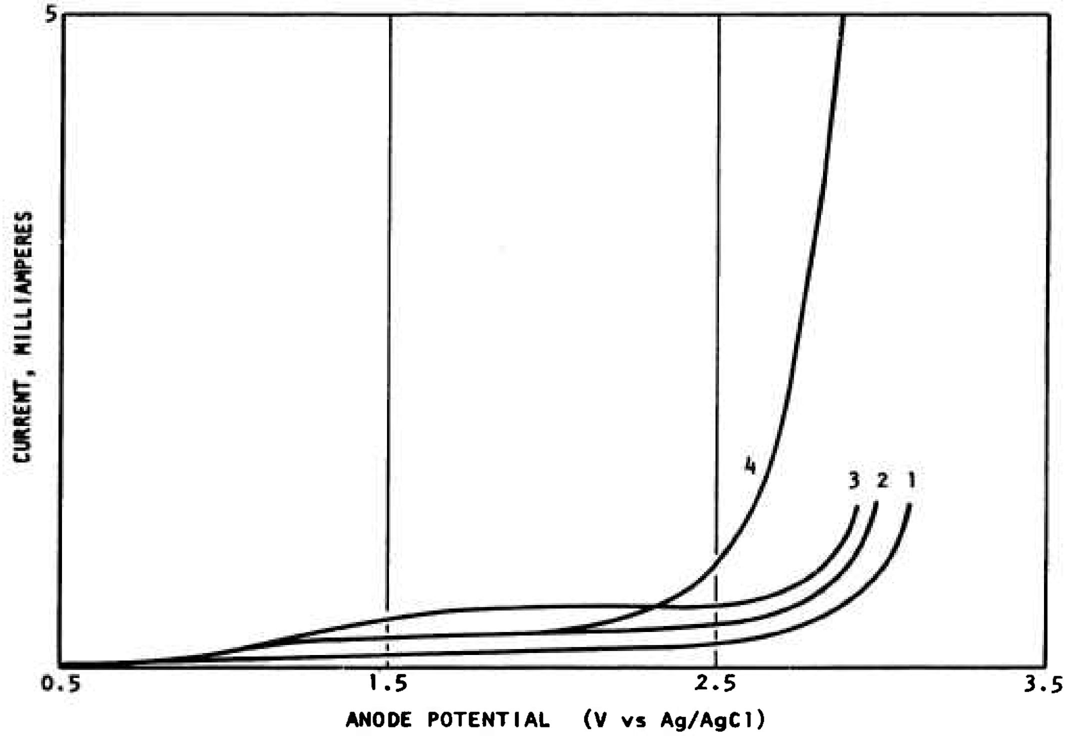


Figure 15. Anodic Polarization Curves for Alkoxyborohydrides on Pt (1.3 cm$^2$) at -5 C, Scan Rate 300 mv/min

1. 0.42 $LiBF_4/CH_3CN$ (20 ml) Followed by the Additions of:
2. 0.5 M $NaB(OCH_2CF_3)_4/CH_3CN$ (2.0 ml)
3. 0.5 M $MaB(OCH_2CF_3)_4/CH_3CN$ (2.0 ml)
4. Sat. $NaB(OCH_3)_3(OCH_2CF_3)/CH_3CN$ (5.0 ml)

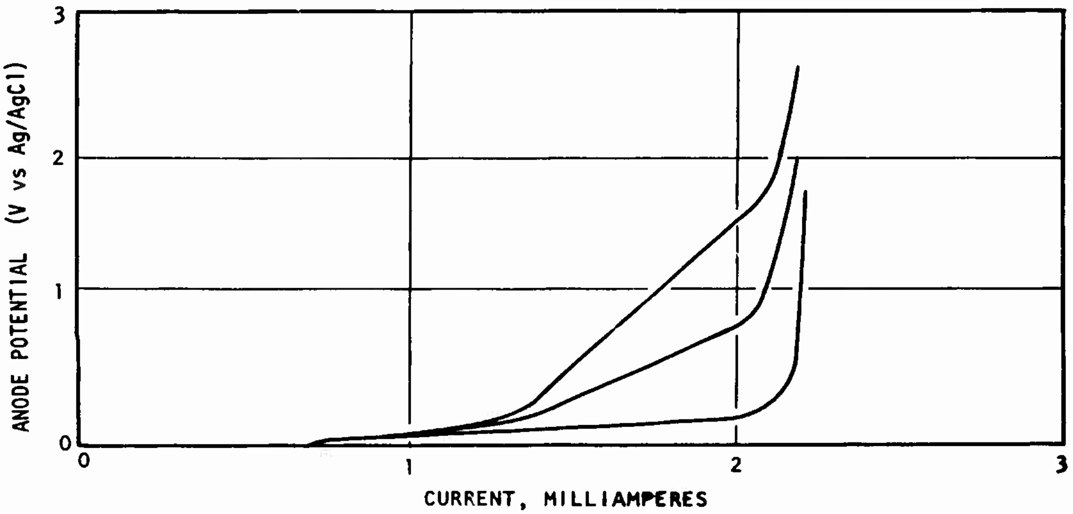


Figure 16. Anodic Polarization Curves for $NaOCH_2CF_3$ on G.E. Pyrolytic Graphite at -5 C, Scan Rate 120 mv/min

1. 0.42 M $LiBF_4/CH_3CN$ (20 ml) Followed by Addition of;
2. 0.15 M $NaOCH_2CF_3/CH_3CN$ (5.0 ml)
3. 0.15 M $NaOCH_2CH_3/CH_3CN$ (5.0 ml)

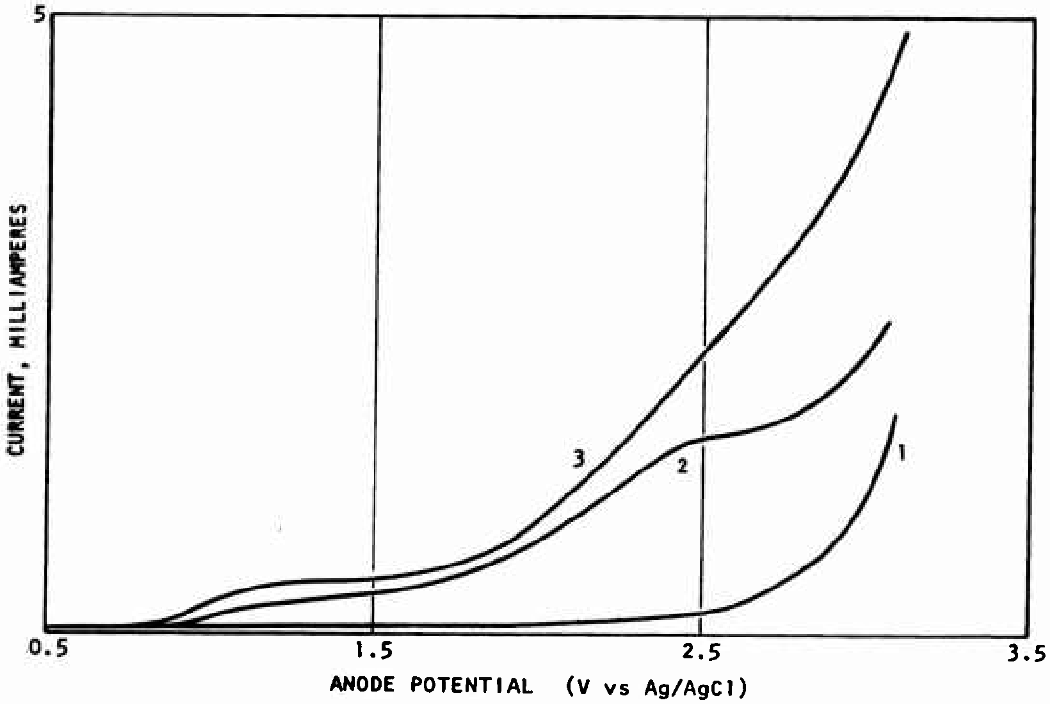


Figure 17. Anodic Polarization Curves for $NaOCH_2CF_3$ on Pt (1.3 $cm^2$) at -5 C, Scan Rate 300 mv/min

1. 0.42 M $LiBF_4/CH_3CN$ (20 ml) Followed by Additions of:
2. 0.15 M $NaOCH_2CF_3/CH_3CN$ (5.0 ml)
3. 0.15 M $NaOCH_2CF_3/CH_3CN$ (5.0 ml)

