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## EXPLOSIVE REACTIONS OF N-F COMPOUNDS WITH HYDROGEN

by

Lester P. Kuhn  
Carl R. Wellman

April 1969

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B A L L I S T I C   R E S E A R C H   L A B O R A T O R I E S

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Lester P. Kuhn

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Interior Ballistics Laboratory

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FOR THE DIRECTOR, ARMY  
RESEARCH OFFICE  
DURHAM, N. C. 27706

RDT&E Project No. 1M223001A211

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B A L L I S T I C   R E S E A R C H   L A B O R A T O R I E S

REPORT NO. 1431

LPKuhn/CRWellman/lkg  
Aberdeen Proving Ground, Md.  
April 1969

EXPLOSIVE REACTIONS OF N-F COMPOUNDS WITH HYDROGEN

ABSTRACT

In order to gain an understanding of the explosive reactions of N-F compounds, a study has been made of the explosive reaction between tetrafluorohydrazine and hydrogen. The explosion is inhibited by substances capable of destroying hydrogen atoms. Tetramethylethylene is the most effective inhibitor of the substances tested. One part of this substance in 10,000 parts of reaction mixture completely suppresses the explosion. The reaction has the properties of a chain reaction initiated by the difluoroamino radical and having hydrogen atoms as one of the chain carriers. The stoichiometry and the products of the reaction depend in an unusual manner upon the presence of inert gas. Mechanisms are proposed for these reactions which are consistent with the experimental data. The intermediates,  $N_2F_3\cdot$  and  $N_2F_2$ , which are believed to be formed in the reaction can react in different ways depending upon the relative abundance of the reactants and upon explosion temperature, thus accounting for the peculiar features of this system.

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## I. INTRODUCTION

Compounds containing the difluoroamino group,  $\text{NF}_2$ , are powerful oxidizers and are therefore of interest to the chemist concerned with propellants and combustion processes. In the search for high energy propellants a number of N-F compounds have been synthesized but their utilization in propellant compositions has been thwarted by their sensitivity and their tendency to detonate rather than burn. The understanding and control of the explosive reactions of N-F compounds with various fuels is therefore of considerable military interest. From the purely scientific point of view these reactions are also of great interest for, in contrast to the hundreds of papers that have been published on explosive reactions of oxygen with various fuels, there has been practically nothing published on explosive reactions of N-F compounds with fuels. The present work is concerned with the explosive reaction of tetrafluorohydrazine with the simplest fuel, hydrogen, a reaction which has not been previously reported in the literature.

In our early experiments we learned that an explosive reaction can occur between tetrafluorohydrazine and hydrogen but the reaction was extremely irreproducible. Thus in a clean dry Pyrex flask a 1:1 mixture of the gases at 30 torr would not explode below  $80^\circ$ . After conditioning of the flask by several explosions, subsequent additions of the same mixture of gases would explode at  $20^\circ$ . By pumping and baking the flask or by washing with water and alcohol and drying thoroughly, the flask could be returned to its initial condition and the 1:1 gas mixture again required a temperature of  $80^\circ$  for explosion when the pressure was 30 torr. Similar results were obtained using a stainless steel reaction vessel. It was just about impossible to get reproducible explosion limits in a Pyrex or stainless steel reaction vessel. Such behavior has often been noted in explosive reactions and is a consequence of the formation or destruction of atoms

or radicals at the wall of the reaction vessel<sup>1,a,b\*</sup>. We were able to overcome this irreproducibility by coating the vessel with Kel-F oil. With this surface coating the explosion limits could be reproduced for a period of several weeks. After this method of obtaining reproducible experiments was discovered all subsequent experiments were carried out in Kel-F coated vessels. In the Kel-F coated vessel the explosion limits were much lower than in the uncoated vessel indicating that the irreproducibility was due to the destruction of radicals at the wall and that these radicals acted as chain carriers.

## II. EXPERIMENTAL

Research grade tetrafluorohydrazine, nitrogen trifluoride and difluorodiazine were obtained from Air Products Co., Allentown, Pa. The diazine contained about 95% of the trans isomer and 5% cis. The gases were used without further purification.

The gases were handled in a Pyrex vacuum line which was connected to a two-stage gas ballast vacuum pump through a liquid nitrogen trap. The pressure of reactants was measured with a Wallace and Tiernan pressure gauge. Between runs the vacuum line, the mixing flask and the reaction flask were evacuated to a pressure of 1 to 2 microns. Stopcocks were lubricated with Kel-F stopcock grease. To prevent the vacuum line from being contaminated by hydrogen fluoride or fluorine the reaction products were never pumped through the vacuum line but through a line which by-passed the vacuum line and led directly to the trap and the pump. If the reaction products were to be analyzed the reaction vessel was disconnected from the vacuum line and connected to the gas sampling valve of the gas chromatograph.

The earlier experiments were carried out by introducing the reactants directly into the reaction flask and then putting the reaction flask into a thermostatted oven at the desired temperature.

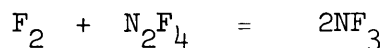
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\* References are listed on page 30.



In later experiments a mixing flask was connected through a T-shaped three-way stopcock to a reaction flask and to the vacuum line. The mixing flask was periodically washed and baked to prevent explosions occurring in it. The reaction flask was a Pyrex flask which had been washed and rinsed several times with acetone and evacuated and heated. Number 10 Kel-F oil was introduced into the warm flask which was then rotated so that the entire surface was coated with the oil. The flask was inverted so that the excess oil drained off and the flask was ready for use.

The reactants were introduced into the mixing flask and were then allowed to diffuse into the reaction flask which was contained in a thermostatted oven at the desired temperature. After explosion the reaction vessel was connected to the gas-sampling valve of the gas chromatograph and analyzed by vpc, using a 2 meter silica gel column at 35° and a flow rate of 40 ml He per minute. The retention times in minutes for the various reactants and products are as follows: hydrogen 0.5, nitrogen 0.7, nitric oxide 0.8, nitrogen trifluoride 1.8, cis difluorodiazine 3.8, trans difluorodiazine 4.4, and tetrafluorohydrazine 8.4. Fluorine, hydrogen fluoride and silicon tetrafluoride do not go through a silica gel column. Hydrogen fluoride was analyzed as such or as silicon tetrafluoride, after reaction with Pyrex, by infrared spectroscopy. Fluorine was determined as nitrogen trifluoride<sup>2</sup> after reaction of the reaction products with tetrafluorohydrazine at 100°,



or it was determined as such by its absorbance at 2850 Å.

