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MECHANISM AND CHEMICAL INHIBITION OF THE
HYDRAZINE-NITROGEN TETROXIDE REACTION

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Flight Accessories Laboratory
Aeronautical Systems Division
Air Force Systems Command
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(Prepared under Contract Nos. AF 33(616)-7757 and AF 33(657)-7617
by Monsanto Research Corporation, Dayton, Ohio; G. B. Skinner,
W. H. Hedley and A. D. Snyder, Authors)

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FOREWORD

This report was prepared under Contract Nr. AF 33(657)-7617, "A Research Program for Understanding the Mechanisms of Flame Inhibition." The contract was initiated under Project Nr. 6075, Task Nr. 607505, by the Flight Accessories Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio with Mr. B. P. Botteri as project engineer.

The work was performed during the period August 1961 through October 1962 at the Dayton Laboratory of Monsanto Research Corporation. The first year's work was performed under Contract Nr. AF 33(616)-7757. Dr. G. B. Skinner was project leader, and Drs. W. H. Hedley and A. D. Snyder worked with him.

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ABSTRACT

The mechanism of the hydrazine-nitrogen tetroxide reaction was investigated by examination of the variation in reaction products and equilibrium reaction temperature with increasing reactant concentration when argon-diluted reactant streams were rapidly mixed in a flow reactor. It is concluded that the reaction proceeds through a thermal reaction mechanism rather than a chain-branched explosion mechanism.

An ignition test was devised to determine the effect of candidate reaction inhibitors. No effective inhibitors were found among 27 gaseous and 28 liquid additives tested. Thiophene, toluene, trimethyl borate, ethyl bromide and benzene produced some inhibition, but only at high concentrations. These results support the conclusions that a thermal mechanism is operative.

This technical documentary report has been reviewed and is approved.

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TABLE OF CONTENTS

	Page
1. INTRODUCTION	1
2. SUMMARY	1
3. SPONTANEOUS IGNITION CHARACTERISTICS	3
3.1 Inhibitor Screening by Spontaneous Ignition Limit	3
3.2 The Preignition Reaction	8
4. INVESTIGATION OF THE HYDRAZINE-NITROGEN TETROXIDE FLAME MECHANISM	8
4.1 High Speed Movies of the Ignition of a Drop of Hydrazine	8
4.2 Spectroscopic Studies of the Hydrazine-Nitrogen Tetroxide Diffusion Flame	10
4.3 Stirred Reactor Studies - Temperature and Product Analysis	12
5. CONCLUSIONS AND RECOMMENDATIONS	18
REFERENCES	28

LIST OF TABLES AND FIGURES

<u>Table</u>		<u>Page</u>
1	Gases Screened as Inhibitors of Spontaneous Ignition of Hydrazine-Nitrogen Tetroxide	5
2	Vaporized Liquids Screened as Inhibitors of Spontaneous Ignition of Hydrazine-Nitrogen Tetroxide	6
3	Ultimate Effectiveness of Inhibitors for Hydrazine-NO ₂ * Reaction	7
4	Gas Product Analysis and Equilibrium Temperature Rises for Argon-Diluted Hydrazine-NO ₂ Stirred Reactions	15
5	Known and Possible Sub-reactions in the Hydrazine-Nitrogen Tetroxide Reaction	19

<u>Figure</u>		
1	Spontaneous Ignition Apparatus	4
2	High Speed Photographs of Hydrazine Droplet Ignition in NO ₂ *-Argon Atmosphere	9
3	Hydrazine-Nitrogen Tetroxide Diffusion Flame Burner	11
4	Stirred Reactor for Hydrazine-Nitrogen Tetroxide Ignition Studies	14
5	Equilibrium Temperature Rise and Product Distribution as a Function of Reactant Concentrations in the Stirred Reactor	17
6	Possible Reaction Sequences in Hydrazine-Nitrogen Tetroxide Flame Reaction	23
7	Low Pressure Burner, after Wolfhard (Ref. 20)	27

1. INTRODUCTION

As part of a long-range program to elucidate the mechanisms of flame inhibition, research to find effective inhibitors of the hypergolic reaction between hydrazine and nitrogen tetroxide was undertaken. This report describes the results of that investigation. The general approach included:

1. Literature survey of existing literature on the over-all reaction, and all sub-reactions that might be pertinent in the over-all mechanism.
2. Definition of the ignition characteristics of the reactant system under inert gas diluent conditions.
3. Definition of an ignition procedure by which potential inhibitors could be tested for effectiveness in retarding the reaction rate.
4. Clarification of the preflame reaction mechanism by analytical and spectroscopic techniques.