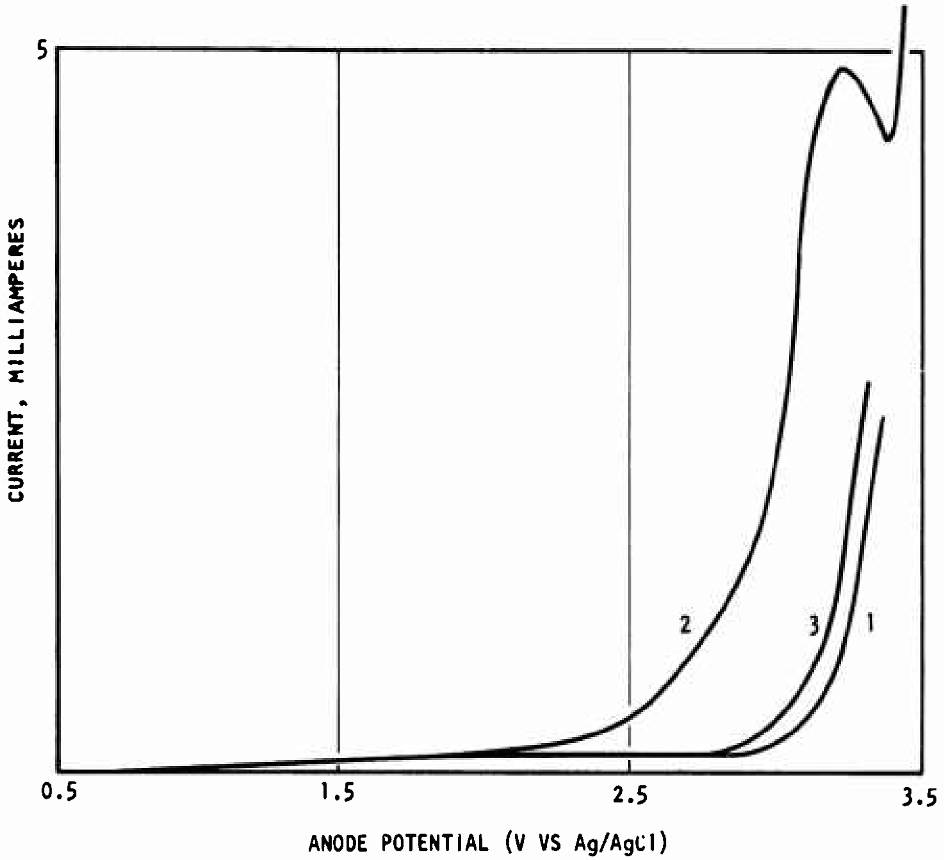


Figure 18. Anodic Polarization Curves for $NaOCH_2CF_3$ on Pt (1.0 $cm^2$) at -22 C, Scan Rate 300 mv/min

1. 0.42 M $LiBF_4/CH_3CN$ (20 ml) Followed by the Additions of:
2. Slurry of $NaOCH_2CF_3$ (5 mmoles) in 0.42 M $LiBF_4/CH_3CN$ (10 ml)
3. $(CF_3)_2CO$ (6 mmoles)

with the solvent was partially responsible for the erratic voltammetric behavior. Further characterization of the oxidizable species was then sought through macroscale electrolysis and product analysis.

(C) In Table 10 , the data on three electrolyses involving $NaOCH_2CF_3$ and $HNF_2$ are presented. In each case, the trifluoro ethoxide was introduced as a freshly prepared slurry in $LiBF_4/CH_3CN$ solution. Electrolysis No. 22 was intended to be as uncomplicated as possible and offer a good possibility of cooxidation with $HNF_2$:THF complex. The cell was warmed to 0 C in the hope of increasing solubility of the trifluoro ethoxide. However, the discoloration of the anolyte during the electrolysis indicated that some undesirable side reactions may have occurred. The only volatile product formed was a small amount of a mixture which we tentatively indentified as $CF_3CH_2OCF_3$ and $(CF_3CH_2O)_2$ by mass spectral analysis (Table 11). A search of the indexed literature indicated that they are probably new compounds. These products presented a positive indication of a primary electrode process involving the trifluoroethyoxide anion; i.e., an oxidation of the anion to the trifluoro ethoxy radical,

$$CF_3CH_2O^- \longrightarrow CF_3CH_2O\cdot + e^- \qquad (41)$$

some of which underwent a decomposition to formaldehyde and the trifluoromethyl radical,

$$CF_3CH_2O\cdot \longrightarrow \cdot CF_3 + CH_2O \qquad (42)$$

followed by radical coupling to give the observed ether,

$$CF_3CH_2O\cdot + \cdot CF_3 \longrightarrow CF_3CH_2OCF_3 \qquad (43)$$

and dimerization to give the peroxide,

$$2\ CF_3CH_2O\cdot \longrightarrow CF_3CH_2OOCH_2CF_3 \qquad (44)$$

### TABLE 10

### THE ELECTROLYSES OF $NaOCH_2CF_3$ AND ITS HEXAFLUOROACETONE COMPLEX WITH $HNF_2$ IN ACETONITRILE

| No. | Electrolyte and Solvent | Initial Reagent Concentrations in Anolyte | Temperature, C | Anode |  |  | $\frac{i\ t}{96.5}$ coulomb, mF | Results and Comments |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Material and Area | Potential (V) vs Ag/AgCl | Current Density, ma/$cm^2$ |  |  |
| 22 | 0.42 M $LiBF_4$ in $CH_3CN$ | 0.08 M $HNF_2$<br>0.2 M $(CH_2)_4O$<br>$NaOCH_2CF_3$<br>(5.0 mmoles)<br>q | 0 | Pt<br>1.0 $cm^2$ | 3.4v | 25 ±5 | 4.6 | Volatile product: small amount of a compound tentatively identified by mass spectrometer as $CF_3CH_2OCF_3$, no $N_2F_4$. |
| 23 | 0.42 M $LiBF_4$ in $CH_3CN$ | 0.08 M $HNF_2$<br>0.2 M $(CH_2)_4O$<br>$NaOCH_2CF_3$<br>(5.0 mmoles)<br>$(CF_3)_2CO$<br>(6.0 mmoles) | 0 | Pt<br>1.0 $cm^2$ | 3.5v | 0.4 ±0.1 | 0.34 | Volatile product: candidate $CF_3CH_2OCF_3$ (0.2 mmole), $(CF_3)_2C{=}O$, no $N_2F_4$ |
| 24 | 0.42 M $LiBF_4$ in $CH_3CN$ | 0.08 M $HNF_2$<br>$NaOCH_2CF_3$<br>(5.0 mmoles)<br>KF (2.0 mmoles) | -24 | Pt<br>1.0 $cm^2$ | 3.5v | 6 ±3 | 1.6 | Volatile products: $N_2F_4$, $N_2O$, and an unidentified C-F compound (total 4.6 cc), no $N_2F_4$ |

## TABLE 11

## MASS SPECTRUM OF THE PRODUCT MIXTURE (-112 C FRACTION) FROM THE ANODIC OXIDATION OF $CF_3CH_2OC(CF_3)_2$ ONa and $HNF_2 \cdot O(CH_2)_4$ in $CH_3CN$

(Electrolysis No. 23, Table I)

| M/E Peak | Tentative Ion Assignment for $CF_3CH_2OCF_3$ | Tentative Ion Assignment for $CF_3CH_2OOCH_2CF_3$ |
|---|---|---|
| 30 | $CH_2O$ | $CH_2O$ |
| 31 | CF | CF |
| 33[a] | $(CH_2F)$ | $(CH_2F)$ |
| 50 | $CF_2$ | $CF_2$ |
| 62 | $CF_2C$ | $CF_2C$ |
| 69 | $CF_3$ | $CF_3$ |
| 78 | $CF_2CO$ | $CF_2CO$ |
| 91 | $CF_2CHOC$ | |
| 92 | $CF_2CH_2OC$ | |
| 94 | | $CF_2COO$[b] |
| 96 | | $CF_2CH_2OO$[b] |
| 97 | | |
| 99 | $CF_3CH_2O$ | $CF_3CH_2O$ |
| 110 | $CF_3CHOC$ | |
| 111 | $CF_3CH_2OC$ | |
| 127[a] | | $CF_3CH_2OOC$ |
| 130 | $CF_3CH_2OCF$ | |
| 146[a] | | |
| 149 | $CF_3CH_2OCF_2$ | |
| 164[a] | | |
| 178[a] | | |

[a] These peaks may be derived from the $CH_2FCH_2OH$ in the $CF_3CH_2OH$ starting material. Mass spectrum of the latter showed a fairly strong m/e = 33 ($CH_2F$ peak).

[b] Note that the infrared spectrum shows no carbonyl absorption

The fact that no $N_2F_4$ was found strongly indicated that little $(CH_2)_4O:HNF_2$ oxidation took place. At an anode potential of 3.4 v vs Ag/AgCl, one would expect a fairly rapid oxidation of the $HNF_2$ complex as well as some oxidation of the free THF. There is insufficient polarization data at this time to verify the possibility that the platinum anode became passive to the $HNF_2$-THF oxidation in the presence of the trifluoroethoxide.