Face shield, equipment shields, and stopcock turning extensions were routinely used since explosion sometimes occurred unexpectedly.

### III. RESULTS

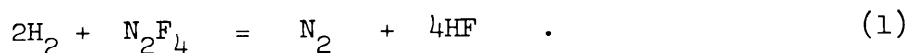
#### A. Effect of Varying Ratio of Reactants

In order to get a material balance for the reaction, various mixtures of hydrogen and tetrafluorohydrazine were allowed to explode and the reaction products were determined. The results are shown in Table I.

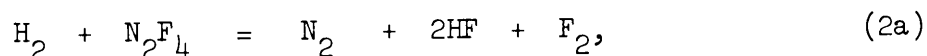
Table I. Yield of Products of Hydrogen - Tetrafluorohydrazine  
Explosion in 100 ml Kel-F Coated Pyrex Flask at 90°.

Reactants		Products			
(torr)		(torr)			
N <sub>2</sub> F <sub>4</sub>	H <sub>2</sub>	N <sub>2</sub>	NF <sub>3</sub>	HF	F <sub>2</sub>
2	4	2	0	8	0
3	3	3	trace	6	3
4	2	2.7	2.6	4	2

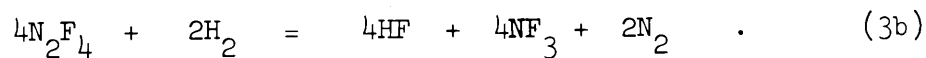
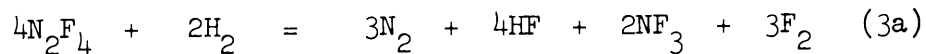
An interesting feature of this reaction is that the products and the stoichiometry of the reaction depend upon the ratio of the reactants. When the ratio H<sub>2</sub>/N<sub>2</sub>F<sub>4</sub> is 2 the reaction can be represented by the equation



When the ratio of reactants is 1 the reaction can be represented by the equation



and when the ratio of reactants is 0.5 the reaction cannot be represented by a simple stoichiometric equation but requires two equations indicating the occurrence of two or more simultaneous processes



## B. The Effect of Inert Gas

The addition of inert gas such as helium or xenon has no effect upon the product composition or yield when the ratio of reactants,  $H_2/N_2F_4$ , is 2. When this ratio is 1 or 0.5, on the other hand, the inert gas has a profound and unusual effect upon the product composition and yield. This is shown in Table II which gives the yield of reaction products from the explosion of a mixture of hydrogen (3 torr), tetrafluorohydrazine (3 torr) and varying amounts of helium. With increasing amounts of helium the yield of nitrogen gradually decreases and finally reaches a limiting value; the yield of nitrogen trifluoride is initially very small and rises to a maximum at a total pressure of about 50 torr and then gradually falls off to a limiting value. Under all conditions hydrogen is completely consumed. Tetrafluorohydrazine is completely consumed at total pressure up to about 50 torr. In the pressure range where the yield of nitrogen trifluoride diminishes a certain amount of tetrafluorohydrazine appears in the products.

Table II. The effect of Helium on the Yield of Products from the Explosive Reaction Between Hydrogen (3 torr) and  $N_2F_4$  (3 torr) at  $90^\circ$ .  
All numbers are in torr

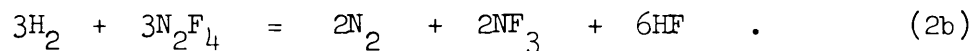
He	$N_2$	$NF_3$	$F_2$	HF	$N_2F_4$
0	2.8	0.2	2.7	6	0
6.5	2.6	0.7	2.0	6	0
19	2.5	0.8	1.8	6	0
31.5	2.4	1.3	1.0	6	0
44	2.3	1.6	0.6	6	0
69	1.9	1.2	0.2	6	0.5
94	1.9	0.9	0.6	6	0.4
144	1.8	0.84	0.2	6	0.8
194	1.8	0.75	0.3	6	0.8

Similar data for the reaction between hydrogen (2 torr) and tetrafluorohydrazine (4 torr) are given in Table III. Again the yield of nitrogen trifluoride goes through a maximum, but this time the maximum occurs at a much lower pressure of helium. Unreacted tetrafluorohydrazine again appears in the region where the yield of nitrogen trifluoride is decreasing.

Table III. Reaction Products from the Explosive Reaction of Hydrogen (2 torr) and Tetrafluorohydrazine (4 torr) in the Presence of Helium at 90°. All numbers are in torr

He	N <sub>2</sub>	NF <sub>3</sub>	F <sub>2</sub>	HF	N <sub>2</sub> F <sub>4</sub>
0	2.7	2.7	2.0	4	0
1.6	2.1	3.8	0.3	4	0
3.2	2.3	3.5	0.7	4	0
6.2	2.2	3.4	0.7	4	0.1
9.5	2.0	3.0	0.5	4	0.5
12.8	1.7	2.4	0.4	4	1.0
19	1.7	2.0	0.4	4	1.3
44	1.6	1.3	0.4	4	1.8
69	1.4	0.7	0.4	4	2.3
94	1.5	0.7	0.4	4	2.3
155	1.3	0.5	0.3	4	2.5
193	1.3	0.5	0.3	4	2.5

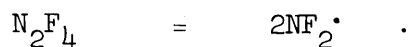
The effect of helium is shown graphically in Figure 1 where the ratio,  $NF_3/N_2$ , found in the reaction products is plotted against helium pressure for the three reaction mixtures. At the pressure when  $NF_3/N_2$  is at a maximum, reaction (2a) is largely replaced by reaction (2b) and 3a) is replaced by (3b)



When xenon is used instead of helium the effect is the same as that shown in Figure 1 but more xenon is required. A comparison of the effect of xenon and helium on the reaction between  $N_2F_4$  (3 torr) and  $H_2$  (3 torr) is shown in Figure 2. The ratio  $NF_3/N_2$  is at a maximum of 0.86 when the helium pressure is 44 torr or the xenon pressure is 100 torr. A similar plot of the effect of helium upon the product ratio for a series of experiments, in which the ratio of reactants was kept constant at 1 but the total pressure of reactants was varied, is shown in Figure 3. The pressure of helium required to produce a maximum in  $NF_3/N_2$  increases with increasing pressure of reactants; the value of  $(NF_3/N_2)_{max}$  is fairly constant being in the range of 0.7 to 0.86. These results all point to the conclusion that the inert gas acts by lowering the temperature during the explosion. Helium has a much higher thermal conductivity than xenon and thus allows the heat generated by the explosive reaction to be lost to the wall more quickly than does xenon. Increasing the pressure of reactants increases the rate of heat production thus requiring higher pressure of helium to lower the temperature to a particular value. The inert gas effect cannot be satisfactorily explained by collisional deactivation or a surface effect.

