

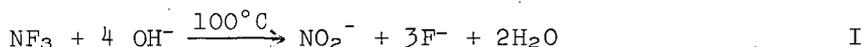
HYDROLYSIS OF THE NITROGEN FLUORIDES

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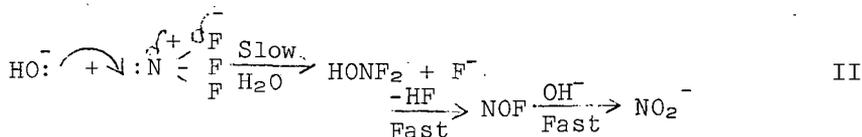
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BASIC HYDROLYSIS OF NF₃

Nitrogen trifluoride is extremely resistant to chemical attack by water and aqueous acid; the compound can be recovered quantitatively after one week in contact with excess dilute acid (HNO₃, H₂SO₄, HClO₄) or pure water at 133°C. In the presence of aqueous base, however, slow hydrolysis occurs at 100°C yielding nitrite and fluoride.

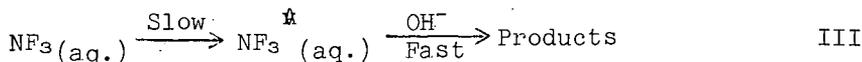


This behavior differs sharply from that of nitrogen trichloride, which is known to give ammonia and hypochlorite under similar conditions. The latter products are readily explained in terms of nucleophilic attack directed at the chlorine atoms, a mechanism which appears reasonable in view of the fact that the electronegativities of N and Cl are very nearly the same and that the halogen may easily expand its valence shell. Obviously, these considerations cannot be applied to the nitrogen trifluoride molecule since fluorine is considerably more electronegative than nitrogen and it has no available d orbitals. Although the nitrogen atom also has no free orbitals, the relatively low electron density would at least offer less resistance to the approach of a nucleophile

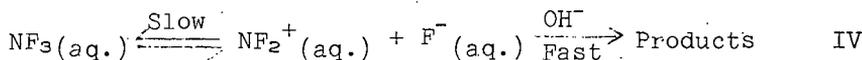


The proposed intermediate HONF₂ would be expected to be unstable with respect to the loss of HF, as is apparently the case with the unknown perfluoro alcohols.¹

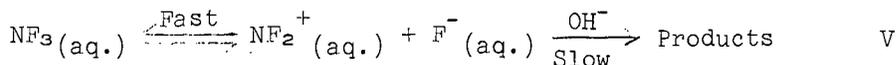
Two other reaction modes worth considering include the formation of an intermediate activated complex with water



and the intriguing but unlikely reversible ionization of NF₃.



or



Preliminary experiments indicated that the rate of reaction of gaseous NF_3 with caustic soda solution in a static system was first order with respect to NF_3 with little dependence on the initial concentration of the base. Although these observations are apparently consistent with the first order equations III and IV more detailed studies show that these results are misleading.

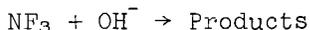
If the reactions were first order in NF_3 only, the rate of decrease of the partial pressure (P) of NF_3 with time (T) in a closed system should be given by the following equations

$$\frac{dP}{dT} = \frac{KV_c}{V_o} P$$

$$\frac{V_o}{V_c} \log \frac{P_o}{P} = K T$$

where V_o is the volume available to gaseous NF_3 , V_c is the volume of the caustic soda solution and P_o is the initial pressure of NF_3 . The assumption is made that a Henry's law equilibrium is established between gaseous and dissolved NF_3 .

In Fig. 1 the results of a number of experiments are shown plotted according to the integrated form of the rate equation. The points of line "B" and group "A" were calculated from data furnished by H. J. Bronaugh. The line "B" was obtained from a series of experiments in which samples of NF_3 (4.83-7.16 mmole) at a constant initial pressure of one atmosphere were allowed to react with 20 ml of 0.5 N NaOH for varying lengths of time. The curvature of the line clearly suggested that the steadily decreasing hydroxyl ion concentration (up to 90% neutralization) does indeed tend to decrease the reaction rate, but the effect is much less than would be expected for the 2nd order equation