(U) We have also investigated the possibility of converting $CF_3CH_2ONa$ to a less basic anionic derivative which might be highly soluble in acetonitrile. The oxidation of selected derivatives should also give the desired trifluoroethyoxy radical. We envisioned the preparation of one such derivative by the following reaction:

$$CF_3CH_2ONa + CF_2O \xrightarrow[-40°C]{CH_3CN} CF_3CH_2OCF_2ONa \tag{45}$$

When this reaction was attempted on a 5-mmole scale, nearly the stoichiometric amount of $CF_2O$ was absorbed but a white precipitate formed immediately and an infrared spectrum of the volatile products showed a C-F carbonyl compound. The reaction probably went as follows,

$$CF_3CH_2ONa + CF_2O \longrightarrow CF_3CH_2O\overset{\overset{O}{\|}}{C}F + NaF \tag{46}$$

A similar reaction of the trifluoroethoxide with hexafluoroacetone (HFA) was apparently more successful. A slurry of $CF_3CH_2ONa$ (5.0 mmoles) in $CH_3CN$ (15 ml) at -30 C was treated with $(CF_3)_2C{=}O$ (5.5 mmoles) in an effort to carry out the following reaction:

$$CF_3CH_2ONa + (CF_3)_2C{=}O \xrightarrow[-35°C]{CH_3CN} CF_3CH_2OC(CF_3)_2ONa \tag{47}$$

A clear, colorless solution was obtained and the volatile products contained only a small amount of unreacted hexafluoroacetone. Removal of the solvent gave a white solid residue which could be redissolved in acetonitrile. Anodic polarization data for the redissolved product are presented in Fig. 19 . The desired electrochemical reaction was:

$$CF_3CH_2OC(CF_3)_2O^- \longrightarrow CF_3CH_2OC(CF_3)_2O\cdot + e^- \qquad (48)$$

followed by the loss of HFA to give the trifluoroethoxy radical as shown in the equation,

$$CF_3CH_2OC(CF_3)_2O\cdot \longrightarrow CF_3CH_2O\cdot + (CF_3)_2C{=}O \qquad (49)$$

The polarization data showed well-defined oxidation waves related to the concentration of the trifluoroethoxide-hexafluoroacetone complex in the anolyte.

(C) The next logical step in the investigation would have been an electrolysis of the complex alone to characterize its oxidation products prior to attempting a cooxidation with $HNF_2$. Instead, we tried directly to set up the conditions for a cooxidation of the two reagents, but the results of the electrolysis (Table 10 , No. 23) indicated that only the oxidation of the $CF_3CH_2ONa$/HFA complex was achieved. In that experiment, an attempt was made to form the $CF_3CH_2O(CF_3)_2ONa$ complex <u>in situ</u> by passing HFA into the anolyte solution containing a slurry of $CF_3CH_2ONa$. A clear solution was not obtained, and the sequence of polarization curves shown in Fig. 19 revealed the unexpected suppression of the oxidation current that followed the addition of $(CF_3)_2C{-}O$ to the anolyte. In spite of this undesirable condition, $HNF_2$-THF was added and the electrolysis No. 23 was carried out. The extremely low anode current density obtained at 3.5 v vs Ag/AgCl was an additional indication that a passive film had formed on the platinum surface. The electrolysis was run overnight at 0 C to accumulate enough products for infrared and mass spectral analyses. In addition to hexafluoroacetone, a major product of the electrolysis was the fluorocarbon mixture, again tentatively identified as $CF_3CH_2OCF_3$ and $(CF_3CH_2O)_2$. The high current yield of the product mixture suggested a fairly long life for the $CF_3CH_2O\cdot$ radical before the loss of formaldehyde as indicated in

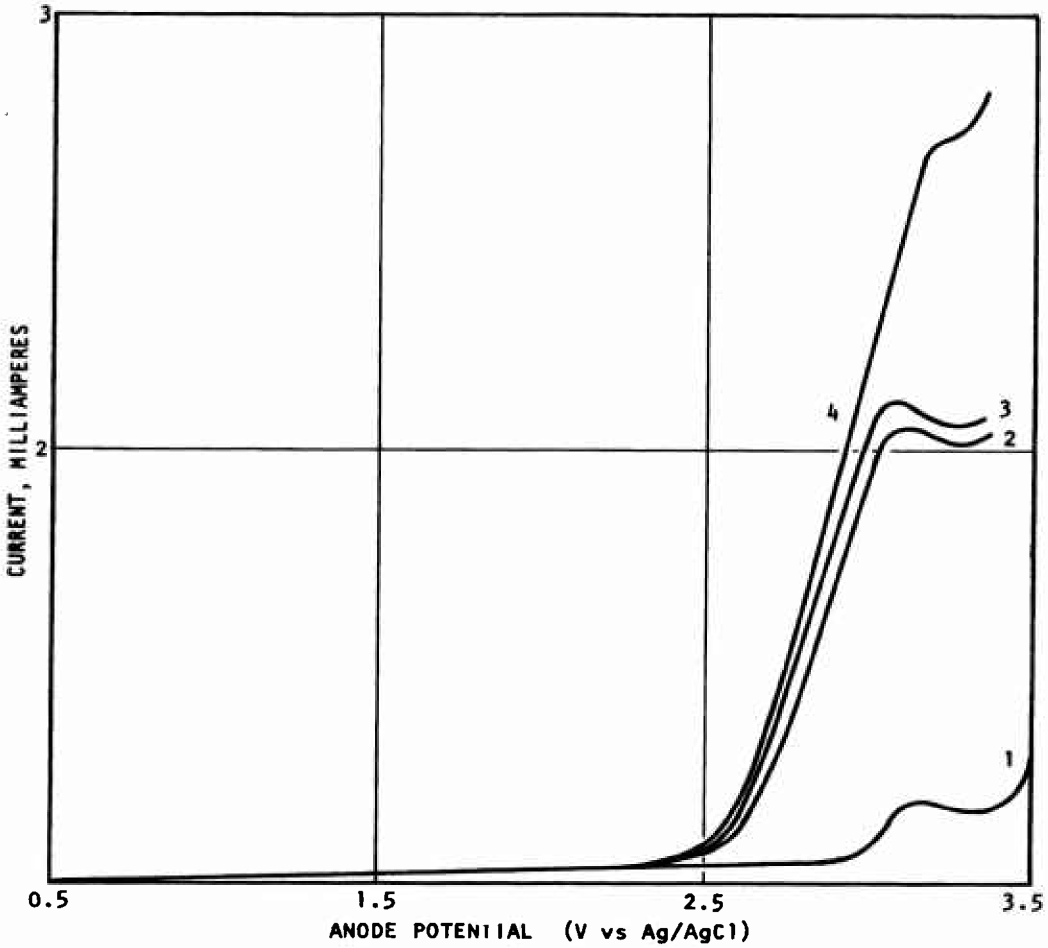


Figure 19. Anodic Polarization Curves for $NaOC(CF_3)_2OCH_2CF_3$ on Pt (1.0 $cm^2$), Scan Rate 300 mv/min

1. 0.42 M $LiBF_4/CH_3CN$ (20 ml) at -20 C Followed by Addition of:
2. Sat. $NaOC(CF_3)_2(OCH_2CF_3)/CH_3CN$ (5.0 ml)
3. The Temperature was Increased to -10 C
4. Sat. $NaOC(CF_3)_2(OCH_2CF_3)/CH_3CN$ (3.0 ml) at -10 C

Eq. 42. In fact, the intermediate radical formed in this case according to Eq. 48 may have an appreciable life also, and may be capable of capturing $\cdot NF_2$. Because no $N_2F_4$ was found, very little oxidation of $HNF_2$ evidently took place.

(C) Electrolysis No. 24 was an attempt to employ the unstable $KF\cdot HNF_2$ complex as a source of $\cdot NF_2$ radicals in a low-temperature anodic oxidation. Although the decomposition of the complex to $N_2F_2$ was neither fast nor quantitative under these conditions, there was no evidence of $\cdot NF_2$ radical formation during the electrolysis. An attack by:NF diradicals on the alkoxide may have been the initial step in the formation of $N_2O$ and the fluorocarbon product observed.

(U) Polarization data for the oxidation of the mixed alkoxy borohydride $NaB(OCH)_3OCH_2CF_3$ is presented in Fig. 15 , curve 4. The material appeared to be readily oxidized on platinum at about 2.7 v vs Ag/AgCl. Without additional studies on a macroscale we cannot know whether it was behaving as a $CH_3O\cdot$ or as a $CF_3CH_2O\cdot$ radical source. No further work was done with this compound.

## CHEMICAL STUDIES

### Chemical Synthesis of Alkyl-ONF$_2$ Compounds

(C) Free Radical Coupling Reactions. The synthesis of R-O-NF$_2$ compounds, where R stands for an alkyl group, could be achieved by either of the following two free radical reactions:

$$RO\cdot + NF_2 \longrightarrow RONF_2 \qquad (50)$$

or

$$R\cdot + ONF_2 \longrightarrow RONF_2 \qquad (51)$$

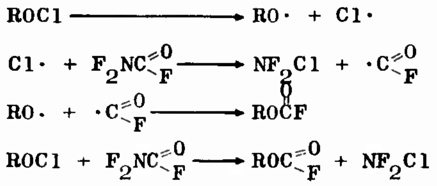
Because both the alkoxy and the NF$_2$ radical (Ref. 13 and 14) can be readily prepared and possess a reasonable lifetime, the first approach appeared more promising.