Since very little was known about the mechanism of the hydrazine-nitrogen tetroxide reaction, a good deal of effort was expended on section 4 above. Although our results have not completely defined the reaction mechanism, we believe a significant advance has been made.

2. SUMMARY

Studies of the hydrazine-nitrogen tetroxide reaction indicate that a thermal reaction mechanism is operative which is initiated and propagated primarily by molecular interaction. No evidence for a chain branching explosion mechanism was found. If this is true, one would not expect small quantities of inhibitor to appreciably decrease the over-all reaction rate. In the chain branched reaction, minute quantities of inhibitor effectively reduce reaction rate through removal of active free radicals from the prereaction zone. In the case of a thermal molecular reaction, only two inhibitor mechanisms exist, both requiring major inhibitor concentrations. The first occurs when the agent competes with one reactant for the other, resulting in a lower net heat release. The second involves

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application of an agent which removes the exothermic heat of reaction to maintain the equilibrium temperature below the ignition temperature.

The conclusion, that a thermal reaction mechanism is operative, is supported by experimental results obtained in reaction mechanism studies, and investigations of the effect of candidate inhibitors on the ignition limit of argon-diluted reactants. In reaction mechanism investigations, the distribution of products and the equilibrated reaction temperatures resulting from the mixing of argon-diluted reactants were studied as a function of reactant concentration. Under dilute conditions, below 2 mole % of each reactant, a preignition reaction was found to proceed, yielding as major products ammonium nitrate and nitrous oxide. At concentrations of 2 mole % and higher of each reactant, the preignition reaction product analyses indicated a regular increase in nitrogen and nitric oxide at the expense of nitrous oxide. At 3 mole % of each reactant and above, the major gaseous products were nitrogen and nitric oxide, along with minor quantities of nitrous oxide and ammonia. At 5 mole % of each reactant spontaneous ignition occurred, and at 6 mole % the reaction flask was uniformly enveloped in flame. The experiments were conducted by rapidly mixing the two argon-diluted reactant streams with a high speed stirrer in an insulated reaction flask.

The emission spectrum from the nitrogen tetroxide-hydrazine flame indicated the presence of NH_2 , NH and OH radicals after the flame front. It was not possible to conduct emission measurements in the preflame region where the presence of free radicals would imply a chain-branched reaction mechanism. High speed schlieren movies of the ignition of a hydrazine droplet in an argon-nitrogen dioxide-nitrogen tetroxide atmosphere were of qualitative interest, but offered no quantitative insight into reaction mechanism.

A modified spontaneous ignition technique was employed to screen 27 gaseous and 28 liquid inhibitor candidates for the hydrazine-nitrogen tetroxide reaction. Of these, only five were found to inhibit the hypergolic reaction, and these to only a small extent. They are thiophene, toluene, trimethyl borate, ethyl bromide and benzene. No explanation for their effectiveness can be advanced. The relative concentration of inhibitor studied was quite large. It seems reasonable that no inhibitor acting by removal of a critical intermediate was found for the hydrazine-nitrogen tetroxide reaction since this type of inhibition requires a relatively small amount of the active agent.

3. SPONTANEOUS IGNITION CHARACTERISTICS

In preliminary studies, when a high concentration of nitrogen tetroxide was added to low concentrations of argon-diluted hydrazine, hypergolic ignition resulted at room temperature even when only 2 mole % hydrazine was present. On the other hand, when liquid hydrazine was admitted to argon-diluted nitrogen tetroxide, there was found a limiting nitrogen tetroxide concentration below which spontaneous ignition did not occur at a given constant temperature. Similar behavior was noted by the Bureau of Mines (Ref. 1) during spontaneous ignition measurements on hydrazine-unsym.-dimethylhydrazine (UDMH)-nitrogen tetroxide-air mixtures.