VI

The group of points "A" was derived from reactions involving samples of NF_3 at initial pressures ranging from 0.25 to 2 atmospheres (1.7-8.7 mmole) and 30 ml of 0.5 NaOH. The positions of the top four points of this group, which were obtained from simultaneous runs, again indicate that the extent of conversion of NF_3 depends on the concentration of OH^- . Thus the height of the individual points decreases inversely with the corresponding degree of neutralization of the caustic soda. More important, however, is the fact that group "A" lies well below "B" showing that the reactions involving 20 ml of base were more than 2/3 as fast as those with 30 ml. Since the

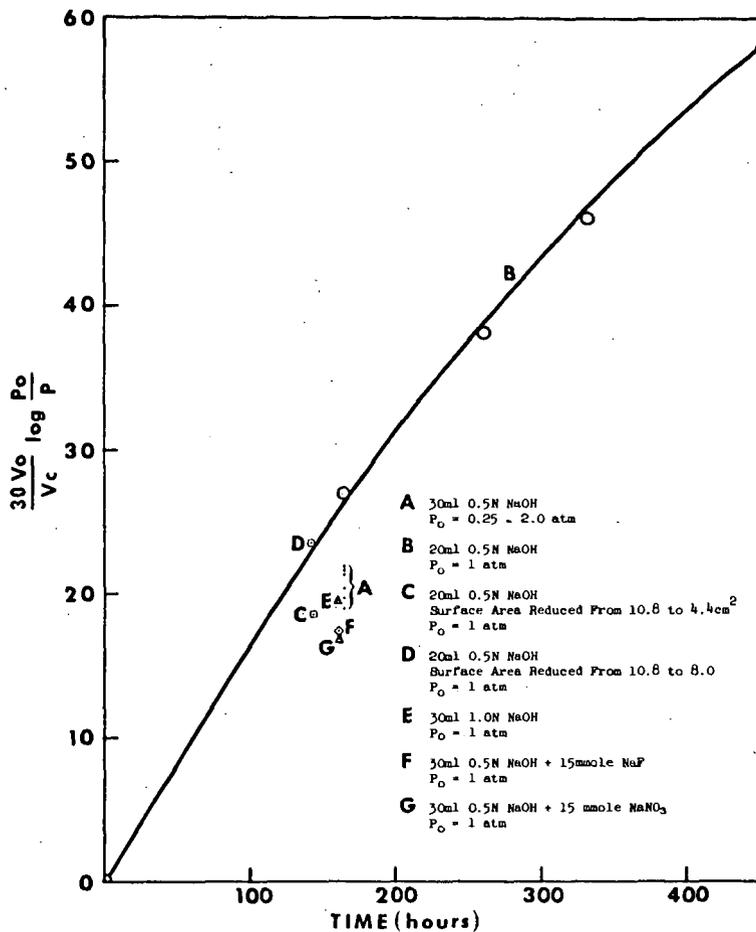


FIG. 1

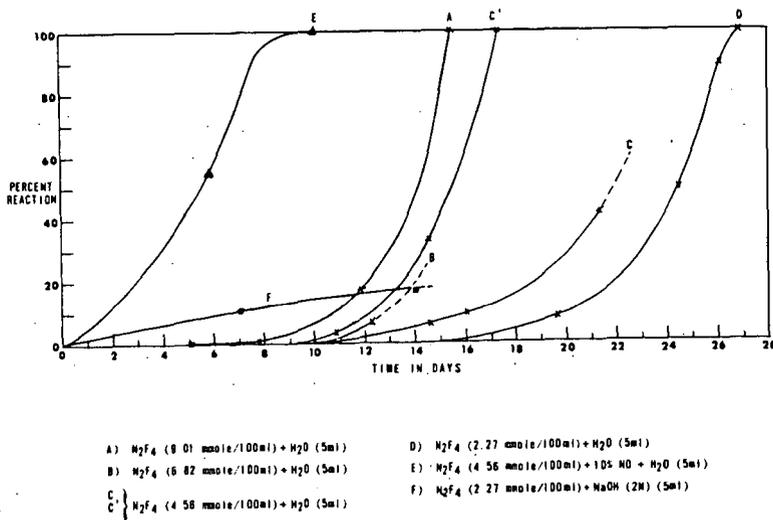


FIGURE 2 - HYDROLYSIS OF N_2F_4 AT 60°C

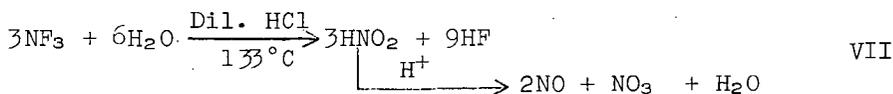
solutions were contained in upright "Teflon" cups of identical diameter in each case, the data indicate that the rate of conversion of NF_3 was significantly influenced by the available surface area. Presumably, the NF_3 failed to reach an equilibrium concentration in solution in spite of the long reaction times. The dependence of the reaction rate on the area of the gas-liquid interface was confirmed in the experiment represented by points "D" and "C" in which the surface areas of the solutions (20 ml 0.5 N NaOH) were reduced from 10.8 cm^2 to 8.0 and 4.4 cm^2 respectively.