### C. Reaction With Nitrogen Trifluoride

Mixtures of hydrogen, nitrogen trifluoride or of hydrogen, and difluoramine do not react below  $100^\circ$ , however the addition of tetrafluorohydrazine causes an explosive reaction to occur readily. The ability of tetrafluorohydrazine to react readily with hydrogen and to sensitize the reaction of hydrogen with both nitrogen trifluoride and difluoramine can be reasonably attributed to the fact that tetrafluorohydrazine is in equilibrium with the difluoramino radical<sup>3</sup> and this radical initiates the explosion



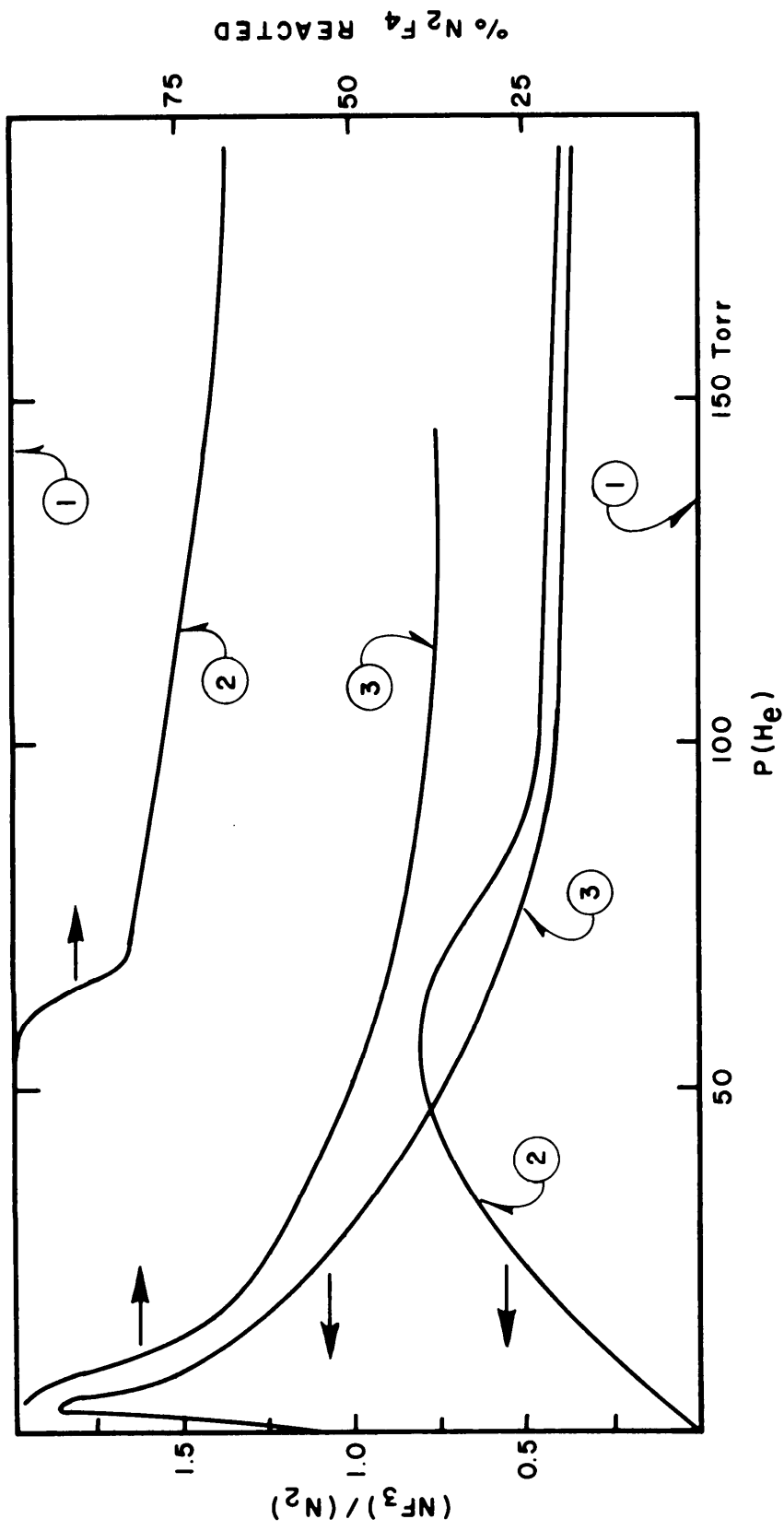


Figure 1. The Effect of Helium on the Percent  $N_2F_4$  Reacted and Upon Ratio,  $NF_3/N_2$ , Produced in the Explosion of Three Different  $N_2F_4 - H_2$  Mixtures: (1)  $4 H_2 + 2N_2F_4$ , (2)  $3H_2 + 3N_2F_4$ , and (3)  $2H_2 + 4N_2F_4$ , (Torr).

