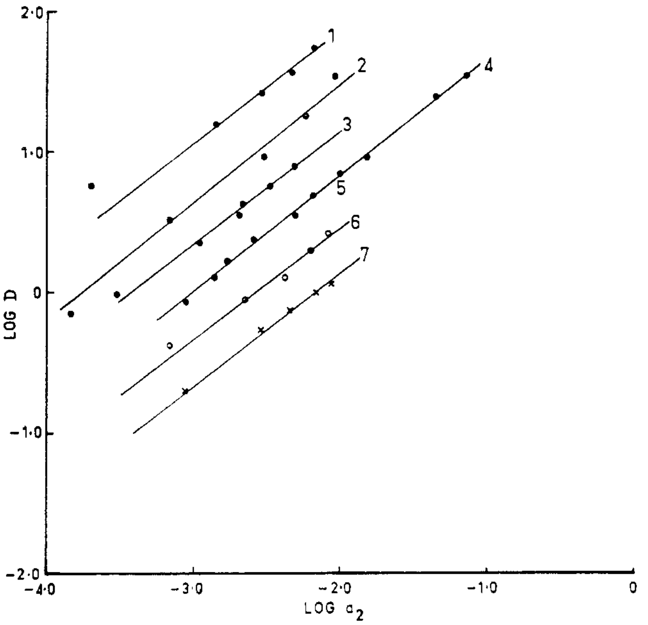

Figure 7.—Log D vs. the logarithm of the uncomplexed amine sulfate dimer concentration (a_2): line 7 (0.8); 6 (0.8); 5 (0.8); 3 (0.8); 1 (0.8); 2 (0.9); 4 (0.9).

Figure 7, and the straight lines obtained have, in fact, slopes close to unity.

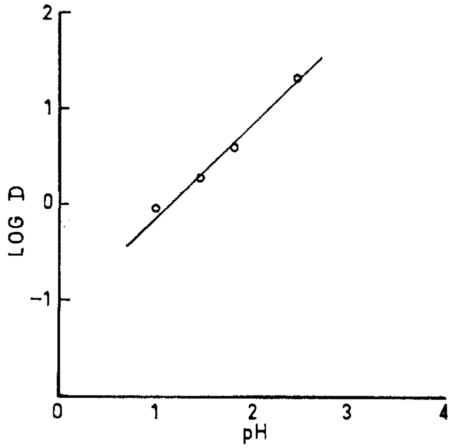

Figure 8.—Log D vs. pH for 0.01 M stoichiometric uncomplexed amine sulfate.

Since it is suggested that the partially hydrolyzed scandium species $ScOHSO_4$ and $(ScOHSO_4)_2$ are involved in the extraction process the distribution ratio for scandium should be first-order dependent on the pH of the aqueous phase.[2] In Figure 8 log D values, which were obtained from Figure 5 for a stoichiometric uncomplexed amine sulfate concentration of 0.01 M, are shown plotted against pH. The straight line obtained has a slope of unity.

These results show that the equilibrium studies are in agreement with the stoichiometry found for the complex; however it is necessary to take into account the aggregation of the sulfate salt in chloroform.

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The Explosive Reaction between Tetrafluorohydrazine and Hydrogen

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Hydrogen and tetrafluorohydrazine have been shown to undergo an explosive chain reaction. The products vary both in type and in stoichiometry depending upon whether the ratio $H_2:N_2F_4$ is 2, 1, or 0.5. In the latter two cases different products are obtained depending upon the presence of inert gas. It is believed that the effect of the inert gas is to lower the explosion temperature. The postulated intermediate, N_2F_2, reacts in different ways depending upon the temperature and upon the relative abundance of the reactants. A weakly exothermic step is believed to predominate at the higher explosion temperature and a strongly exothermic step predominates at the lower temperature.

Introduction

Compounds containing the difluoramino group, NF_2, are powerful oxidizers and are therefore of interest to the chemist concerned with propellants and combustion processes. 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°. After conditioning of the flask by several explosions, subsequent additions of the same mixture of gases would explode at 20°. 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° 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.[1] 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.

Experimental Section

Research grade tetrafluorohydrazine, nitrogen trifluoride, and difluorodiazine were obtained from Air Products Co., Allentown, Pa. The diazine contained about 95% *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 1–2 μ. 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 thermostated oven at the desired temperature. 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 thermostated oven at the desired temperature. After explosion the reaction vessel was connected to the gas-sampling valve of the gas chromatograph and analyzed, using a 2-m silica gel column at 35° and a flow rate of 40 cm^3 of He/min. 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[2] after reaction of the reaction products with tetrafluorohydrazine at 100°, $F_2 + N_2F_4 = 2NF_3$, 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.