The apparently small effect of the initial OH^- concentration on the rate of hydrolysis of NF_3 is probably due not only to the surface area phenomenon described above, but also to a reduction in the solubility of the gas resulting from increased ionic strength. The proposed "salting-out" effect is demonstrated in the experiments represented by points "E", "F" and "G". In "E", 1.0 N NaOH (30 cc) was used in place of the 0.5 N caustic soda employed by H. J. Bronaugh for group "A", yet the extent of reaction was approximately the same. Half normal NaOH was also used in "F" and "G" but the total ionic strength of the solutions was increased to the equivalent of 1.0 N NaOH by the addition of NaF and NaNO_3 respectively. In each of the latter experiments the reaction rate was significantly lowered, indicating that inhibition due to rising ionic strength tends to partly offset the acceleration associated with increasing OH^- concentration. In this connection it should be noted that concentrated NaOH (12 N) reacts extremely slowly with NF_3 .

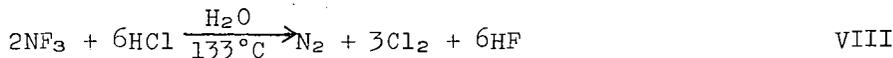
It is of interest that the rate of basic hydrolysis is decreased to exactly the same extent (within the experimental accuracy) by equivalent amounts of NaF or NaNO_3 . If the reaction involved mechanism V, NaF would be expected to act as an inhibitor by shifting the equilibrium to the left. Thus it appears that the reaction proceeds via the nucleophilic mechanism given in equation II.

REACTION OF NF_3 WITH AQUEOUS HCl

Additional support for the proposed nucleophilic mechanism of the basic hydrolysis has been provided by a study of other aqueous systems such as hydrochloric acid. Although NF_3 is unaffected by prolonged contact with either pure HCl or pure water at 133°C, the compound reacts slowly with aqueous HCl at this temperature, yielding products which vary with the concentration of the acid. Nitric oxide and nitric acid are formed by the dilute solution (0.5 N)



while the more highly concentrated reagent (4 N) yields elementary nitrogen and chlorine.

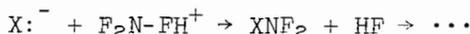
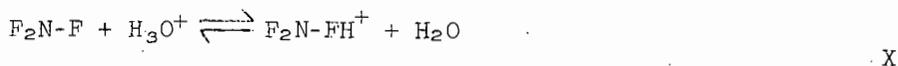


As in the case of the basic hydrolysis the rate of conversion of NF_3 was found to vary only slightly with the strength of the solution. The fact that NF_3 reacts with aqueous HCl but not with the pure compound clearly suggests that ionic attack is involved. The active species in the reaction is almost undoubtedly Cl^- since it has been shown that while NF_3 is inert to many acids, it reacts readily with hot, neutral sodium chloride solution (4 N).



REACTION OF NF_3 WITH AQUEOUS NUCLEOPHILES

Further indirect evidence for the postulated nucleophilic behavior of Cl^- and OH^- has been obtained from a series of experiments in which NF_3 was allowed to react with solutions containing anions of varying nucleophilic strength. It was found that for those species tested the extent of reaction within a given time and temperature range increased monotonically with the accepted value² of the nucleophilicity of the anion. Furthermore, although NF_3 did not react with acid solutions of weak nucleophiles, the reaction rate with halides was increased by the presence of hydronium ion, as would be expected for an $\text{S}_{\text{N}}2$ mechanism involving the loss of fluoride



The results of a number of experiments involving nucleophilic reagents are listed in Table I. In the strictest sense it is not possible to compare the relative degrees of reaction solely on the basis of the nucleophilicity of the starting material because reactive intermediates may influence the overall conversion rate. The varying stoichiometries also impose restrictions for those experiments which involve small quantities of aqueous reagent and are thus subject to unequal changes in concentration for a given amount of NF_3 reacted. In spite of these limitations the data clearly indicate that the reaction rates increase with nucleophilic strength in the order