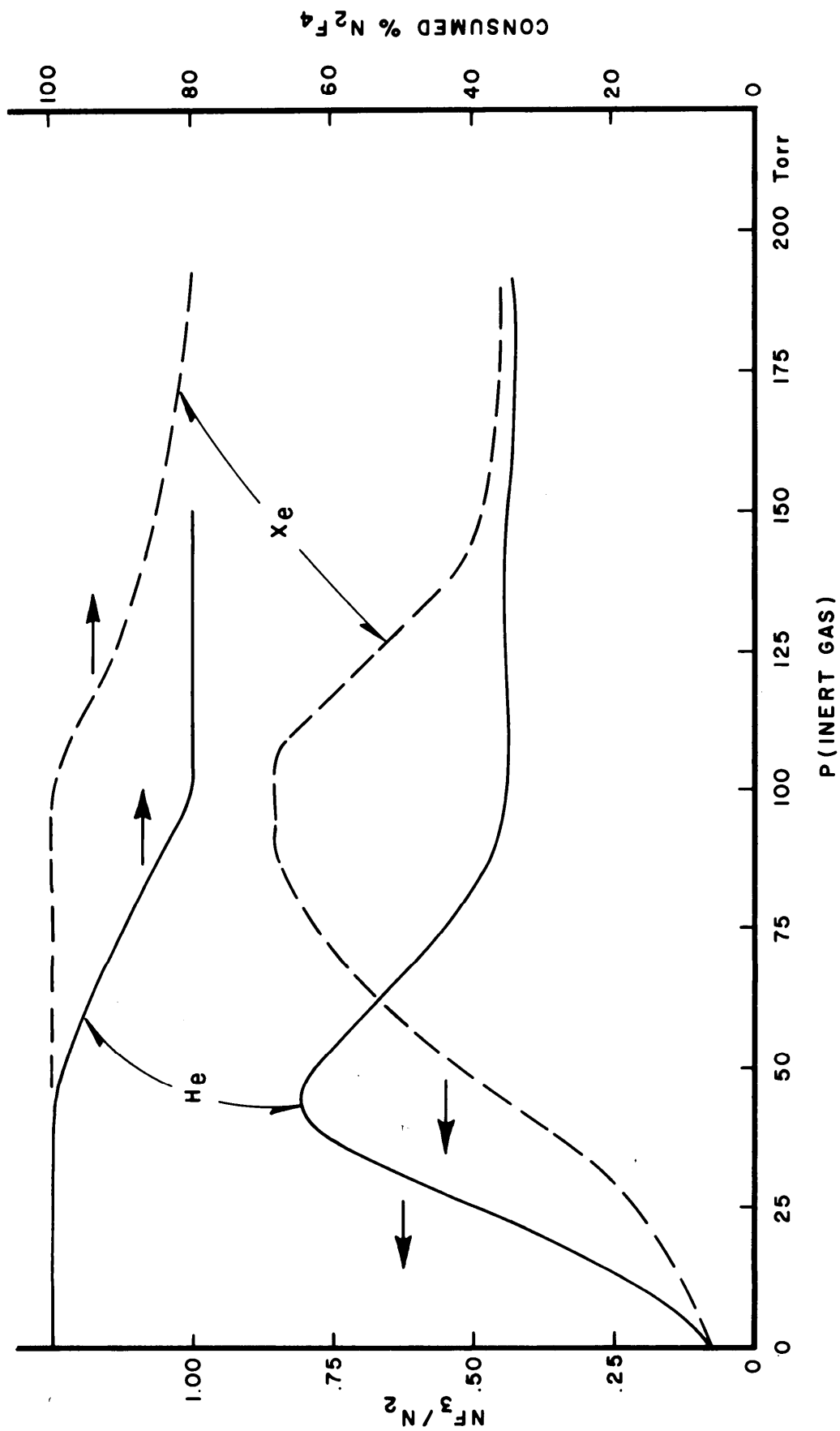


Figure 2. Comparison of the Effect of Helium and of Xenon on the Yield Ratio,  $NF_3/N_2$ , and on the Percent  $N_2F_4$  Consumed in the Explosive Reaction of Hydrogen (3 Torr) and Tetrafluorhydrazine (3 Torr).

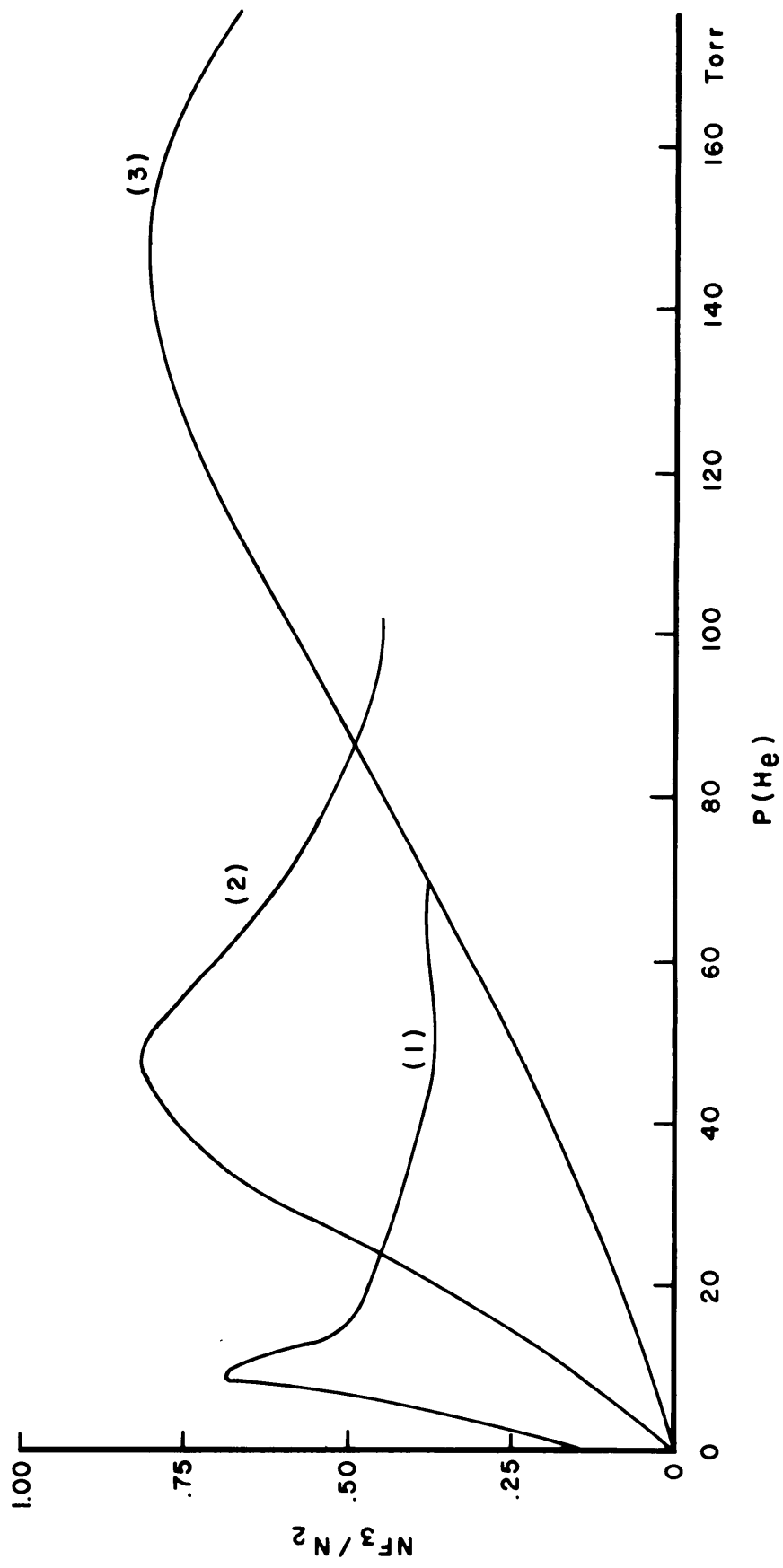


Figure 3. Effect of Helium on the Yield Ratio,  $NF_3/N_2$ , Formed in the Explosive Reaction of a 1:1 Hydrogen -  $N_2F_4$  Mixture at Different Pressures of Reaction Mixture (1) 3 Torr (2) 6 Torr and (3) 12 Torr.