Results

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 THE HYDROGEN–TETRAFLUOROHYDRAZINE EXPLOSION IN A 100-ML KEL-F-COATED PYREX FLASK AT 90°

(Reactants), Torr		(Products), Torr			
N_2F_4	H_2	N_2	NF_3	HF	F_2
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 $H_2:N_2F_4$ is 2, the reaction can be represented by the equation

$$2H_2 + N_2F_4 = N_2 + 4HF \qquad (1)$$

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

$$H_2 + N_2F_4 = N_2 + 2HF + F_2 \qquad (2a)$$

and when the ratio of reactants is 0.5, the reaction cannot be represented by a simple stoichiometric equation but appears to follow two or more simultaneous processes such as

$$4N_2F_4 + 2H_2 = 3N_2 + 4HF + 2NF_3 + 3F_2 \qquad (3a)$$

$$4N_2F_4 + 2H_2 = 4HF + 4NF_3 + 2N_2 \qquad (3b)$$

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

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°

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

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[1] (a) C. N. Hinshelwood and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, **A138**, 311 (1932); (b) B. Lewis, *J. Amer. Chem. Soc.*, **55**, 4001 (1933).

[2] J. Levy and B. K. W. Copeland, *J. Phys. Chem.*, **69**, 3700 (1965).

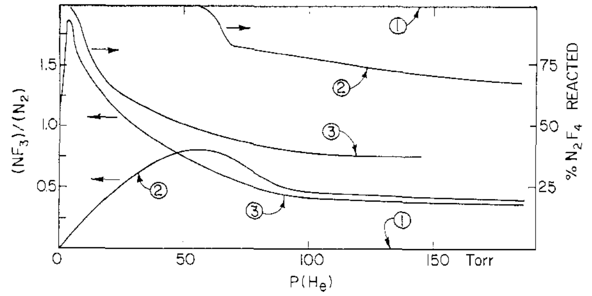

Figure 1.—The effect of helium on the per cent of N_2F_4 reacted and upon the $NF_3:N_2$ ratio produced in the explosion of three different N_2F_4–H_2 mixtures: (1) $4H_2 + 2N_2F_4$; (2) $3H_2 + 3N_2F_4$; (3) $2H_2 + 4N_2F_4$ (pressures in Torrs).

(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 pressures 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. 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. 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

$$3H_2 + 3N_2F_4 = 2N_2 + 2NF_3 + 6HF \qquad (2b)$$

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 0.7–0.86. 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 a 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.

TABLE III

REACTION PRODUCTS FROM THE EXPLOSIVE REACTION OF HYDROGEN (2 TORR) AND TETRAFLUOROHYDRAZINE (4 TORR) IN THE PRESENCE OF HELIUM AT 90°

Torr					
He	N_2	NF_3	F_2	HF	N_2F_4
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
19.0	1.7	2.0	0.4	4	1.3
44.0	1.6	1.3	0.4	4	1.8
69.0	1.4	0.7	0.4	4	2.3
94.0	1.5	0.7	0.4	4	2.3
155.0	1.3	0.5	0.3	4	2.5
193.0	1.3	0.5	0.3	4	2.5

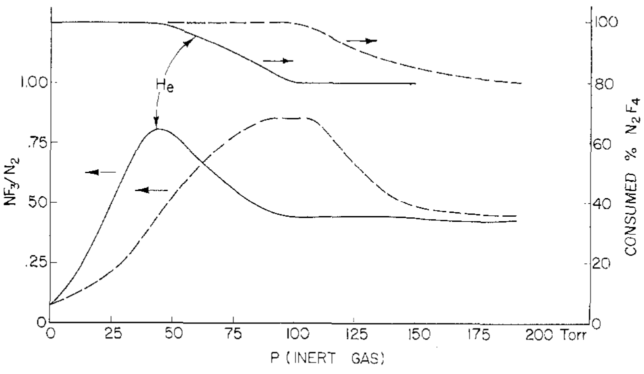

Figure 2.—Comparison of the effect of helium and of xenon on the $NF_3:N_2$ yield ratio and on the per cent of N_2F_4 consumed in the explosive reaction of hydrogen (3 Torr) and tetrafluorhydrazine (3 Torr).