REACTIONS OF NF_3 WITH ELECTROPHILES

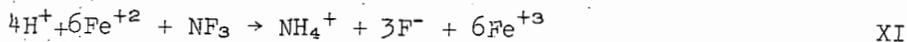
In his early work on NF_3 Ruff³ reported that the compound was stable to AlCl_3 at red heat. Investigations in this laboratory show that NF_3 does react with AlCl_3 under mild conditions (80°C , 4 days) to produce nitrogen and chlorine. Chlorine is liberated rapidly at 135°C . The reaction presumably involves coordination of a fluorine atom of NF_3 to the vacant orbital of the aluminum atom, as is believed to be the case with the chlorination of fluorocarbons by AlCl_3 . Reactions conducted in a Teflon IR cell gave no evidence for the formation of gaseous intermediates such as NF_2Cl .

TABLE I - REACTIONS OF NF₃ WITH NUCLEOPHILES IN AQUEOUS SOLUTION

Reagent	Molarity Volume (ml)	Temp. (°C)	Reaction Time (hrs)	Reaction Initial NF ₃ (mmole)	Po NF ₃ At Reaction Temp. (atm)	NF ₃ Reacted (%)	Product (mmoles)
HClO ₄	0.5-20	133	159	2.14	0.585	1.0	-
HNO ₃	0.5-20	133	159	2.10	0.574	1.0	-
H ₂ SO ₄	0.5-20	133	159	3.34	0.99	1.0	-
H ₂ SO ₄	4 -20	133	159	3.52	1.02	1.0	-
HCl	0.5-20	133	235	3.00	1.00	54.4	NO 0.73; NO ₂ ⁻ 0.12; NO ₃ ⁻ 0.81; F ⁻ 4.74
HCl	4 -20	133	235	3.16	1.02	63.6	N ₂ 1.06; Cl ₂ 2.75; F ⁻ 5.38
HCl	0.5-20	133	159	2.14	0.636	13.5	Cl ₂ 0.12
NaCl	4 -20	133	306	4.37	1.047	24.7	N ₂ 0.33; NO ₃ ⁻ 0.42
HBr	0.5-20	133	159	1.98	0.633	67.7	N ₂ 0.31; N ₂ O .06; Br ₂ 2.44; F ⁻ 3.84
NaCl	0.5-30	100	160	2.97	0.936	1.0	-
HCl	0.5-30	100	160	2.98	0.939	1.0	N ₂ ; Cl ₂
NaBr	0.5-30	100	160	3.07	0.957	14.0	NH ₄ ⁺ 0.44; F ⁻ 1.37
HBr	0.5-30	100	160	3.01	0.938	22.6	N ₂ 0.1; NH ₄ ⁺ 0.33; F ⁻ 1.74, Br ₂ 0.94
NaOH *	0.5-30	100	160	3.01	0.939	38.2	NO ₂ ⁻ 1.15; F ⁻ 3.35
NaI	0.5-30	100	160	2.97	0.91	50.8	N ₂ 0.50; N ₂ O 0.05; NH ₄ ⁺ 0.72; F ⁻ 4.84
HI	0.5-30	100	160	3.15	0.952	71.8	NH ₄ ⁺ 2.11; I ₂ 5.05
Na ₂ S ₂ O ₃	0.5-30	100	160	2.79	0.837	61.3	S 5.1; F ⁻ 3.75; NH ₄ ⁺ 1.50

* NaOH reaction data were calculated.

Nitrogen trifluoride is readily converted to ammonium ion by acidic or neutral ferrous sulfate solution at 60°C.

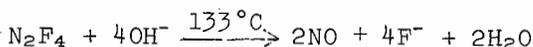


In a typical experiment NF_3 (3.18 mmole, $P_0 = 0.69$ atm) was maintained in contact with the aqueous salt (20 ml, 0.5 N) for 12 days, resulting in the destruction of about 44 per cent of the NF_3 .

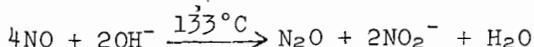
Ferric chloride solutions react very slowly with NF_3 at 100°C; the FeCl_3 acts as a hydrolysis catalyst, yielding nitric oxide and nitrate. This catalysis is not a general property of the transition metal ions as shown by the total inertness of NF_3 to solutions of CoCl_2 , MnSO_4 , CuSO_4 and NiSO_4 at 100°C over periods up to seven days.