(C) The t-butoxy radical was chosen as the alkoxy radical based on the following assumption. The electronegativity of the NF$_2$ group is comparable to that of chlorine (Ref. 15). Hence, the relative stability of the hypothetical alkyl-O-NF$_2$ compounds should be comparable to that of the known alkyl hypochlorites. Because tertiary alkyl hypochlorites have the highest stability and primary alkyl hypochlorites have the lowest one (Ref. 16 through 18), one could expect a similar trend for the alkyl-O-NF$_2$ compounds. The t-butoxy radical can be easily generated by decomposition of t-butyl hypochlorite or t-butyl peroxide. The NF$_2$ radical can be generated from various sources such as perfluoroformamide (Ref. 19) or its alkali metal salts (Ref. 20), N$_2$F$_4$, or NHF$_2$.

(U) When t-butyl hypochlorite was reacted with the potassium salt of perfluoroformamide (PFA) at -31 C in CH$_3$CN solution, the following reaction took place quantitatively:

$$F_2NCF_2O^-K^+ + (CH_3)_3COCl \longrightarrow NF_2Cl + COF_2 + K^+(CH_3)_3CO^- \qquad (52)$$

(U) When the reaction was carried out at ambient temperature in the absence of a solvent using perfluoroformamide itself instead of its potassium salt, again complete conversion of the starting materials occurred. The main products were $NF_2Cl$, $CO_2$, $(CH_3)_3CNF_2$, and $(CH_3)_3CO\overset{O}{C}F$. These products could be rationalized in terms of the following reactions:



$$ROCl \longrightarrow RO\cdot + Cl\cdot \qquad (53)$$

$$Cl\cdot + F_2NC\begin{smallmatrix}{\diagup}O\\ {\diagdown}F\end{smallmatrix} \longrightarrow NF_2Cl + \cdot C\begin{smallmatrix}{\diagup}O\\ {\diagdown}F\end{smallmatrix} \qquad (54)$$

$$RO\cdot + \cdot C\begin{smallmatrix}{\diagup}O\\ {\diagdown}F\end{smallmatrix} \longrightarrow RO\overset{O}{C}F \qquad (55)$$

$$ROCl + F_2NC\begin{smallmatrix}{\diagup}O\\ {\diagdown}F\end{smallmatrix} \longrightarrow ROC\begin{smallmatrix}{\diagup}O\\ {\diagdown}F\end{smallmatrix} + NF_2Cl \qquad (56)$$

and by assuming the formation of $(CH_3)_3COC\text{-}NF_2$ as an unstable intermediate, which can decompose according to:

$$(CH_3)_3CO\overset{O}{\overset{\|}{C}}\text{-}NF_2 \longrightarrow (CH_3)_3C\text{-}NF_2 + CO_2 \qquad (57)$$

The intermediate $(CH_3)_3CO\overset{O}{\overset{\|}{C}}\text{-}NF_2$ was observed only indirectly by the presence of its decomposition products $(CH_3)_3CNF_2$ and $CO_2$. However, in the electrochemical study of the perfluoroformamide - $NaB(OCH_3)_4$ system at -80 C, the corresponding $CH_3O\overset{O}{C}\text{-}NF_2$ was isolated in nearly quantitative yield (see above).

(C) To suppress the undesired sidereaction (Eq. 56) in the t-butyl hypochlorite-PFA system, PFA was substituted by $N_2F_4$, hoping that the following reaction would occur.

$$(CH_3)_3COCl + F_2N - NF_2 \xrightarrow{?} (CH_3)_3CONF_2 + NF_2Cl \qquad (58)$$

When t-butyl hypochlorite was combined with $N_2F_4$ at ambient temperature, no reaction occurred. Similarly, uv irradiation of the mixture contained in a Pyrex container or brief exposure (~10 minutes) to uv in a quartz container resulted only in unreacted starting materials. When the mixture in a quartz container was exposed for 3 hours to uv irradiation, about 30 percent of the $N_2F_4$ was converted to $N_2O$, whereas most of the t-butyl hypochlorite was converted to $(CH_3)_3CF$ and $CH_3COCH_3$. These products suggest that the desired product, $(CH_3)_3CONF_2$, if formed may be either unstable or reactive with glass (expecially under uv irradiation).

(C) Because of its apparently low reactivity, $N_2F_4$ was replaced by the more reactive difluoramine. However, instead of the desired reaction

$$(CH_3)_3COCl + HNF_2 \xrightarrow{?} HCl + (CH_3)_3CONF_2 \qquad (59)$$

the following reaction had taken place quantitatively:

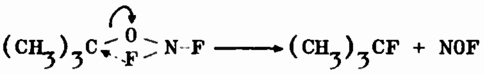
$$(CH_3)_3COCl + HNF_2 \longrightarrow NF_2Cl + (CH_3)_3COH \qquad (60)$$

The fact that $NF_2Cl$ and not HCl is formed indicates that the mainly covalent organic hypochlorites react in the same manner as the ionic inorganic hypochlorites (Ref. 21). We had hoped that a free radical decomposition of an organic hypochlorite might favor the reaction described by Eq. 59. In spite of the fact that this reaction did not result in the desired product, $(CH_3)_3CONF_2$, it constitutes a novel and convenient synthetic method to prepare $NF_2Cl$. A short note on this subject (see Appendix) has been submitted to Inorganic Chemistry for publication.

(C) In all reactions involving a starting material containing a positive chlorine atom (such as t-butyl hypochlorite), it appeared that $NF_2Cl$ and not $RONF_2$ was the favored reaction product. Consequently, ROCl was replaced by the peroxide ROOR, thus precluding $NF_2Cl$ formation. In the absence of uv irradiation, $N_2F_4$ and t-butyl peroxide did not interact at ambient temperature. Ultraviolet irradiation of the mixture in a Pyrex container at ambient temperature gave a reaction as in Eq. 61:

$$(CH_3)_3COOC(CH_3)_3 + N_2F_4 \longrightarrow N_2O + CH_3NF_2 + (CH_3)_3CF + CH_3COCH_3 \qquad (61)$$

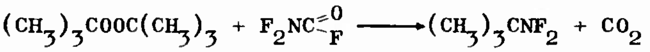
When the reaction was carried out in a quartz vessel, the same products were obtained but there was a higher conversion of the starting materials. The observed product, $(CH_3)_3CF$, could have arisen from decomposition of an unstable $(CH_3)_3CONF_2$ according to:



(62)

$$(CH_3)_3C\cdots\overset{O}{\underset{F}{}}\cdots N{-}F \longrightarrow (CH_3)_3CF + NOF$$

with the NOF attacking glass to form nitrogen oxides and silicon tetrafluoride as observed. The elimination of NOF from $(CH_3)CONF_2$ could easily proceed through an internal nucleophilic substitution ($S_Ni$) mechanism (Ref. 22) as postulated for the analogous decarboxylation of alkyl chloroformates (Ref. 23) and aryl fluoroformates (Ref. 24). Hence, the following changes were made: (1) the use of uv irradiation was avoided, and (2) $N_2F_4$ was replaced by compounds which could more readily generate $NF_2$ radicals. The first system studied was t-butyl peroxide and perfluoroformamide. The conversion of the starting materials was low and the following products were observed:



(63)

$$(CH_3)_3COOC(CH_3)_3 + F_2NC\overset{\leq O}{\underset{\diagdown F}{}} \longrightarrow (CH_3)_3CNF_2 + CO_2$$

This indicates that $(CH_3)_3CO\overset{O}{\overset{\|}{C}}NF_2$ may have been again the intermediate as in the reactions of perfluoroformamide with $(CH_3)_3COCl$ or as in the electrochemical synthesis (see above).

When difluoroamine was used in place of perfluoroformamide, only unreacted starting materials were recovered.