3.1 Inhibitor Screening by Spontaneous Ignition Limit It was observed that when a drop of hydrazine, originally at room temperature, is dropped into an Erlenmeyer flask filled with an NO_2^* (equilibrium-nitrogen tetroxide-nitrogen dioxide mixture)-argon mixture at 75°C , spontaneous ignition occurs when the concentration of NO_2^* in argon exceeds 11 mole %. If the mixture contains less than 11 mole % NO_2^* , a nonflame reaction occurs. These observations agree qualitatively with those of Perlee, Imhof and Zabetakis (Ref. 2) who found the concentration limit at 75°C to be 13.2 mole % of NO_2^* in air.

A series of experiments were designed by means of which the effect of selected candidate inhibitors on this ignition limit could be studied rapidly. It was reasoned that an effective inhibitor would displace the ignition limit to higher concentrations of NO_2^* .

The apparatus for studying the spontaneous ignition of a hydrazine drop in an atmosphere containing NO_2^* vapor is presented in Figure 1. Argon, NO_2^* , and gaseous inhibitor are metered through rotameters. The gases mix and flow into a 250-ml Erlenmeyer flask, thermostatted at 75°C in a water bath. When all air has been displaced from the flask, gas flow is stopped, and after 30 seconds, during which turbulence in the flask diminishes, a drop of hydrazine is allowed to fall into the flask, and results are noted. To enable screening of vaporized liquids as inhibitors, the apparatus includes a heated injector. The liquid, fed into the injector by a variable speed syringe driving motor, is vaporized in the injector and admitted into the main stream through a fine slot.