HYDROLYSIS OF N_2F_4

Dinitrogen tetrafluoride reacts more readily than NF_3 with aqueous solutions; at 133°C it is rapidly destroyed by contact with acidic, basic and neutral solutions. The reaction with caustic soda produces mainly nitrous oxide and nitrite along with a trace of nitrogen.



XII



With water and aqueous HCl significant quantities of nitrogen and nitrate are formed in addition to nitric oxide. Surprisingly, the amount of nitrogen produced was found to be greater with water than with 4 N HCl, and in neither instance was as much N_2 formed as in the corresponding reaction of NF_3 with 4 N HCl. At lower temperatures (60-100°C) N_2F_4 is nearly quantitatively converted to NO by water and dilute HCl (0.5 N).

The results of a number of experiments on the kinetics of the N_2F_4 - H_2O system are summarized in Figure 2. The hydrolytic mechanism is obviously complex as indicated by the long induction periods and the subsequent exponential increase in the reaction rates. The total time required to completely destroy the N_2F_4 shows a difficultly reproducible inverse dependence on the initial pressure of this compound. The effect of N_2F_4 pressure on the overall reaction rate has been confirmed in other experiments. In a typical series, N_2F_4 samples at concentrations of 0.65, 1.27, 2.53, 3.85 and 5.22 mmole/100 ml were heated with water for 5 days at 35°C, 6 days at 50°C and 6 days at 60°C. The first three samples (low pressures) were recovered quantitatively while the fourth and fifth samples reacted to the extent of 6% and 100% respectively.

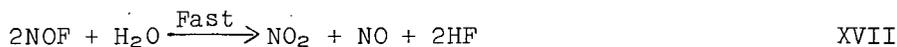
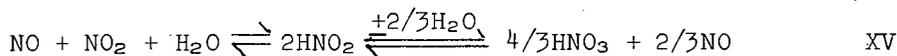
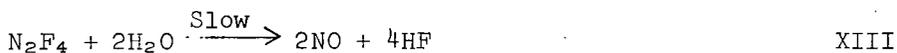
The marked acceleration of the hydrolysis with time is apparently a result of secondary reactions initiated by the product nitric oxide. The fastest and slowest reaction ["E" and "D"] illustrated in Fig. 2 were conducted under identical conditions except for the addition of

10 mole % of nitric oxide to the N_2F_4 in "E". The hydrofluoric acid formed also exerts a positive influence on the rate, but to a lesser degree than nitric oxide.

Both hydrochloric acid (0.5 N) and sodium hydroxide (2 N) profoundly alter the reaction. The halide causes the complete destruction of N_2F_4 at low pressures in less than 10 days while the hydroxide produces a slow, steady reaction with no indication of an induction period or increasing rate with time (line "F").

Experimental results on the N_2F_4 - H_2O reaction were very difficult to duplicate; the lines C and C', which are vastly different, were obtained from supposedly identical runs, using N_2F_4 and water from the same sources. The large variations in reaction rate are believed to be due to minute amounts of oxygen remaining in the starting materials even after careful purification including boiling and vacuum degassing of the water. In control experiments, oxygen was found to be at least 10 times as effective as nitric oxide in promoting the reaction; the addition of about one mole per cent of the gas (based on N_2F_4) to the mixture reduced the total conversion time by a very conservatively estimated factor of four.

The above observations are consistent with the following reaction scheme:

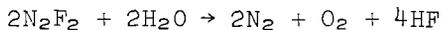


The formation of some nitrogen dioxide (eq. XIV) at 60°C appears likely in view of the fact that large quantities of this gas were observed in the products of similar reactions at higher temperatures (133°C). Experiments in this laboratory have confirmed that N_2F_4 is readily attacked by NO_2 (eq. XVI) giving NOF, which would in turn rapidly hydrolyze and thus regenerate the NO_2 (eq. XVII). Increasing acidity would favor higher concentrations of free NO_2 by shifting the equilibrium (XV) to the left. By analogy to the chemistry of NF_3 , caustic soda might be expected to be more efficient than water in the direct (nucleophilic) attack on N_2F_4 , but secondary reaction would be inhibited by the removal of NO_2 . Obviously oxygen would immediately convert any NO present to NO_2 .