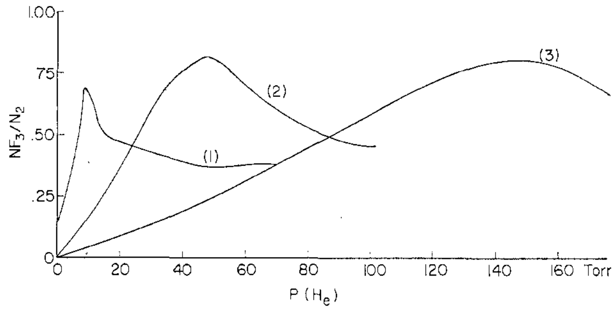

Figure 3.—Effect of helium on the $NF_3:N_2$ yield ratio formed in the explosive reaction of a 1:1 hydrogen–N_2F_4 mixture at different pressures of reaction mixture: (1) 3 Torr; (2) 6 Torr; (3) 12 Torr.

Reaction with Nitrogen Trifluoride.—Mixtures of hydrogen and nitrogen trifluoride or of hydrogen and difluoramine do not react below 100°; 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[3] ($N_2F_4 = 2NF_2\cdot$) and this radical initiates the explosion. Since nitrogen trifluoride and difluoramine do not give rise to radicals under our experimental conditions, they do not react with hydrogen.

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°. The times required for a mixture of hydrogen (40 Torr) and tetrafluorohydrazine (20 Torr) at 100° 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 0.01 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 0.035 Torr of butene-1 no explosion occurs in 1 hr. To determine the effectiveness of various inhibitors the amount of inhibitor required to produce an induction period of 10 min for the explosion of our standard mixture at 110° 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: $CH_2{=}CH_2 < CH_2{=}CHCH_3 < CH_3CH{=}CHCH_3 < CH_3CH{=}C(CH_3)_2 < (CH_3)_2C{=}C(CH_3)_2$. Analysis of the reaction mixture during the induction period shows that the inhibitor is being destroyed by chemical reaction during the induction period.

TABLE IV
AMOUNT OF INHIBITOR REQUIRED TO PRODUCE AN INDUCTION PERIOD OF 10 MIN

Inhibitor	Pressure, Torr	Inhibitor	Pressure, Torr
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	0.007
Butadiene	0.06	Tetramethylethylene	0.002

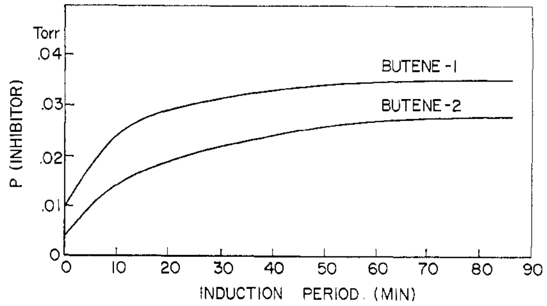

Figure 4.—Effect of inhibitor on induction period.

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.[4] The inhibitors destroy hydrogen atoms as follows

$$CH_4 + H\cdot \longrightarrow H_2 + CH_3\cdot$$

$$CH_2{=}CH_2 + H\cdot \longrightarrow CH_3CH_2\cdot$$

$$CH_3CH{=}CH_2 + H\cdot \longrightarrow H_2 + \cdot CH_2CH{=}CH_2$$

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 primary alkyl radicals) and because they contain more allylic hydrogen atoms.

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. 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.

TABLE V
EXPLOSIVE REACTIONS OF MIXTURES OF HYDROGEN–DIFLUORODIAZINE–TETRAFLUOROHYDRAZINE

(Reactants), Torr			(Products), Torr			
H_2	N_2F_4	N_2F_2	N_2	HF	NF_3	F_2
25[a]	0	20	20	40	0	0
30	10	5	15	50	0	0
20	20	10	29	40	0	30
0[b]	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 nonexplosive reaction of the series. It has a half-life of about 1 hr at 110°.

Discussion

Although a complete understanding of the mechanism of these explosive hydrogen–tetrafluorohydrazine re-

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(3) F. Johnson and C. Colburn, *J. Amer. Chem. Soc.*, **83**, 3043 (1961).

(4) D. Dalgleish and J. Knox, *Chem. Commun.*, 917 (1966).

actions 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 eq 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 difluoramino radical.