Since nitrogen trifluoride and difluoramine do not give rise to radicals under our experimental conditions they do not react with hydrogen.

#### D. Effect of Hydrocarbons

The explosion limit of the hydrogen-tetrafluorohydrazine reaction, i.e. the temperature required for explosion at a given pressure of reactants, was found to be extremely sensitive to the presence of small amounts of hydrocarbons. Thus a mixture of hydrogen (40 torr) and tetrafluorohydrazine (20 torr) explodes on mixing below room temperature; the addition of butene-1 (0.1 torr) to this mixture completely suppresses the explosion at temperatures up to  $100^{\circ}$ . The time required for a mixture of hydrogen (40 torr) and tetrafluorohydrazine (20 torr) at  $100^{\circ}$  to explode (induction period) in the presence of different amounts of butene-1 and of butene-2 are shown in Figure 4. We see that when the pressure of butene-1 is less than .01 torr the mixture explodes instantly but when larger amounts of butene-1 are used an induction period of increasing duration occurs until at a pressure of .035 torr of butene-1 no explosion occurs in 1 hour. To determine the effectiveness of various inhibitors the amount of inhibitor required to produce an induction period of 10 minutes for the explosion of our standard mixture at  $110^{\circ}$  was determined. The results are shown in Table IV. The smaller the number the more effective is the inhibitor. Saturated hydrocarbons are less effective than unsaturated hydrocarbons. Substituted ethylenes have the following order of increasing effectiveness:  $\text{CH}_2=\text{CH}_2 < \text{CH}_2=\text{CHCH}_3 < \text{CH}_3\text{CH}=\text{CHCH}_3 < \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 < (\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ . Analysis of the reaction mixture during the induction period shows that the inhibitor is being destroyed by chemical reaction during the induction period.

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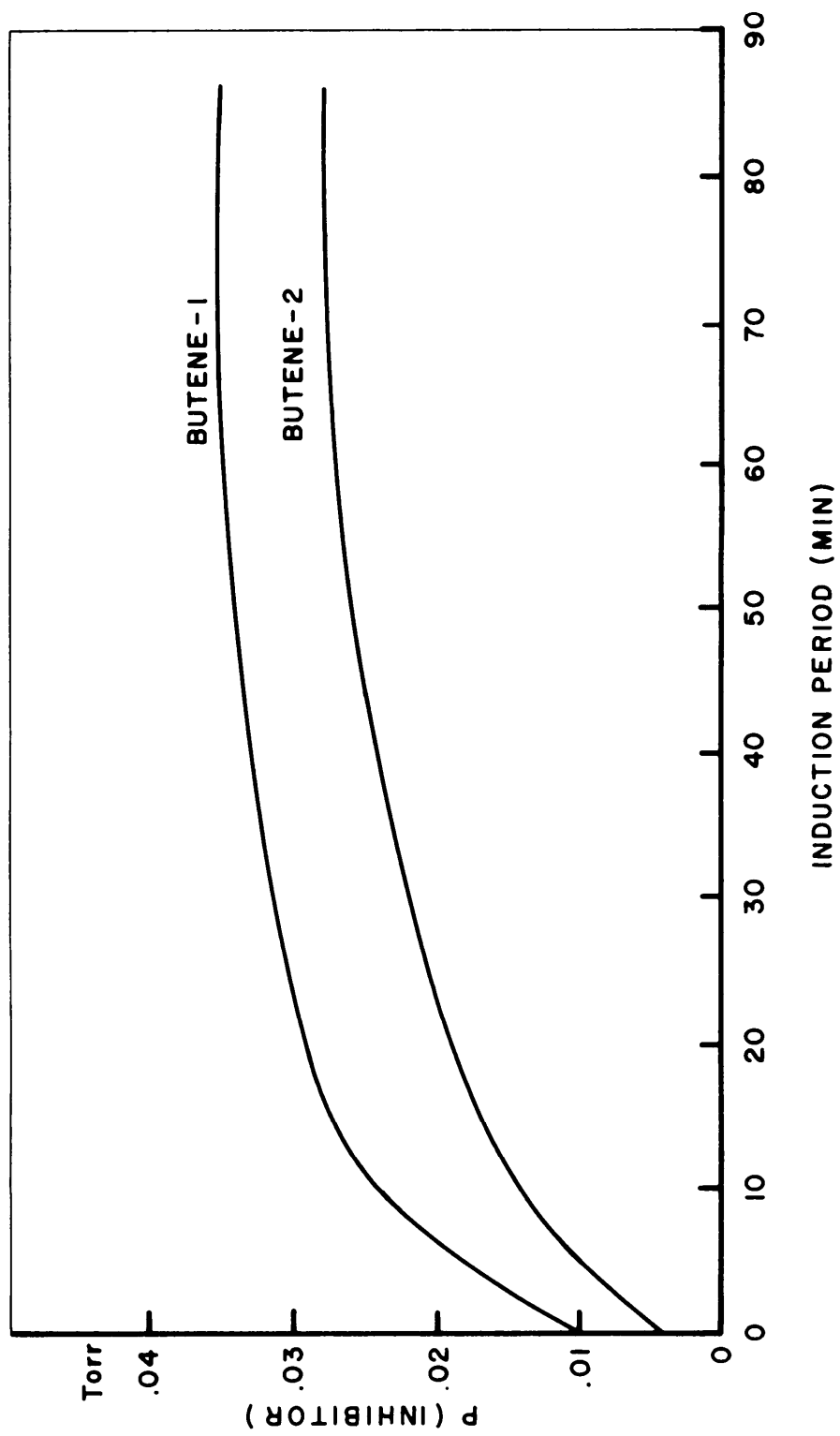