HYDROLYSIS OF cis- AND trans- N_2F_2

Few authors who have worked with difluorodiazine have failed to

comment on the "vast" difference in the reactivities of the two isomers. It is therefore surprising that trans-N₂F₂ is only moderately more resistant than cis-N₂F₂ to attack by water. Both materials are unaffected by excess water at 60°C over a period of 15 hours. The cis-isomer hydrolyzes slowly at 74°C (30% in 17 hours) while the trans- compound reacts at a similar rate at 89°C. In each case the major products are nitrogen, oxygen and hydrogen fluoride.



XVIII

Nitrous oxide is also formed, but only in minor quantities (< 3%).

The results of a number of hydrolytic experiments with the cis- and trans-N₂F₂ are summarized in Figures 3 and 4.

The data in Figure 3 were obtained by allowing samples of trans-N₂F₂ at 89°C to react with 5 ml portions of water, aqueous NaOH (2 N) or aqueous HCl (0.5 N) in Pyrex ampoules. The line "A", drawn through the circled points, shows the logarithmic rate of change in the number of millimoles of trans-N₂F₂ in contact with water. Line "B" was derived by plotting the function $\log(N_0 - 2/3n)$ where N₀ is the initial concentration of trans-N₂F₂ and n is the total amount of non-condensable gas produced at any given time. The lines "C" and "D" were obtained from experiments involving aqueous NaOH (2 N) and aqueous HCl (0.5 N) respectively and were plotted on the same basis as line "A".

If the reaction proceeded quantitatively according to equation XVIII, lines "A" and "B" should be superimposed. The difference between these lines is at least partly due to the formation of nitrous oxide. Also, infrared spectroscopic studies on the original and partially reacted trans-N₂F₂ suggest that the material may have contained a small amount of undetectable impurity which would have caused a slight but proportionally consistent overestimation of the amount of N₂F₂ present.

A similar set of experiments involving a mixture of cis- and trans-N₂F₂ (67% cis) at 74°C is recorded in Fig. 4. The reaction rates of trans- and cis-N₂F₂ are given by lines "E" and "F" respectively. The points enclosed by squares express the rate of formation of non-condensable gases (N₂ and O₂) from cis-N₂F₂ in terms of the function $\log[N_0 - 2/3n - \Delta]$ where N₀ is the initial amount of the cis isomer, n is the total amount of non-condensable gas produced in the given time and Δ is the amount of trans-isomer reacted as calculated from line "E". The excellent agreement between the non-condensable function and line "F" is probably somewhat fortuitous since detectable quantities of N₂O were also formed.

After the completion of the preceding experiment, the remaining isomeric mixture was allowed to react with 2 N NaOH under similar conditions of temperature and pressure. No change in the reaction rate occurred as is indicated by the points in parentheses in Fig. 4.

The above data suggest two important conclusions:

1. The reactions of cis- and trans-N₂F₂ with water are each first order with respect to the nitrogen fluoride.

HYDROLYSIS OF A MIXTURE OF CIS & TRANS-N₂F₂ AT 74°C

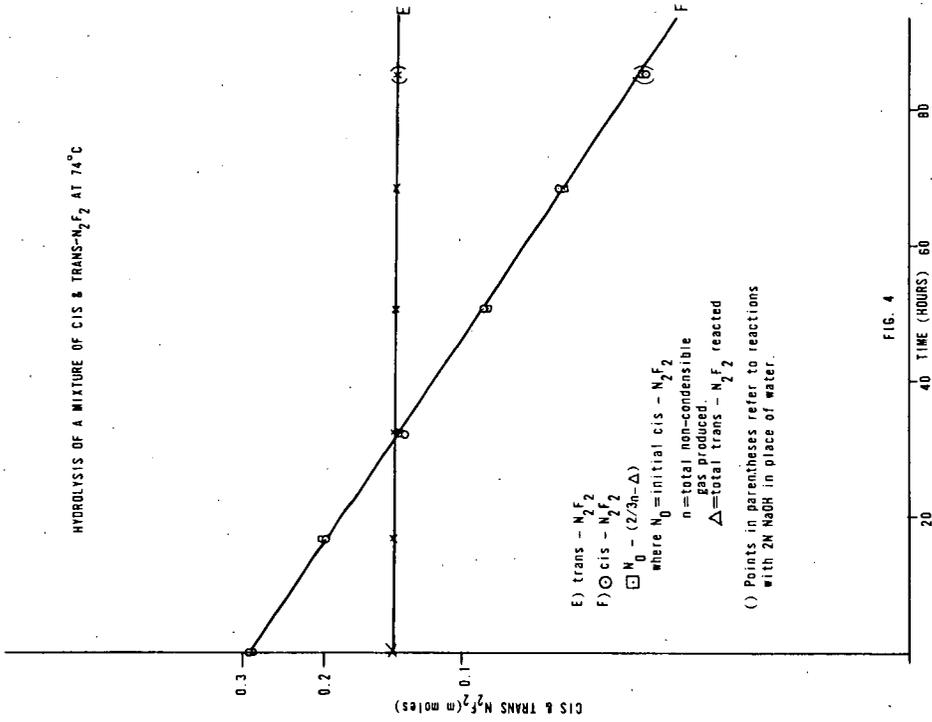


FIG. 4

HYDROLYSIS OF trans-N₂F₂ AT 89°C

- A) trans - N₂F₂ + H₂O (5ml)
 - B) trans - N₂F₂ + H₂O (5ml)
 - C) trans - N₂F₂ + NaOH (5ml, 2N)
 - D) trans - N₂F₂ + HCl (5ml, 0.5N)
- ORDINATE = M₀ - 2/3n
 where M₀ = initial N₂F₂
 n = total non-condensable gas produced

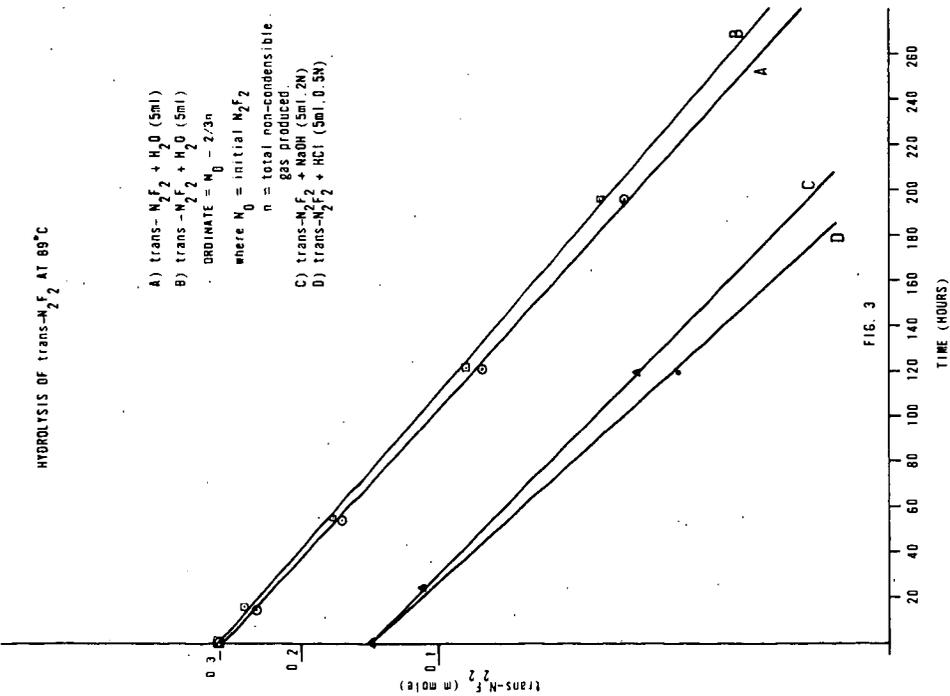
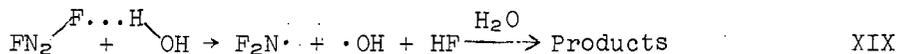


FIG. 3

2. The hydrolyses do not proceed via nucleophilic attack on N_2F_2 .

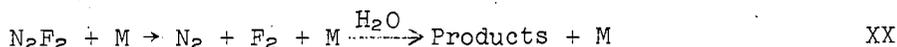
The second conclusion is based on the observations that the strong nucleophile OH^- does not significantly accelerate the reactions, and on the fact that very little nitrous oxide is produced.

Because N_2F_2 is a strongly endothermic⁴ compound, it is necessary to consider not only direct chemical attack by water



but also the thermal decomposition of the nitrogen fluoride to the elements. The reported reactivity⁵ of *cis*- N_2F_2 toward glass poses an additional question of possible competing reactions with the container walls.