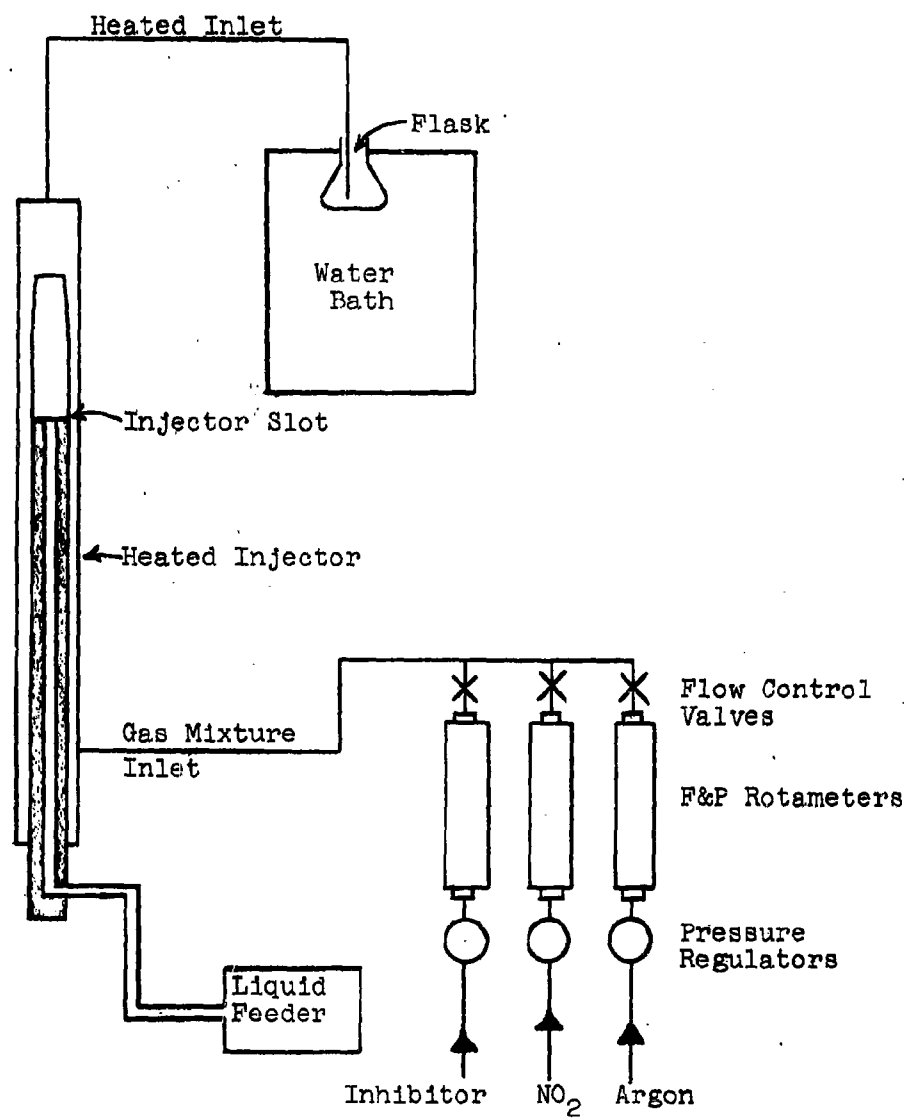


Figure 1. Spontaneous Ignition Apparatus

It was decided that an effective inhibitor might raise the NO_2^* concentration ignition limit from 11 mole % to 15 mole %. Therefore, gas mixtures containing 15 mole % of NO_2^* , 5% inhibitor and 80% argon were tested. None of the 27 gaseous inhibitors tested prevented ignition under these conditions. Some might have increased the concentration limit slightly above 11% NO_2^* , but if so the change was insignificant and no effort was made to check the point. The gaseous inhibitor candidates tested are presented in Table 1.

Table 1. GASES SCREENED AS INHIBITORS OF SPONTANEOUS IGNITION OF HYDRAZINE-NITROGEN TETROXIDE

Methane	1,1-Difluoroethylene
Methyl chloride	n-Butane
Methyl bromide	1,3-Butadiene
Trifluoromethane	Hydrogen bromide
Carbon tetrafluoride	Hydrogen chloride
Bromotrifluoromethane	Hydrogen sulfide
Bromochlorodifluoromethane	Ammonia
Dibromodifluoromethane	Carbon monoxide
Ethyl chloride	Carbon dioxide
Chlorotrifluoromethane	Nitrous oxide
1,1-Difluoroethane	Sulfur dioxide
Dichlorotetrafluoroethane	Sulfur hexafluoride
Ethylene	
Ethylene oxide	
Vinyl chloride	

The liquid inhibitors were tested similarly. The liquids were syringe-driven into the injector, vaporized, and injected into the NO_2^* -argon stream through a heated line (to prevent condensation). The mixtures were again 15 mole % NO_2^* , 5% additive and 80% argon.

The 28 vaporized liquid candidate inhibitors are presented in Table 2. Of these 8 appeared to be effective.

Table 2. VAPORIZED LIQUIDS SCREENED AS INHIBITORS
OF SPONTANEOUS IGNITION OF HYDRAZINE-
NITROGEN TETROXIDE

Ineffective	Effective
Acetone	Benzene
Acetic acid	Diethyl ether
Acetonitrile	Dimethyl sulfide
Bromobenzene	Ethyl bromide
Bromochloromethane	n-Octane
Carbon disulfide	Thiophene
Carbon tetrachloride	Toluene
Chloral	Trimethyl borate
Chlorobenzene	
Chloroform	
Dibromotetrafluoroethane	
Ethyl iodide	
Iron pentacarbonyl (a)	
Methanol	
Nitromethane	
Phosphorous trichloride	
Silicon tetrachloride	
Tetramethyl lead (a)	
Titanium tetrachloride (a)	
Water	

(a) Plugged inlet tube

Three of the compounds tested (iron pentacarbonyl, tetramethyl lead, and titanium tetrachloride) reacted with NO_2^* to such an extent that they plugged the inlet tube, and could not be properly tested.

To determine their ultimate effectiveness, the inhibitory materials were tested at 5% concentration in mixtures containing greater than 15% NO_2^* . The results are listed in Table 3.