## Fluorination Reactions of Methoxyamine

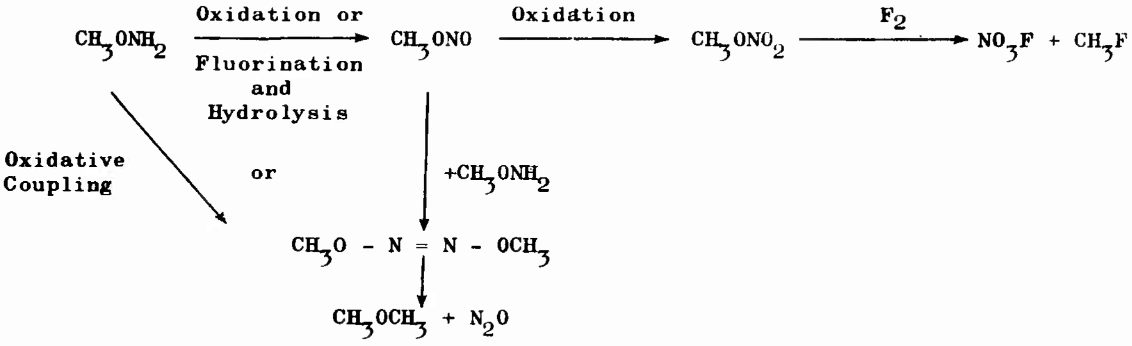
(C) The fluorination of salts derived from methoxyamine has previously been studied. For example, sodium methoxysulfamate was fluorinated with elementary fluorine in aqueous solution and sulfolane (Ref. 25); however, no evidence for the formation of the desired compound, $CH_3ONF_2$, was obtained. Similarly, the fluorination of the methoxyamine hydrochloride in the presence of NaF as a diluent in a fluidized bed did not result in $CH_3ONF_2$ (Ref. 26). Since Shants (Ref. 27) has recently demonstrated the importance of the pH-value for the direct fluorination of $-NH_2$ groups, the fluorination of $CH_3ONH_2$ itself was studied in a bicarbonate buffered agueous solution and in the anhydrous $CH_3CN$ system. The desired reaction was:

$$CH_3ONH_2 + F_2 \longrightarrow CH_3ONF_2 + 2HF \qquad (64)$$

The aqueous fluorination of $CH_3ONH_2$ was carried out at 0 C in a bicarbonate buffer solution to maintain a weakly alkaline reaction medium and to bind the by-product HF. The following reaction products were observed:

$$CH_3ONH_2 \xrightarrow[NaHCO_3]{F_2} CH_3ONO + CH_3ONO_2 + NO_3F + CH_3F + N_2O + CO_2$$

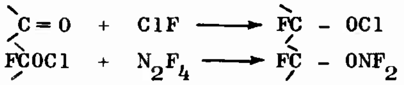
(U) According to mass spectral analysis, the fraction consisting mainly of $CH_3ONO_2$ contained also some small amounts of $CH_3ON:=:NOCH_3$ and partially fluorinated dimethyl ethers. The nitrogen material balance (98.5 percent recovery) indicates that within experimental error essentially all nitrogen containing products were collected. No material balance for the carbon containing products was possible owing to the large amounts of $CO_2$ evolved from the bicarbonate buffer. Most of the reaction products found can be rationalized by the following reaction scheme:



Because the desired $CH_3ONF_2$ may have formed but may be hydrolytically unstable, the fluorination reaction of $CH_3ONH_2$ was repeated in $CH_3CN$ solution at -10 C. Again, no evidence for the presence of $CH_3ONF_2$ was obtained, the major products being $N_2O$, $CH_3ONO$, $CO_2$, and $CH_3F$. Thus, as in the nonaqueous systems, the intermediary of $CH_3ONF_2$ is quite probable with $CH_3ONO$ arising through the $S_Ni$ reaction scheme.

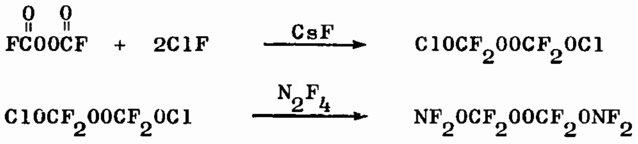
## (C) Intermediates for $ONF_2$ Compound Synthesis

(C) Several carbonyl compounds have been selected to extend the utility of new reactions discovered at Rocketdyne. These new reactions have provided a new route to $ONF_2$ compounds as in the following equations:



The extent to which the above reactions can be utilized is unknown with respect to the effects of substituents on the carbonyl carbon. Further, the stability of the hypochlorites may be limited and it would be desirable to establish reaction systems wherein both chlorofluorinations and subsequent reactions with $N_2F_4$ are carried out <u>in situ</u>.

(C) The first carbonyl for test was bis (fluoroformyl) peroxide, FC(0)OOC(0)F (BFFP). The desired reactions were

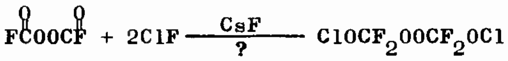


$$F\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}F + 2ClF \xrightarrow{CsF} ClOCF_2OOCF_2OCl$$

$$ClOCF_2OOCF_2OCl \xrightarrow{N_2F_4} NF_2OCF_2OOCF_2ONF_2$$

The resulting peroxide would represent a high-energy oxidizer as a liquid and its properties could aid considerably in projecting both new applications and new reaction systems.

The ternary system $N_2F_4$-ClF-BFFP did not give the expected bis (perfluoroaminoxy methyl) peroxide $(F_2NOCF_2O)_2$. The expected outcome was based on an assumed initial formation of a bis chloroxy species which in turn would react with $N_2F_4$ to form the $ONF_2$ derivative:

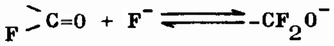


$$F\overset{O}{C}OO\overset{O}{C}F + 2ClF \xrightarrow[?]{CsF} ClOCF_2OOCF_2OCl$$

$$(ClOCF_2O)_2 + 2N_2F_4 \xrightarrow{?} (NF_2OCF_2O)_2 + 2ClNF_2$$

Not only did the reaction fail to yield any $ONF_2$ species but a complex mixture was obtained.

(U) Rather than attempt to resolve the mixture arising from the ternary reactant system it was decided to evaluate a control reaction of BFFP and CsF. The control reaction was essential in determining the nature of the possible decomposition products which could participate in the chlorofluorination step. Further, it was recognized that complex formation could occur as in



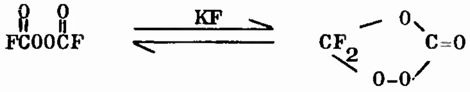
$$F{>}C{=}O + F^- \rightleftharpoons {-CF_2O^-}$$

to serve as a competing reaction. A minimal of complexing was expected inasmuch as the addition of CsF to an acyl fluoride normally is facile only in solution.

(U) The action of CsF on BFFP was found to give two principal products, these being $CF_3OO\overset{O}{C}F$ and $(CF_3OO)_2C{=}O$. The low reaction temperature of -80 C, coupled with reaction periods as long as 40 days, sufficed in achieving complete reaction. The fluoroformyl trifluoromethyl peroxide, $CF_3OOC(O)F$, was formed in yields up to 25 percent and the bis (trifluoromethyl) bis (peroxy) carbonate, $(CF_3OO)_2C{=}O$ was consistently over 20-percent yield.

These syntheses are refreshingly simple and are in marked contrast to their synthesis as reported by Talbot (Ref. 28) from the action of $CF_2N_2$ on BFFP. It is suspected that both peroxides are evolved from a common intermediate, $CF_3OO^-$, which when coupled with $COF_2$ in the appropriate stoichiometry yields the two carbonates. Some insight into the possible reaction mechanism was acquired through a study of the BFFP-KF system.

The action of KF does not result in any of the peroxides discussed above. Instead, the BFFP was found to isomerize both reversibly and reproducibly. At low temperatures, the following equilibrium was observed:



with "yields" as high as 23 percent being obtained.* The cyclic isomer was confirmed through $F^{19}$ nmr, mass spectrometry and molecular weight.

The $F^{19}$ chemical shift was found to be -60.4 $\phi$. Further, the resonance was a singlet as predicted. The chemical shift is entirely consistent with a $CF_2$ in a similar environment; i.e., bonded to two oxygens.

(U) The mass pattern is unambiguous in confirming the structure of the BFFP isomer, 2,3,5-trioxa-4,4-difluorocyclopentanone. The stable pattern includes the following species (m/e, ion, abundance X 100): 82, $CF_2O_2^+$, 100; 66, $CF_2O^+$, 39.46; 63, $CFO_2$, 11.21; 60, $CO_3^+$, 1.43; $CF_2^+$, 22.42; 44, $CO_2^+$, 80.72; and 32, $O_2^+$, 47.98. The high intensity of the $CF_2$ containing ions (m/e 82, 66, and 50) confirms the presence of the $CF_2$ linkage in the molecule inasmuch as rearranged species would have very low intensities. A parent peak (m/e 126) was neither expected nor observed. However, the molecular weight from the measured vapor density was found to be 124 and in excellent agreement with the calculated 126. The infrared trace is shown in Fig. 20.

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*Because an equilibrium is involved, the yield computation includes the decomposition products $COF_2$ and $CO_2$. The degree of isomerization cannot be even qualitatively assessed since it is not known whether decomposition to $COF_2$ and $CO_2$ occur through BFFP or its isomer.