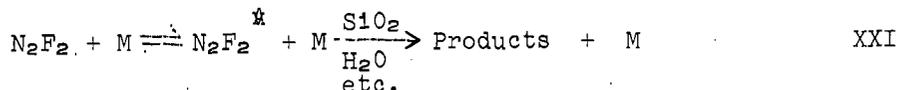
In an effort to resolve these problems a study was made of the decomposition of N_2F_2 in glass, both alone and in the presence of elementary nitrogen. The experimental results given in Table II indicate that both isomers decompose slowly at the previously established hydrolysis temperatures and that the reaction rates increase with the total pressure of the system. Variations in the available glass surface area apparently do not significantly alter the rates. These observations suggest that the hydrolytic reactions may proceed, at least in part, via a simple decomposition mechanism of the type



where M is any molecule. Hydrolytic attack is not completely precluded by the above evidence since water vapor (in equilibrium with the liquid) was found to be approximately twice as efficient as an equal pressure of nitrogen in destroying the isomers. In this connection it may be noted that nitric oxide was considerably more active than water under similar conditions.

The sensitivity of the decomposition rate to pressure offers a reasonable explanation for the reported high degree of reactivity of *cis*- N_2F_2 (under high pressures) toward glass⁵ at ambient temperatures as compared with the relative inertness (at low pressures) of this system observed in this laboratory.

Obviously, all of the above experimental results may be equally well interpreted in terms of the reversible formation of an activated intermediate



at least in the case of the *trans* isomer, mechanism XXI is supported by the work of Schaap, Nevitt and Zletz⁶ which indicates that the compound is stable in steel at 82°C under pressures as high as 3,400 atm. The *cis* isomer was reported to detonate under similar conditions.

TABLE II
 DECOMPOSITION OF cis- AND trans-N₂F₂ IN GLASS

Initial N ₂ F ₂ (mmole)	Initial Pressure of N ₂ F ₂ At Reaction Temp. (mm Hg)	Initial Partial Pressure Of N ₂ (mm Hg)	Surface Area -cm ⁻¹ Volume	Reaction Temp. (°C)	Time (hrs)	Decomposition (%)
trans (0.240)	40	500	1.8	89	18	9
trans (0.246)	40	500	1.8	89	16	11
trans (0.229)	40	nil	1.8	89	16	5
trans (0.217)	36	nil	1.9	89	18	5
trans (0.412)	69	nil	1.8	89	16	5
trans (0.412)	69	500	1.9	89	16	10
trans (0.040)	67	500	6.7	89	16.5	11
cis (0.028) trans (0.137)	cis (6) trans (29)	300	1.9	75	18	cis (15) trans (nil)
cis (0.024) trans (0.437)	cis (5.1) trans (29)	nil	1.9	75	18	cis (8) trans (nil)
cis (0.104) trans (0.063)	cis (18) trans (10)	nil	6.7	75	18	cis (9) trans (nil)
trans(0.246)	-	500	1.8	-	-	nil

* Control run to establish efficiency of recovery technique.

In a study of the isomerization of trans-N₂F₂ in copper, Colburn et al. ⁵ noted that extensive decomposition to the elements occurred at temperatures above 300°C. Similar experiments in this laboratory have shown that this reaction also occurs at much lower temperatures (175-200°C) and that the rate is strongly pressure-dependent. The results of a typical series of runs, as given in Table III, demonstrate that the extent of decomposition increases greatly with the pressure. The relatively low ratio of cis- to trans-N₂F₂ recovered in Experiment 1 suggests that the cis isomer is more rapidly destroyed than the trans compound.

TABLE III
ISOMERIZATION OF trans-N₂F₂

Expt.	Pressure (mm)	Reaction Time (sec)	Reaction Temp. (°C)	Total N ₂ F ₂ Recovered (%)	cis-N ₂ F ₂ In Recovered N ₂ F ₂ (%)
1	370	30	175-200	16	29
2-7	14-20	90	175-200	70	67

EXPERIMENTAL

Sealed pyrex ampoules (ca. 135 ml) equipped with one or more break seals were used for all hydrolytic reactions. In the experiments involving NF₃ and caustic soda, the base was contained in loose-fitting Teflon cups within the ampoules to prevent attack on the glass. Infrared spectroscopy was generally used for the analysis of gaseous products.

Nitrogen trifluoride and dinitrogen tetrafluoride were obtained from Peninsular ChemResearch Inc. and Air Products Inc. respectively. Difluorodiazine was prepared by the reaction of N₂F₄ with AlCl₃ at -78°C. ⁷

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