Table 3. ULTIMATE EFFECTIVENESS OF INHIBITORS FOR HYDRAZINE-
NO₂* REACTION

Material	Inhibited at, % NO ₂ * in Mixture	Failed at,
n-Octane (a)	23.8	24.8
Diethyl ether (a)	22.5	23.8
Dimethyl sulfide (a)	22.5	23.8
Thiophene	18.7	19.5
Toluene	18.6	19.6
Trimethyl borate	17.2	18.6
Ethyl bromide	16.4	17.2
Benzene	15.6	17.2

(a) Not actually inhibitors - see text

n-Octane, diethyl ether, and dimethyl sulfide appeared to react directly with the NO₂*, with considerable heat release. The hydrazine drop provided enough additional heat to ignite the NO₂*-inhibitor mixture, after which no NO₂* remained to burn with hydrazine. With the other inhibitors, the NO₂* disappeared slowly during the experiment, reacting with hydrazine by the nonflame reaction. Therefore, these last five materials acted as true inhibitors, though not extremely good ones. The first three cannot be considered inhibitory.

It can be seen from Table 3 that 5% of inhibitor was effective in neutralizing no more than 8% of NO₂*. The inhibiting effects could plausibly result from a preferential chemical reaction of the inhibitor to remove either the fuel or the oxidizer, or else by an increase in the specific heat or heat transfer rate of the gas mixture. Either of these mechanisms would require a relatively large amount of added material. It seems reasonable that no inhibitor acting by removal of a critical intermediate was found for the hydrazine-NO₂* reaction, since this type of inhibition requires a relatively small amount of the active agent.

This reaction is an acid-base reaction, hence proceeds rapidly to completion. Since the hydrazine-NO₂* reaction starts spontaneously, its rapid exothermic character carries the first stage to completion as soon as the reactants are combined. In view of the high spontaneous heat release of this reaction and the failure to find any highly effective inhibitors out of 55 candidates tried, it seems improbable that any ignition inhibitors exist.

3.2 The Preignition Reaction Early in the spontaneous ignition studies it was observed that when the nitrogen tetroxide was sufficiently diluted with inert gas, the hydrazine-nitrogen tetroxide reaction produced ammonium nitrate (solid) and nitrous oxide (gas). The solid product (not previously reported for this reaction) was identified by x-ray diffraction measurements, while gas analysis was obtained by infrared. Because of this reaction premixed flame studies at near-atmospheric pressures could not be carried out.

4. INVESTIGATION OF THE HYDRAZINE-NITROGEN TETROXIDE FLAME MECHANISM

Since the mechanism of the hydrazine-nitrogen tetroxide combustion process was almost entirely unknown, it was necessary that our research include a study of the uninhibited reaction. It was hoped that understanding of the mechanism might suggest specific inhibitors not previously tested.

4.1 High Speed Movies of the Ignition of a Drop of Hydrazine To gain more insight into the ignition process that occurs when a drop of hydrazine falls into NO_2^* -argon, high speed movies were taken at about 1500 frames per second. The NO_2^* -argon mixture contained 20% NO_2^* , and was originally at room temperature, as was the hydrazine. The gas mixture, contained in a 2-inch square glass cell, was viewed through the schlieren system, which made it easier to see flow patterns and density changes. Flow of NO_2^* -argon was shut off a few seconds before addition of the hydrazine to avoid gas motion not due to the ignition process.

A sequence of individual frames selected from a 100-ft roll of film (about 4000 frames total) is shown in Figure 2 along with the time in milliseconds after the drop hit the bottom of the glass cell. From these photographs, the ignition process may be divided into seven stages. Stage 1 shows the hydrazine drop entering the glass cell. The tube to the far left is the NO_2^* -argon entrance tube and the droplet is about to contact a small glass plate located on the bottom of the cell. Stage 2 illustrates a preignition reaction during which hydrazine vaporizes into the NO_2^* atmosphere,

Stage

1



2



62

99

137

180

260

3



378

456

531

745

811

4



932

941

5



960

994

1023

6



1077

1089

1102

1118

1145



1190

1198

1220

1258

1300

Figure 2. High Speed Photographs of Hydrazine Droplet Ignition
(Numbers refer to time in milliseconds from start of test)

forming a growing particulate cloud of ammonium nitrate. During this time a spherical droplet appears to take form on the glass plate.

From the photographs it is not clear whether ignition occurs at Stage 3 (ca 378 millisecc) or at Stage 4 (932 millisecc). During Stage 3 what appears to be a flame is formed while the amount of smoke gradually decreases until at 811 millisecc only a faint wisp remains. During Stage 3 a conical inner core appears directly on the glass plate surface and becomes sharply defined. This core may represent a surface of reaction or a pool of liquid hydrazine.