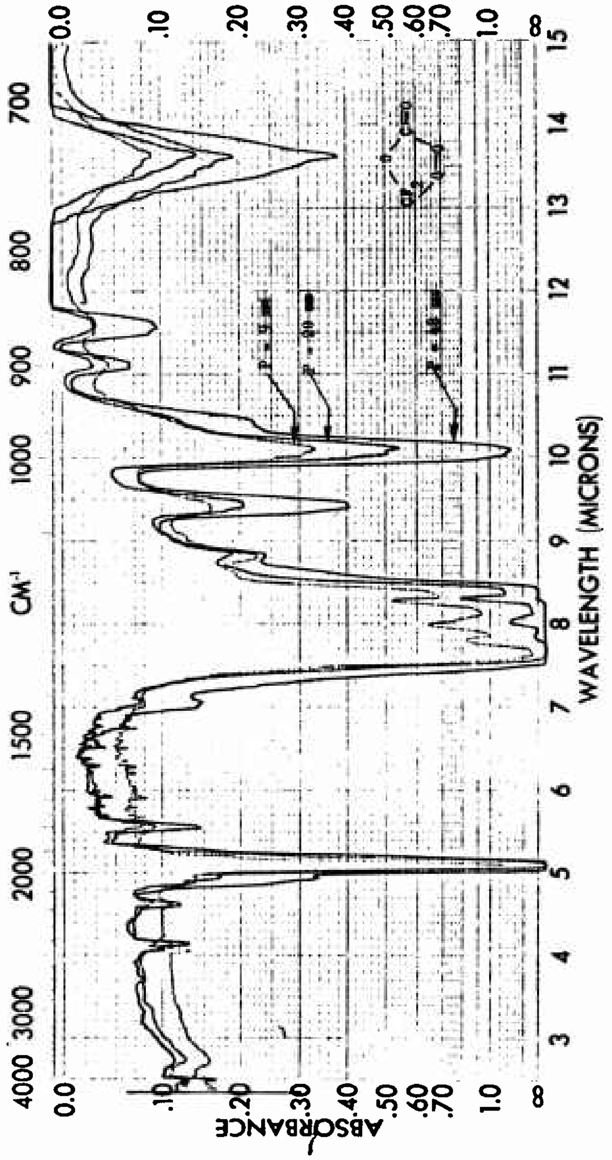
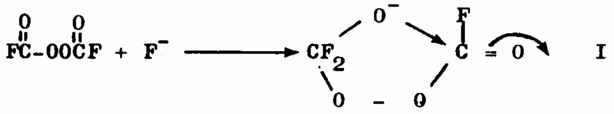


Figure 20. Infrared Spectrum of BFFP Isomer

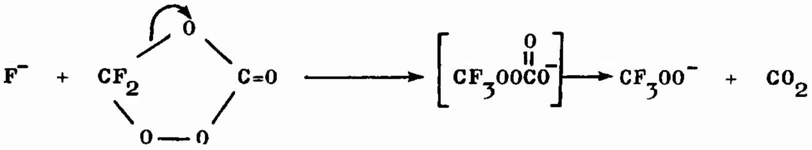
The formation of $CF_3OO\overset{O}{\overset{\|}{C}}F$ and $(CF_3OO)_2C{=}O$ may now be readily explained as well as identifying the difference in alkali fluoride activity. The isomerization step no doubt occurs through a $F^-$ addition followed by a



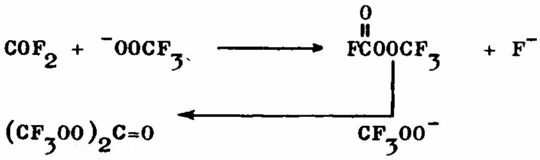
displacement on the remaining acyl group:

The principal action of KF on the cyclic peroxide is limited to a reversal of the reaction to BFFP.

(U) On the other hand, CsF is considerably stronger than KF as a base and can effect two different displacements. One, of course, is identical to the action of KF. The other involves a displacement of O from the difluoromethylene group followed by $CO_2$ elimination:



Coupling with $COF_2$ (generated by BFFP decomposition) then may give the peroxides:

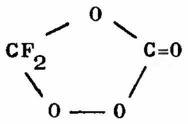


$$COF_2 + {}^-OOCF_3 \longrightarrow F\overset{O}{\overset{\|}{C}}OOCF_3 + F^-$$

$$F\overset{O}{\overset{\|}{C}}OOCF_3 + CF_3OO^- \longrightarrow (CF_3OO)_2C{=}O$$

Both of these peroxides are now available for conversion to hypochlorites and subsequently to $ONF_2$ compounds.

(U) The BFFP isomer, 2,3,5-trioxa-4,4 difluorocyclopentanone



deserves some comment. This novel compound can be considered as an ozonide of difluoroketene and constitutes the first known example of a perfluorinated ozonide. Furthermore, the fact that it was prepared without the use of ozone, is very remarkable.

## SECTION IV

## EXPERIMENTAL DETAILS

### ELECTROCHEMICAL STUDIES

### Instrumentation and Apparatus

(U) The potentiostatic anodic polarization data were obtained using a three-electrode system in which the anode potential was varied linearly with respect to the reference electrode by means of an electronic potentiostat (Elektronischer Potentiostat nach Wenking made by G. Bank Elektronik) fed a linear control signal from a motor-driven potentiometer (Motor potentiometer MP 165 by Erwin Halstrup). The anode vs reference potential was monitored by an electrometer (Keithley Model 621) the output of which was recorded on an X-Y recorder (Moseley Autograph). The cell current response was recorded on the opposite axis of the X-Y recorder as the potential across a low value resistance.

(U) The Wenking was also used as the power supply for some of the constant potential electrolyses. For the constant current electrolyses, an electronic power supply was used (Constant Current Power Source; Model C630, Electronic Measurements Co., Inc.) and the anode vs reference potential was monitored with the electrometer and recorder.

(U) In some cases, all of the above functions were accomplished with one integrated instrument (Electroscan 30, Beckman Instruments, Inc.).

(U) For the electrochemical cell body, a variation of the standard H-form was used in most of the experiments. The cell compartments each had a capacity of 60 ml and were separated by a short arm which housed an 0.5-inch-diameter fine-fritted glass disk. The head was attached to the anode compartment by means of a large spherical joint. Three standard taper joints in the head were used to introduce the anode/reference electrode assembly (Fig. 21), the mechanical stirring shaft, and a Teflon catheter tube for the introduction of liquid reagents. The gaseous reagents were introduced in the $N_2$/He carrier gas stream which entered the cell through the hollow stirring shaft, 3/16-inch diameter. When a rotating anode was used, a platinum foil sleeve was fitted to a 7/16-inch-diameter stirring shaft mounted in a special cell and head assembly. All condensible products were trapped at -196 C and the carrier was vented through a halocarbon oil bubbler.

### Reference Electrodes

(U) 1. Ag/AgBr. The silver-silver bromide electrode was prepared by anodizing a silver wire in aqueous 0.05 M KBr solution. The anodized electrode was rinsed in distilled water and dried under nitrogen at room temperature. The electrode was placed in the reference probe cavity containing a saturated solution of LiBr in acetonitrile. A sketch of the anode and reference electrode assembly is presented in Fig. 21.

(U) 2. $Ag/Ag^+$. A thermal-electrolytic silver-silver couple was prepared by a variation of the procedure of Ives and Janz, (Ref. 20). A thermally deposited silver electrode was anodized in a divided micro cell containing about 0.5 ml of the anolyte solution of the electrochemical system to be studied (e.g., 0.5 M $KPF_6$ in acetonitrile or 0.5 M $KPF_6$ in N,N-dimethyl acetamide/tetrahydrofuran (70/30). The anodized electrode and its anolyte were then placed in the reference probe cavity.

(U) 3. Ag/AgCl. The silver-silver chloride couple was prepared by the fusion of optical-grade rolled silver chloride to a coil of silver wire in an open flame. The electrode was placed in the reference probe cavity containing 1.0 M $(Et)_4NCl.4H_2O$ in acetonitrile. This type of electrode was the most stable, reproducible, and durable of the three used.