Figure 4. Effect of Inhibitor on Induction Period

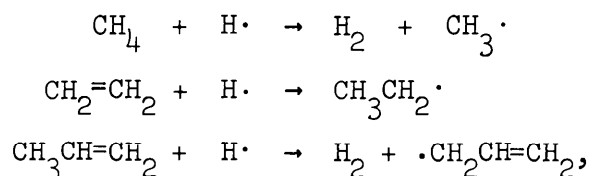
Table IV. Amount of Inhibitor Required to Produce an Induction

Period of 10 Minutes

All numbers are in torr

<u>Inhibitor</u>	<u>Pressure</u>	<u>Inhibitor</u>	<u>Pressure</u>
methane	6	ethylene	0.30
acetylene	1.9	propylene	0.03
ethane	1.4	butene-1	0.025
propane	0.62	butene-2	0.014
n-butane	0.33	trimethylethylene	.007
butadiene	0.06	tetramethylethylene	.002

The sensitivity of the explosive reaction to inhibition by small amounts of hydrocarbons indicates that the reaction is a chain reaction, that the chains are long, and that the inhibitor breaks the chains by destroying the chain carrier which is probably the hydrogen atom, on the basis of the observed relationship between structure and effectiveness of the inhibitor<sup>4</sup>. The inhibitors destroy hydrogen atoms in the following manner:



forming new radicals which are not capable of sustaining the chain. The more highly substituted ethylenes are more effective as inhibitors because they form more stable radicals (tertiary alkyl radicals are more stable than secondary alkyl radicals which are more stable than primary alkyl radicals) and because they contain more allylic hydrogen atoms.

### E. The Effect of Difluorodiazine

Since it is quite possible that difluorodiazine,  $N_2F_2$ , is an intermediate in the reaction of hydrogen with tetrafluorohydrazine, some experiments were carried out with binary and ternary mixtures of hydrogen, difluorodiazine, and tetrafluorohydrazine. The results are shown in Table V.

Table V. Explosive Reactions of Mixtures of Hydrogen-Difluorodiazine-Tetrafluorohydrazine

<u>Reactants (torr)</u>			<u>Products (torr)</u>			
<u>H<sub>2</sub></u>	<u>N<sub>2</sub>F<sub>4</sub></u>	<u>N<sub>2</sub>F<sub>2</sub></u>	<u>N<sub>2</sub></u>	<u>HF</u>	<u>NF<sub>3</sub></u>	<u>F<sub>2</sub></u>
25 <sup>a</sup>	0	20	20	40	0	0
30	10	5	15	50	0	0
20	20	10	29	40	0	30
0 <sup>b</sup>	40	40	40	0	80	0
5	20	10	20	10	20	15

- a. This reaction required a temperature of 130°, the other reactions were carried out at 90°.
- b. This is the only non-explosive reaction of the series. It has a half-life of about 1 hour at 110°.

We see that difluorodiazine can react explosively with hydrogen without added tetrafluorohydrazine although a higher temperature is required than for the hydrogen-tetrafluorohydrazine reaction. The difluorodiazine-hydrogen reaction is also strongly inhibited by small amounts of olefins indicating that it too is a chain reaction. The ternary mixtures undergo explosive reactions which result in the complete destruction of the difluorodiazine and yield products in which the ratio,  $NF_3/N_2$ , is the same as is found in the absence of difluorodiazine. This means that difluorodiazine is, or is converted to, an intermediate in the hydrogen-tetrafluorohydrazine reaction.

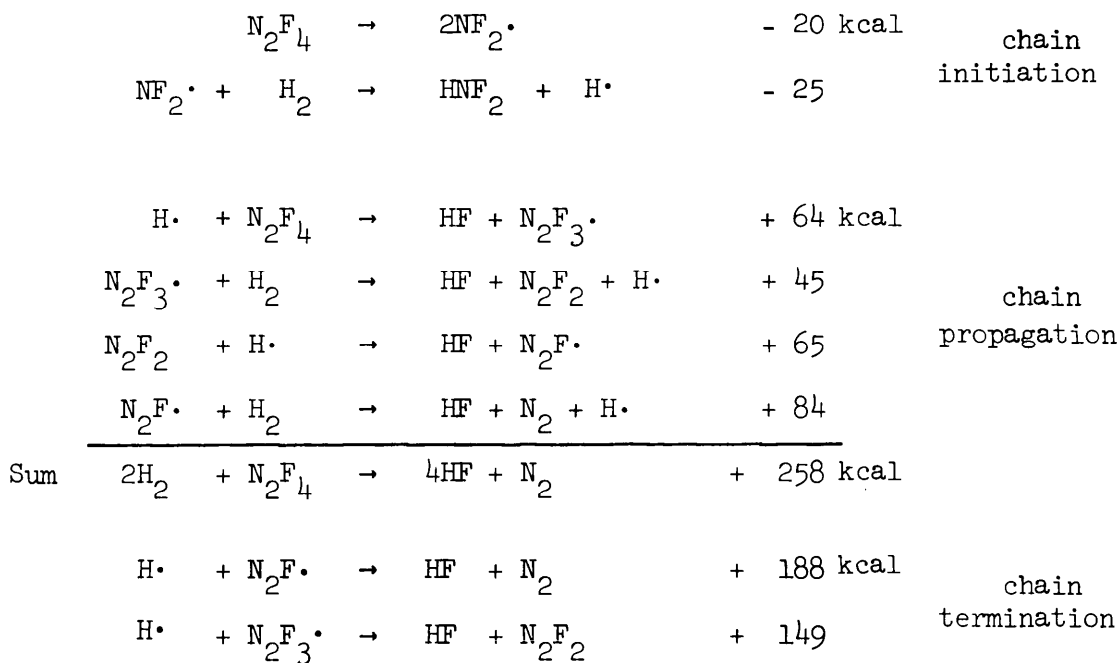
#### IV. DISCUSSION

Although a complete understanding of the mechanism of these explosive hydrogen-tetrafluorohydrazine reactions must await quantitative data on explosion limits which will be the subject of a subsequent publication, it is possible to draw a number of conclusions concerning the mechanism on the basis of the data at hand. It will be convenient to consider the reactions represented by equations 1, 2, and 3 as separate reactions each having its own mechanism. For reasons given above each of these is believed to be a chain reaction initiated by the difluoroamino radical.