An alternate explanation would be that the apparent flame boundaries in Stage 3 represent ammonium nitrate streams which are directed upward due to their low bulk density and under the influence of the exhaust duct located directly above the apparatus. The sudden disappearance of the conical core in Stage 4 would then represent the onset of ignition.

In Stage 5 the reacting surface is established, while Stage 6 follows a representative cycle termed "flicker" of the flame. In this cycle an established surface separates at the base of the flame, gradually lifting off while a new surface is being formed. In Stage 7 the "flicker" of the flame was repeated. The total film time was over 2000 millisecc.

So as to clearly define the onset of ignition, the apparatus was modified. A photomultiplier tube was placed perpendicular to the schlieren axis which fed a signal to a trigger circuit. This triggered an intense high voltage spark source in line with the schlieren axis when ignition occurred. The apparatus worked perfectly; however, the mode of ignition appeared nonreproducible, and the experiments were discontinued.

4.2 Spectroscopic Studies of the Hydrazine-Nitrogen Tetroxide Diffusion Flame The emission spectrum of a hydrazine-nitrogen tetroxide flame produced with the diffusion burner (Figure 3) was studied employing the Jarrell-Ash Model 82000 spectrometer. Argon-diluted streams of nitrogen tetroxide and hydrazine preheated to 85°C were metered up through the concentric tubes. The spectrum was taken near the top of the yellow rounded inner cone.

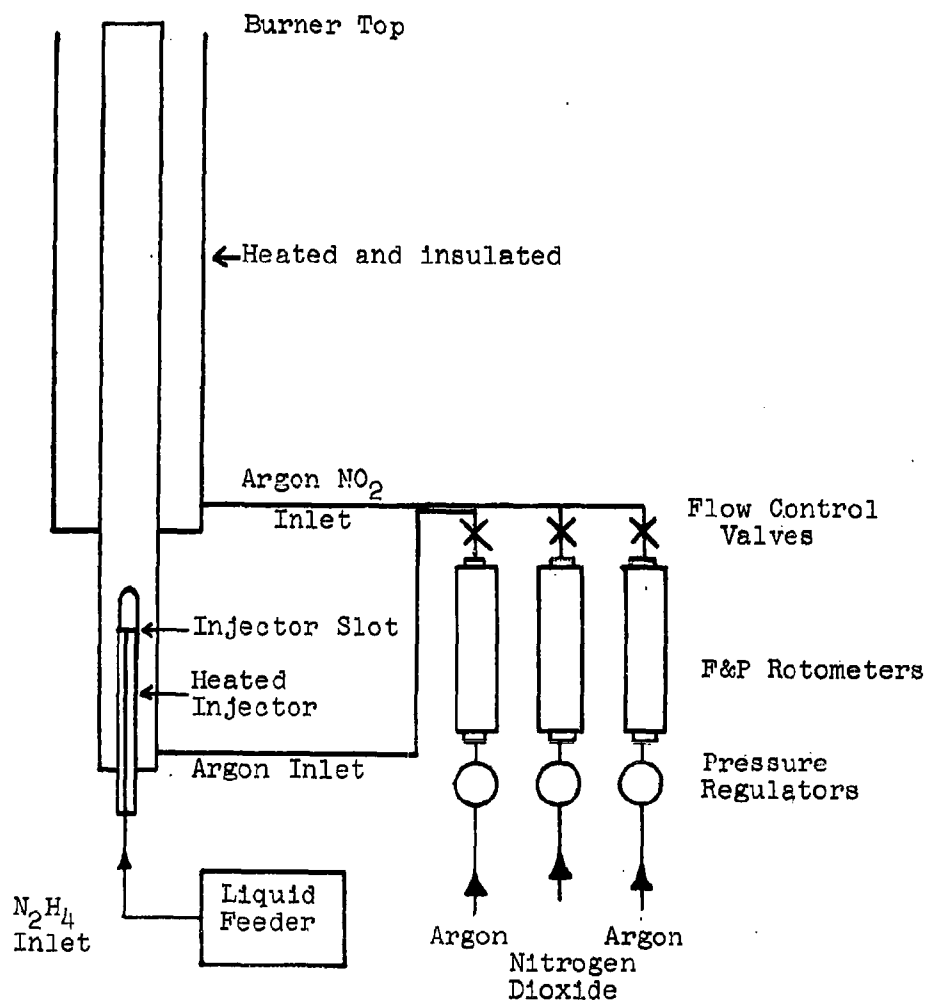
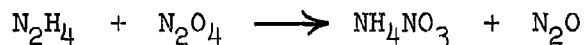