A. Reaction between 2 Mol of Hydrogen and 1 Mol of Tetrafluorohydrazine, Reaction 1.—A reasonable mechanism of this reaction which is consistent with the data is mechanism 1

Chain initiation

$$\begin{array}{rr} N_2F_4 \longrightarrow 2NF_2\cdot & (-20\ \text{kcal}) \\ NF_2\cdot + H_2 \longrightarrow HNF_2 + H\cdot & (-25\ \text{kcal}) \end{array}$$

Chain propagation

$$\begin{array}{rr} H\cdot + N_2F_4 \longrightarrow HF + N_2F_2 + F\cdot & (+78\ \text{kcal}) \\ F\cdot + H_2 \longrightarrow HF + H\cdot & (+31\ \text{kcal}) \\ N_2F_2 + H\cdot \longrightarrow HF + N_2 + F\cdot & (+118\ \text{kcal}) \\ F\cdot + H_2 \longrightarrow HF + H\cdot & (+31\ \text{kcal}) \\ \hline \text{sum}\quad 2H_2 + N_2F_4 \longrightarrow 4HF + N_2 & (+258\ \text{kcal}) \end{array}$$

Chain termination

$$\begin{array}{rr} H\cdot + F\cdot \longrightarrow HF & (+135\ \text{kcal}) \end{array}$$

The change in enthalpy accompanying each step was calculated from published values[5] of heats of formation, ΔH_f (kcal): N_2F_4, −2; $NF_2\cdot$, +9.8; HNF_2, −17; $H\cdot$, +52; HF, −65; NF_3, −30; $F\cdot$, +18.5; N_2F_2, +19.

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

B. Reaction between 1 Mol of Hydrogen and 1 Mol of Tetrafluorohydrazine, Reaction 2.—The initiation steps are the same as in the previous mechanism. The chain propagation steps are as follows in mechanism 2a

$$\begin{array}{rr} H\cdot + N_2F_4 \longrightarrow HF + N_2F_2 + F\cdot & (+78\ \text{kcal}) \\ F\cdot + N_2F_2 \longrightarrow F_2 + N_2 + F\cdot & (+19\ \text{kcal}) \\ F\cdot + H_2 \longrightarrow HF + H\cdot & (+31\ \text{kcal}) \\ \hline \text{sum}\quad N_2F_4 + H_2 \longrightarrow N_2 + 2HF + F_2 & (+128\ \text{kcal}) \end{array}$$

The fluorine is believed to arise from the attack of a fluorine atom on N_2F_2. When excess hydrogen is present, as in the previous mechanism, the N_2F_2 is reduced to nitrogen and hydrogen fluoride and no fluorine is formed. The above mechanism also accounts 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.

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 is

$$\begin{array}{rr} H\cdot + N_2F_4 \longrightarrow HF + N_2F_2 + F\cdot & (+78\ \text{kcal}) \\ F\cdot + H_2 \longrightarrow HF + H\cdot & (+31\ \text{kcal}) \\ N_2F_2 + NF_2\cdot \longrightarrow NF_3 + N_2 + F\cdot & (+41\ \text{kcal}) \\ F\cdot + H_2 \longrightarrow HF + H\cdot & (+31\ \text{kcal}) \\ \hline \text{sum}\quad 1.5N_2F_4 + 1.5H_2 \longrightarrow NF_3 + N_2 + 3HF & (+181\ \text{kcal}) \end{array}$$

As stated earlier, the inert gas acts by lowering the reaction temperature. We assume the N_2F_2 can react in two ways. It can react with a fluorine atom, as in mechanism 2a, which is exothermic by about 19 kcal or it can undergo reaction with $NF_2\cdot$, as in 2b, which is exothermic by about 41 kcal. We propose that the less exothermic step predominates at the higher temperature and that the more exothermic step predominates at the lower temperature. It has frequently been noted that in a series of related reactions, the less exothermic reactions have higher activation energies than the more highly exothermic reactions.[6]