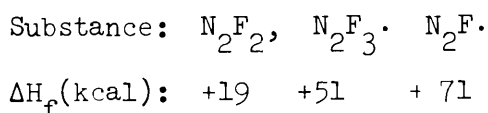
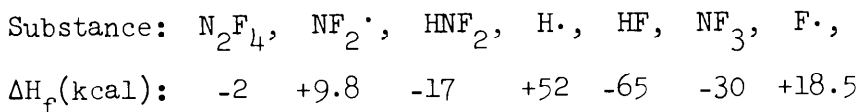
##### A. Reaction Between 2 Moles of Hydrogen and 1 Mole of Tetrafluorohydrazine, Reaction 1

A reasonable mechanism of this reaction which is consistent with the data is as follows:

Mechanism 1.



The change in enthalpy accompanying each step was calculated from published values<sup>5</sup> of heats of formation,  $\Delta H_f$ , shown in the accompanying table:



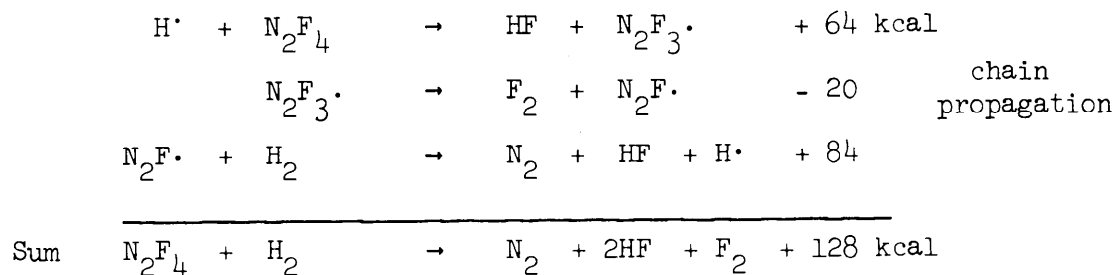
The last two values were calculated from the reactions,  $N_2F_4 + 71 \text{ kcal} = N_2F_3\cdot + F\cdot$ , and  $N_2F_2 + 71 = N_2F\cdot + F\cdot$ , 71 being the accepted value for the average bond strength of the N-F bonds in  $N_2F_4$ .

The chain initiation steps are endothermic but the chain propagation steps are highly exothermic as is required of a chain reaction leading to explosion.  $H\cdot$ ,  $N_2F_3\cdot$ , and  $N_2F\cdot$  are the chain carriers;  $N_2F_2$  is an intermediate and it too is destroyed by a chain process.

B. The Reaction Between 1 Mole of Hydrogen and 1 Mole of Tetrafluorohydrazine, Reaction 2

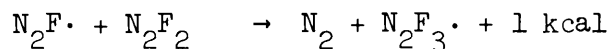
The initiation steps are the same as in the previous mechanism. The chain propagation steps are as follows:

Mechanism 2a.

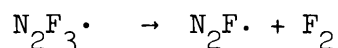


The fluorine is believed to arise from the decomposition of the  $N_2F_3\cdot$  radical. When excess hydrogen is present, as in the previous mechanism, the  $N_2F_3\cdot$  is reduced to  $N_2F_2$  and no fluorine is formed.

To account for the observation that the explosion of a ternary mixture, containing  $N_2F_2$  and equal parts of hydrogen, and  $N_2F_4$ , yields nitrogen and fluorine we suggest the following additional step:

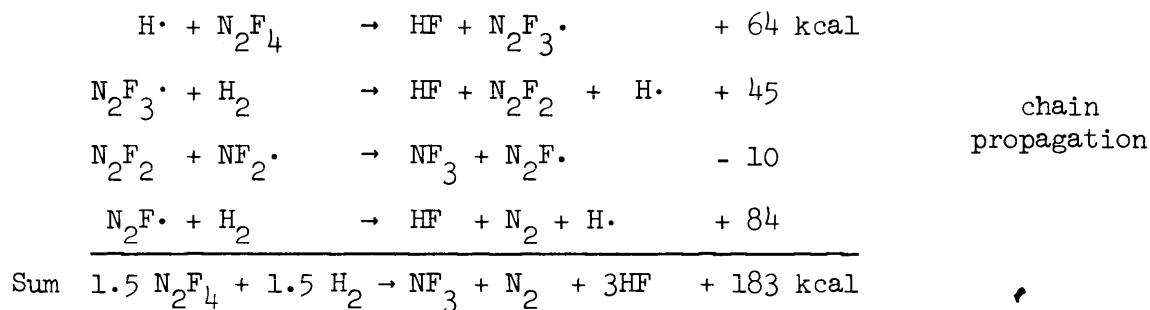


which coupled with the decomposition step



constitutes a chain reaction for the conversion of difluorodiazine into fluorine and nitrogen. To account for the peculiar effect of helium on the course of the reaction shown in Table II we propose that mechanism 2b gradually replaces mechanism 2a as the pressure of helium is increased.

Mechanism 2b.



As stated earlier, the inert gas acts by lowering the reaction temperature. We assume that  $N_2F_3\cdot$  can react in two ways. It can undergo a unimolecular decomposition, as in mechanism 2a, which is endothermic by about 20 kilocalories or it can undergo reaction with hydrogen, as in 2b, which is exothermic by about 45 kilocalories. We propose that the endothermic step predominates at the higher temperature and that the exothermic step predominates at the lower temperature. It has frequently been noted that endothermic reactions have higher activation energies than exothermic reactions<sup>6</sup>. To determine whether it is reasonable to expect the rates of these two reactions to cross over as the temperature is lowered, calculations were made of their rates at 600 and 1000°K. The endothermic

unimolecular decomposition of  $N_2F_3\cdot$  was assumed to obey the equation,

$$k_{(\text{endo})} = 10^{13} e^{-32000/RT}$$

and the exothermic bimolecular reaction of  $N_2F_3\cdot$  with hydrogen was assumed to obey the equation,

$$k_{(\text{exo})} = 10^{11} e^{-11000/RT} \quad .$$

These are believed to be reasonable values for the activation energies and frequency factors<sup>7</sup>. The results of these calculations are shown in Table VI. In order to compare the rate of the endothermic unimolecular reaction with the rate of the exothermic bimolecular reaction it is necessary to multiply the exothermic rate constant by the concentration of hydrogen which in our experiments was about  $10^{-4}$  moles per liter. The last column in Table VI shows that at  $1000^\circ\text{K}$  the endothermic reaction is 25 times faster than the exothermic reaction whereas at  $600^\circ\text{K}$  the endothermic reaction is about 1000 times slower than the exothermic reaction.