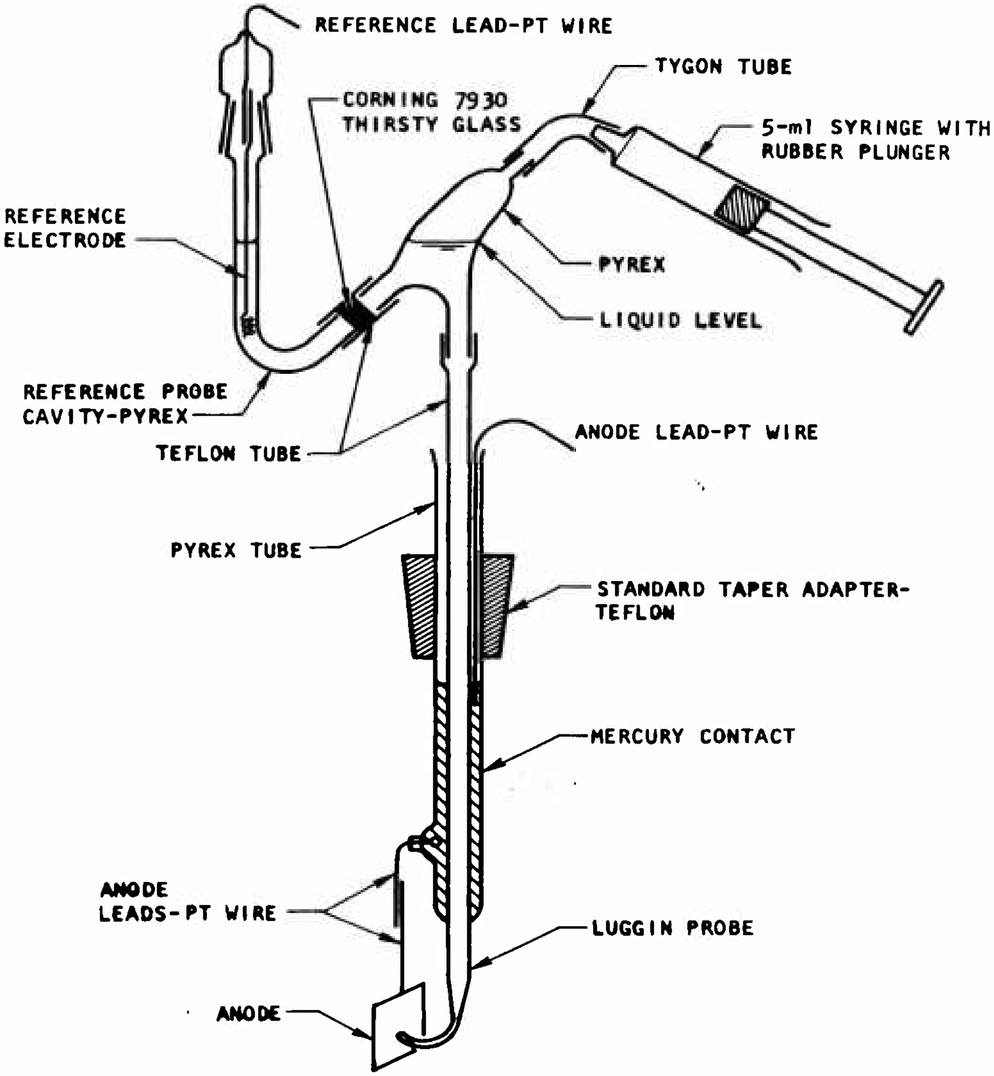


Figure 21. The Anode and Reference Electrode Assembly

## (U) Preparation of $Na\ B(OCH_2CF_3)$

A 50-ml microflask fitted with a thermometer, magnetic stirrer, and a gas outlet protected by a $CaSO_4$ drying tube was loaded with $CF_3CH_2OH$ (8.00 grams; 80 mmoles) cooled to 15 C. Solid $NaBH_4$ (0.378 grams; 10.0 mmoles) was slowly added under dry nitrogen with stirring. The slow evolution of $H_2$ began after about 5 minutes. While stirring overnight at 15 to 25 C, the volume of gas collected was 900 cc (40 mmoles) indicating completion of the reaction. The mixture was warmed to 50 - 60 C for an additional hour and then allowed to cool. No additional $H_2$ evolution was observed. The product was collected on a sintered glass filter and dried in vacuo at ambient temperature. Yield: 3.78 grams, 87.6 percent of theory.

## (U) Preparation of $Na\ B(OCH_3)_3OCH_2CF_3$

To excess $B(OCH_3)_3$ (35 ml) in a 50-ml flask was added solid $NaOCH_2CF_3$ (12.2 grams; 100 mmoles) under nitrogen with stirring at ambient temperature. A mild exotherm accompanied the dissolution of the alkoxide. The solution was stirred overnight. The product was isolated by the removal of excess $B(OCH_3)_3$ in vacuo at 55 C. Pumping was continued for 3 days at 50 C. Yield: 21.99 grams, 86.0 percent of theory.

## FREE RADICAL COUPLING REACTIONS

## (U) Apparatus

All reactions were carried out in a standard, Pyrex-glass, high-vacuum system with joints and stopcocks lubricated with Halocarbon grease. Purification and separation of starting materials and reaction products was achieved by fractional condensation. Compounds were identified by infrared, $F^{19}$ and proton, and mass spectroscopy. All reactions were carried out on a mmole scale, and protective shielding was used during handling operations. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer using a 5-cm Pyrex cell fitted with Ag Cl windows.

### (U) Preparation of Starting Materials

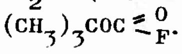
Difluoramine was prepared from difluorourea as reported by Lawton _et al_. (Ref. 30). The compound was always condensed at -142 C and the use of a -196 C bath should be avoided (Ref. 30). Tertiary-butyl hypochlorite was prepared from tertiary-butyl alcohol (Ref. 31). Tertiary-butyl peroxide was purchased from Matheson Coleman and purified by fractional condensation. Methoxyamine was prepared from the hydrochloride as reported by Bissot _et al_. (Ref. 32). Perfluoroformamide and its potassium salt was prepared as reported by Frazer and Shreeve (Ref. 19 and 20) and $N_2F_4$ was purchased from Air Products.

### (U) Reaction Between $F_2NCFO \cdot KF$ and $(CH_3)_3COCl$

A Pyrex ampoule was loaded in the dry nitrogen atmosphere of a glove box with dry KF (5 mmoles) and $CH_3CN$ (1 ml). The latter was distilled from $P_2O_5$ prior to use. The ampoule was connected to the vacuum line and $F_2NCFO$ (2.0 mmoles) was added at -196 C. The contents of the trap were allowed to warm to -31 C and were kept at this temperature for 3 hours. A small amount of volatiles ($COF_2$ and $N_2F_4$) were removed by pumping. Two mmoles of $(CH_3)_3COCl$ were added at -196 C and the mixture was kept at -31 C for 3 hours. The reaction products were separated and identified as described above and consisted of equimolar amounts of $NF_2Cl$, $COF_2$, and $K^+(CH_3)_3CO^-$.

### (U) Reaction Between $F_2NCFO$ and $(CH_3)_3COCl$

Perfluoroformamide (1 mmole) and $(CH_3)_3COCl$ (1 mmole) were combined at -196 C in a U-trap. The mixture was allowed to warm to ambient temperature and was kept there for 2 hours. The reaction products consisted of $NF_2Cl$ (0.5 mmole), $(CH_3)_3CNF_2$ (0.4 mmole), $CO_2$ (0.9 mmole, and some



$(CH_3)_3COC\overset{O}{\underset{F}{\lessgtr}}$.

## (U) Reactions Between $N_2F_4$ and $(CH_3)_3COCl$

Tetrafluorohydrazine (1.01 mmole) and $C(CH_3)_3COCl$ (1.01 mmole) were combined at -196 C. The mixture was allowed to warm up to room temperature and was kept there for 12 hours. Except for a small amount of $(CH_3)_3CF$, only unreacted starting materials were recovered.

(U) In a second experiment, a mixture of $N_2F_4$ (1.10 mmole) and $(CH_3)_3$ COCl (1.02 mmole) in a Pyrex U-trap was exposed to uv irradiation from a 140-watt Hanovia quartz lamp for 3 hours. The reaction products consisted of $N_2F_4$ (1.03 mmole), $(CH_3)_3CF$ (0.3 mmole), and a mixture of organic compounds derived from $(CH_3)_3$ COCl.

(U) In a third experiment, a similar product distribution and conversion of starting materials was obtained when the mixture of starting materials in a quartz bulb was exposed to uv irradiation of a Nestler Pfaust lamp for 15 minutes.

(U) When the latter experiment was repeated (using 1.06 mmole of $N_2F_4$ and 1.06 mmole of $(CH_3)_3COCl$) with 3-hour irradiation from a Hanovia uv lamp, the following product distribution was obtained: $N_2F_4$ (0.65 mmole), $N_2O$ (0.30 mmole), $(CH_3)_3CF$ (0.43 mmole), $CH_3COCH_3$ (0.35 mmole), and a trace of $CH_3NF_2$.

## (U) Reaction Between $(CH_3)_3COCl$ and $NHF_2$

Difluoramine (1.06 mmole) and $(CH_3)_3COCl$ (1.08 mmole) were combined at -146 C in a U-trap. The mixture was allowed to warm up to room temperature and a smooth reaction took place. After 90 minutes, the reaction products were separated and consisted of $ClNF_2$ (1.06 mmole) and $(CH_3)_3COH$.

## (U) Reactions Between $(CH_3)_3COOC(CH_3)_3$ and $N_2F_4$

When $(CH_3)_3COOC(CH_3)_3$ (1.06 mmole) and $N_2F_4$ (1.06 mmole) were combined at -196 C in a Pyrex U-trap and allowed to warm up to ambient temperature, no reaction occurred. When this mixture was irradiated by a Hanovia quartz lamp for 2.5 hours, the following reaction products were obtained: $N_2F_4$ (0.86 mmole), $N_2O$ (0.15 mmole), $(CH_3)_3CF$ (0.10 mmole), $CH_3COCH_3$ (0.06 mmole), and a trace of $CH_3NF_2$.

(U) The reaction was repeated exposing a mixture of 1.06 mmole of $(CH_3)_3COOC(CH_3)_3$ and 1.06 mmole $N_2F_4$ in a quartz container for 3-1/2 hours to uv irradiation by a Hanovia lamp. The following reaction products were obtained: $N_2F_4$ (0.45 mmole), $N_2O$ (0.21 mmole), $CH_3NF_2$ (0.66 mmole), $(CH_3)_3CF$ (0.41 mmole), and $CH_3COCH_3$ (0.56 mmole).