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 exothermic reaction

$$N_2F_2 + NF_2\cdot \longrightarrow N_2 + F\cdot + NF_3 \qquad (+41\ \text{kcal})$$

is replaced by the more exothermic reaction

$$N_2F_2 + H\cdot \longrightarrow N_2 + HF + F\cdot \qquad (+118\ \text{kcal})$$

C. Reaction between 1 Mol of Hydrogen and 2 Mol of Tetrafluorohydrazine, Reaction 3.—This is the most complicated reaction of this series and it is difficult to expound 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 are the same as in the previous mechanisms and difluorodiazine is again the key intermediate which can react with different radicals and thus give different products. In the absence of inert gas a certain amount of the difluorodiazine reacts with fluorine atoms to yield fluorine and nitrogen and regenerate a fluorine atom as in mechanism 2a and the balance reacts with the difluoramino radical to yield trifluoramine. 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 $NF_3{:}N_2$ is a

$$\begin{array}{rr} H\cdot + N_2F_4 \longrightarrow HF + N_2F_2 + F\cdot & (+78\ \text{kcal}) \\ F\cdot + NF_2\cdot \longrightarrow NF_3 & (+58\ \text{kcal}) \\ N_2F_2 + NF_2\cdot \longrightarrow N_2 + NF_3 + F\cdot & (+41\ \text{kcal}) \\ F\cdot + H_2 \longrightarrow HF + H\cdot & (+31\ \text{kcal}) \\ \hline \text{sum}\quad 2N_2F_4 + H_2 \longrightarrow 2NF_3 + N_2 + 2\ HF & (+208\ \text{kcal}) \end{array}$$

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[5] D. Wagman, W. Evans, I. Halow, V. Marker, S. Bailey, and R. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., Oct 1965, part I.

[6] A. Frost and R. Pearson, "Kinetics and Mechanism," 2d ed, John Wiley and Sons, New York, N. Y., 1962, p 106.

maximum. As shown in Figure 1, further addition of inert gas reduces the ratio $NF_3:N_2$ and causes the appearance of unreacted N_2F_4 in the products. This is the same phenomenon that we observed in the explosion of 1:1 mixtures of hydrogen: tetrafluorohydrazine and we explain it in the way we did before, namely, that reaction 3b is replaced by reaction 1 because the exothermic step

$$N_2F_2 + NF_2\cdot \longrightarrow H_2 + NF_3 + F\cdot \qquad (+41\text{ kcal})$$

is replaced by the strongly exothermic step

$$N_2F_2 + H\cdot \longrightarrow N_2 + HF + H\cdot \qquad (+118\text{ kcal})$$

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 are evidence[7] that the reactions

$$N_2F_2 \longrightarrow N_2 + 2F\cdot$$
$$F\cdot + H_2 \longrightarrow HF + H\cdot$$

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

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A Study of the Reactions of Zirconium(IV) Chloride with Some Aliphatic Acids[1]

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The initial reaction of aliphatic acids with zirconium(IV) chloride at −15° yields molecular addition compounds of the type $ZrCl_4\cdot 2RCO_2H$. When heated to 21°, hydrogen chloride is eliminated and products are obtained which appear to have a composition represented by $ZrCl_2(RCO_2)_2\cdot 2RCO_2H$. At temperatures over 100°, using an excess of the aliphatic acid, $Zr(RCO_2)_4$ was obtained. Molecular weights of the tetrasubstituted products indicate monomer formation and a coordination number of 8 is suggested for zirconium.

Introduction

The reaction of zirconium(IV) chloride with aliphatic acids has been studied by several investigators[3-9] and there is much disagreement among the various investigators and little, if any, information available in regard to infrared spectra, molecular weight data, and X-ray diffraction patterns of reaction products. Among the many reported reaction products are mono-, di-, tri-, and tetrasubstituted compounds as well as various compounds containing coordinated aliphatic acid and hydrogen chloride. Also reported are hexaacyloxydizirconium oxides and zirconyl derivatives as products from these reactions.

Some of the contradictory observations reported in the literature are undoubtedly due to the recognized complexity of the chemical behavior of zirconium. Many zirconium compounds have very little stability toward hydrolysis, and, therefore, difficulties are encountered in isolating and characterizing pure products. It is evident that the need for research in this area of zirconium chemistry is great. In view of this, an investigation of the reactions of zirconium(IV) chloride with acetic, propionic, *n*-butyric, and isobutyric acids was undertaken.

Experimental Section

Materials and Apparatus.—The zirconium(IV) chloride was a commercial reactor-grade product from U. S. Industrial Chemical Co. Analysis of this material indicated 99.0% $ZrCl_4$. No appreciable improvement of purity was obtained on subliming the $ZrCl_4$. Thus, the commercial product was used as received, and

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