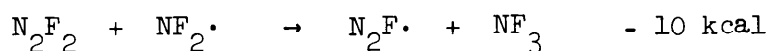
Table VI. Calculation of Reaction Rates of  $N_2F_3\cdot$

Temp. ( $^\circ\text{K}$ )	k endo	k exo	k exo ( $\text{H}_2$ )	Rate(endo)/Rate(exo)
1000	$10^6$	$4 \times 10^8$	$4 \times 10^4$	25
600	2.5	$1 \times 10^7$	$1 \times 10^3$	$2.5 \times 10^{-3}$

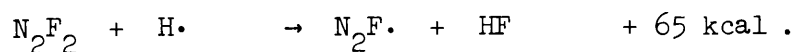
At the temperature where  $NF_3/N_2$  is a maximum about 80% of the reaction goes by mechanism 2b and about 20% by mechanism 2a. Further lowering of the temperature by the addition of more helium leads to a reduction in the ratio,  $NF_3/N_2$ , and at the same time unreacted  $N_2F_4$



is found in the products, indicating that a certain amount of the reaction is occurring by mechanism 1. This time the endothermic reaction

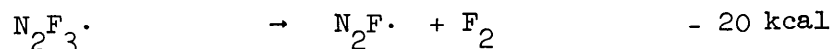


is replaced by the exothermic reaction

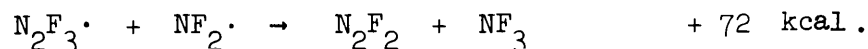
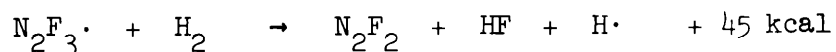


C. Reaction Between 1 Mole of Hydrogen and 2 Moles of Tetrafluoro-hydrazine, Reaction 3

This is the most complicated reaction of this series and it is difficult to come up with a mechanism which uniquely explains all of the experimental data. It is likely that several mechanisms are operating simultaneously. The chain initiation steps leading to the formation of hydrogen atoms is the same as in the previous mechanisms and the  $\text{N}_2\text{F}_3\cdot$  radical is again the key intermediate which determines whether fluorine will be a reaction product. In the absence of inert gas a certain amount of the  $\text{N}_2\text{F}_3\cdot$  radical decomposes as before



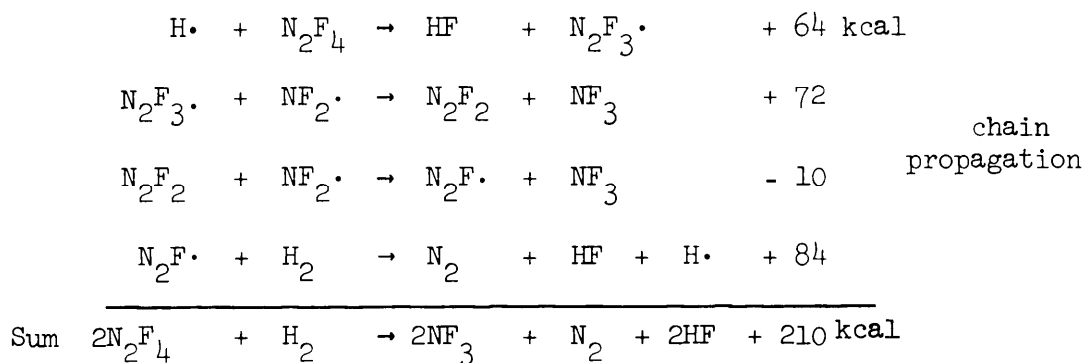
and the balance reacts otherwise



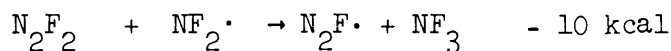
As inert gas is added the reaction temperature is lowered and the exothermic steps not leading to fluorine become most important.

Mechanism 3b is a reasonable mechanism to account for the major reaction, 3b, occurring when the  $\text{NF}_3/\text{N}_2$  is a maximum.

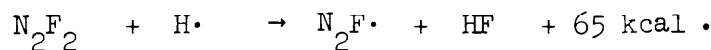
Mechanism 3b



As shown in Figure 1, further addition of inert gas reduces the ratio,  $\text{NF}_3/\text{N}_2$ , and causes the appearance of unreacted  $\text{N}_2\text{F}_4$  in the products. This is the same phenomenon that we observed in the explosions of 1:1 mixtures of hydrogen and tetrafluorohydrazine and we explain it in the way we did before, namely that reaction 3b is replaced by reaction 1 because the endothermic step

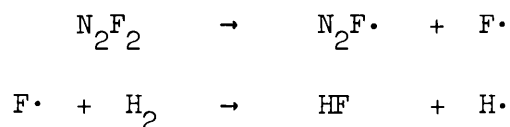


is replaced by the exothermic step



When these mixtures are allowed to explode in the presence of large amounts of helium (> 100 torr) small but easily detectable amounts of difluorodiazine are found in the reaction products by gas chromatography. The finding of the diazine substantiates our hypothesis that it is an intermediate in the reaction and that its rate of disappearance decreases when large amounts of inert gas are present.

The question of whether these explosive reactions are thermal explosions or branching chain explosions has not been brought up. It will be the subject of a future publication. In none of the chain propagation mechanisms that we have proposed is there a step in which the number of radicals increases as is required by a branching chain reaction. The fact that mixtures of hydrogen and difluorodiazine explode without being sensitized by tetrafluorohydrazine and the fact that difluorodiazine is capable of initiating free radical polymerization reactions is evidence<sup>8</sup> that the reactions



may occur and would provide a pathway for branching chain explosions. The extent to which these steps occur has not yet been determined.

#### V. CONCLUSION

Hydrogen and tetrafluorohydrazine have been shown to undergo an explosive chain reaction. Different stoichiometry and different products are observed depending upon whether the ratio  $\text{H}_2/\text{N}_2\text{F}_4$  is 2,1 or 0.5. In the latter two cases different products are obtained depending upon the presence of inert gas. The effect of the inert gas is to lower the explosion temperature. The intermediates,  $\text{N}_2\text{F}_3\cdot$  and  $\text{N}_2\text{F}_2$ , which are believed to be formed, react in different ways depending upon the temperature and the relative abundance of reactants. An endothermic step is believed to predominate at the higher temperature and an exothermic step predominates at a lower temperature. The mechanisms that we have proposed are reasonable and consistent with the experimental data, however they have not been proven. Further measurements of induction periods, explosion limits, pressure - time and temperature - time relationships are necessary to establish their validity or to indicate appropriate modifications.

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