(U) Reaction Between $(CH_3)_3COOC(CH_3)_3$ and $F_2NC\begin{smallmatrix}\nearrow O\\ \searrow F\end{smallmatrix}$

Perfluoroformamide (1.06 mmole) and $(CH_3)_3COOC(CH_3)_3$ were combined at -196 C in a Pyrex U-trap. The mixture was allowed to warm up to room temperature and was kept there for 1.5 hours. The reaction products consisted of $NF_2CFO$ (0.95 mmole), $NHF_2$ (0.06 mmole), $(CH_3)_3CNF_2$ (0.06 mmole), and $CO_2$.

(U) Reaction Between $(CH_3)_3COOC(CH_3)_3$ and $NHF_2$

Difluoramine (1.29 mmole) and $(CH_3)_3COOC(CH_3)_3$ (1.0 mmole) were combined at -142 C in a Pyrex U-trap. The mixture was allowed to warm up to ambient temperature and was kept there for 1.5 hours. The reaction products consisted only of unreacted starting materials.

## FLUORINATION REACTIONS OF $CH_3ONH_2$

### (U) Aqueous Fluorination

Methoxyamine (10 mmole) was placed into a 100-ml three-necked flask. A solution of 6 grams of $NaHCO_3$ in 50 ml of distilled $H_2O$ was added, and a premixed gas stream consisting of 8 parts of He and 1 Part of $F_2$ was passed through the solution at a rate of 70 cc/min. The reaction flask was kept at 0 C by means of an ice bath, and the volatile products were collected in a trap kept at -196 C. The fluorination reaction was completed after about 1 hour as indicated by the disappearance of clouds in the gas phase above the aqueous phase. The reactor was purged for 30 minutes with a stream of He. The contents of the -196 C trap consisted of $CH_3ONO$ (1.46 mmole), $CH_3ONO_2$ (0.26 mmole), $N_2O$ (4.0 mmole), $NO_3F$ (0.13 mmole), $CH_3F$ (0.1 mmole), and a large amount of $CO_2$. Mass spectral analysis revealed the presence of $CH_3ON{=}NOCH_3$ and of partially fluorinated dimethyl ethers in the $CH_3ONO_2$ containing fraction.

## (U) Nonaqueous Fluorination

The fluorination of $CH_3ONH_2$ (9.7 mmole) was carried out similarly to that described above, except for substituting the aqueous buffer solution by 20 ml of dry $CH_3CN$ and keeping the reaction vessel at -10 C by means of a salt-ice mixture. The collected products consisted of $N_2O$ (0.96 mmole), $CH_3ONO$ (2.41 mmole), $CO_2$, $CH_3F$, and some unidentified organic material.

## (U) DISPROPORTIONATION OF BFFP

Into a 75-ml stainless-steel cylinder containing 5 grams of dried CsF was condensed 1 liter (gas) of BFFP ($F\overset{O}{C}O\overset{O}{C}F$) using liquid nitrogen. The cylinder was allowed to warm slowly from -196 to -80 C by placing a dry-ice-liquid nitrogen slush on the cylinder and allowing the liquid nitrogen to slowly boil off. After reaching -80 C, the cylinder was warmed to approximately -40 C and maintained at this temperature for 6 to 40 days. After the desired reaction period, the cylinder was cooled to -196 C and opened to a Teflon U-trap maintained at the same temperature. Noncondensable gases were noted. The product was then fractionated through a series of cold traps at -95, -126, and -196 C to a high-vacuum pumping system. In a typical experiment with a reaction period of 6 days at

-40 C, the -196 C fraction contained 805 cc of $CO_2$ and a small amount of $COF_2$. This fraction was discarded. The -126 C fraction contained 244 cc of $CF_3OO\overset{O}{\overset{\|}{C}}F$ as identified by ir. This represents a 24-percent yield. The -95 C fraction containing approximately 2 ml of a clear liquid at ambient temperature, was refractionated through a -64, -95, -196 C series of traps. The -64 C fraction contained approximately 1.5 ml of liquid at ambient temperature. A vapor sample of this liquid showed $CF_3OO\overset{O}{\overset{\|}{C}}OOCF_3$ and unknown compounds as indicated by ir. The -95 C fraction, approximately 1/2 ml liquid at ambient temperature, contained mainly $CF_3OO\overset{O}{\overset{\|}{C}}OOCF_3$ and a small amount of an unknown. The -196 C fraction contained a small amount of $COF_2$, $CF_3OO\overset{O}{\overset{\|}{C}}F$, and an unknown compound

# APPENDIX

## Preparation of Chlorodifluoramine, $ClNF_2$

by Karl O. Christe

Contribution from Rocketdyne, A Division
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The synthesis of $ClNF_2$ was first reported in 1960 by Petry[1]. Since then, numerous papers dealing with the preparation of this interesting compound have been published.[2-9] The majority of these preparations is based on the reaction of $HNF_2$ with chlorine or chlorine containing compounds.[1,4-6,9] With the exception of the reactions between $HNF_2$ and ClF[9] or inorganic hypochlorites[6], the yields of $ClNF_2$ (based on $HNF_2$) are only about 50% or lower. The remaining methods based on $N_2F_4$,[7,8] $NaN_3$,[3] or $NH_4^+$ containing salts[2] result in only moderate yields of $ClNF_2$ or are hard to control. This paper reports a new, more convenient synthesis of $ClNF_2$ from $HNF_2$ and tertiary-butyl hypochlorite.

This reaction produces $ClNF_2$ in quantitative yield (based on $HNF_2$). In contrast to the reaction between $HNF_2$ and ClF[9], it does not require the use of a metal-Teflon vacuum system but can be carried out in a standard all

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glass vacuum line. Aqueous solutions of inorganic hypochlorites have previously been used[6] to convert $NHF_2$ into $ClNF_2$. However, in aqueous solutions proper control of the pH value and use of a flow reactor are essential to suppress the competing reaction resulting in the formation of $N_2F_4$.

## Experimental

Caution. - Difluoramine is highly explosive[4] and protective shielding should be used during handling operations. The compound was always condensed at -142° and the use of a -196° bath should be avoided.[4]

Materials and Apparatus. - Difluoramine was prepared from difluorourea as reported by Lawton et al.[10] Tertiary-butyl hypochlorite was prepared from tertiary-butyl alcohol.[11] Both compounds were purified by fractional condensation and their purity was determined by infrared spectroscopy. All reactions were carried out in a Pyrex high vacuum line having stopcocks lubricated with Halocarbon grease (from Halocarbon Products Corp.). Infrared spectra were taken on a Perkin-Elmer Model 337 spectrophotometer using a 5-cm Pyrex cell fitted with AgCl windows.

Preparation of $ClNF_2$. - Difluoramine (1.06 mmoles) and tertiary-butyl hypochlorite (1.08 mmoles) were combined at -142° in a U-trap. The mixture was allowed to warm to room temperature and a smooth reaction took place. After 90 minutes the mixture was separated by fractional condensation at -54°, -95°,

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-142°, and -196°. An infrared spectrum of the material trapped at -196° and -142° showed the presence of only $ClNF_2$ (1.06 mmoles). The large bulk of the organic material was trapped at -54°.

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13. ABSTRACT

Anodic cooxidation of $(CH_2)_4O{:}HNF_2$ and $(CH_3)_3COH$ gave $(CH_3)_3CF$. With $CH_3OH$, the products of anodic oxidation in the presence of $(CH_2)_4{:}HNF_2$ were $CH_3OCH_2NF_2$, $CH_3OCH_2NF_2$, $CH_3OCH(NF_2)OCH_3$, and $CH_3OCHO$. The electrolysis of $C_5H_5N{:}HNF_2$ and $B(OCH_3)_4^-$ on graphite gave a mixture of $CH_3ONO$ and $N_2F_4$. The methyl nitrite is believed to be a decomposition product of the desired $CH_3ONF_2$.

The anodic oxidation of the derivatives of 2,2,2-trifluoro ethanol on platinum in acetonitrile gave $CF_3CH_2OCF_3$ and $(CF_3CH_2O)_2$. A cogeneration of $CF_3CH_2O\cdot$ and $\cdot NF_2$ radicals was not achieved.

Perfluoroformamide and its alkali metal salts, $N_2F_4$, and $HNF_2$ with t-butyl hypochlorite and t-butyl peroxide as $(CH_3)_3CO\cdot$ gave no direct evidence for the formation of $(CH_3)_3CONF_2$. Attempts to prepare $CH_3ONF_2$ by direct fluorination of $CH_3ONH_2$ in $H_2O$ or $CH_3CN$ solution were unsuccessful.

A new compound was formed from bis-(fluoroformyl) peroxide, BFFP, and KF and was isomeric with BFFP. Mass spectral data and $F^{19}$ nmr confirmed the structure as the ozonide of difluoroketene (2,3,5-trioxa-4,4-difluorocyclopentanone). Cesium fluoride and BFFP gave good yields of $(CF_3OO)_2C{=}O$ and $CF_3OOC(O)F$. (C)

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