Figure 3. Hydrazine-Nitrogen Tetroxide Diffusion Flame Burner

The most important spectral feature was the spread out emission spectrum of NH_2 , which extended from about 6000 to 4500 Å. In addition, peaks due to NH at 3360 Å and OH near 3100 Å were detected. It must be pointed out that the presence of free radicals in the hydrogen-nitrogen tetroxide flame does not constitute proof that the radicals are involved in the ignition process.

4.3 Stirred Reactor Studies - Temperature and Product Analysis Early work indicated that at low concentrations of nitrogen tetroxide in argon a pre-ignition reaction proceeded when a hydrazine droplet entered the NO_2^* atmosphere. At 2.2% NO_2^* or below, the reaction was found to proceed in nearly 80% conversion to ammonium nitrate and nitrous oxide according to the reaction



Infrared analysis indicated that nitrous oxide was the only nitrogen oxide formed, and therefore it appeared that some NO_2^* was reduced to nitrogen.

While the study of the reaction that occurs when a drop of hydrazine is added to NO_2^* vapor offered some insight into the mechanism, this technique has limitations. The roles of diffusion, convection and heat transfer are important but are difficult to evaluate quantitatively. Of the heat generated by the reactions, some is transferred to unreacted gas, some to the container walls, and some to the vaporizing hydrazine, and some, of course, remains in the reaction products, raising their temperature. It was not possible to determine from these experiments just what temperature and what substances were required to bring about the transition from nonflame to flame reaction.

It was desirable to obtain information as to the course of the precombustion reaction up to the point of spontaneous ignition, in the absence of competing physical processes such as vaporization and mixing. A knowledge of the gaseous reaction products and the reaction temperature as a function of initial reactant concentration would lead to a better understanding of the over-all mechanism. Since the argon-diluted reactants could not be premixed without reaction, a method was devised to permit dilute, prevaporized reactant streams to be mixed instantaneously.

A series of experiments was planned which made use of the instrumented diffusion burner previously employed for the spectroscopic study. A stirred reactor was mounted on the exit of the diffusion burner so that concentric streams of hydrazine-argon and NO_2^* -argon entered through a hole in the bottom of a 200-cc Pyrex flask, where they were rapidly mixed by a paddle-wheel stirrer. The temperature of the product gases was measured by a chromel-alumel thermocouple. Gas samples at equilibrium were withdrawn through a stainless steel capillary for infrared, mass spectrometric and gas chromatographic analysis. The flask was well insulated with asbestos. At higher reactant concentrations it was necessary to substitute a quartz flask since the equilibrated temperature surpassed the temperature capability of Pyrex. The stirred reactor is sketched in Figure 4.

In this reactor, streams of nitrogen dioxide and hydrazine in argon, preheated to 85°C , were rapidly mixed as they entered the flask. After a short period during which the flask and stirrer warmed up, the reactor came to a steady state, with a constant product gas temperature and composition. Employing this method, experiments were conducted in which the nitrogen dioxide and hydrazine streams were at the same concentration in mole per cent, but this concentration was successively increased from 2% nitrogen dioxide - 2% hydrazine - 96% argon to 6% of each reactant and 88% argon.

The gas products were analyzed by one or more of the three analytical techniques used: infrared, mass, or VPC; thus, nitric oxide was analyzed by all three methods, while hydrogen was analyzed only by gas chromatography.

Results by different methods, when used, agreed within the expected accuracy ranges, and average values are therefore reported.

The gaseous product analysis in mole per cent and the temperature rise in $^\circ\text{C}$ for each experiment are presented in Table 4. In the experiments at 4.5, 5.0, and 6.0% reactants, it was first observed that rate of stirring affected the extent of reaction and the final equilibrated temperature. A setting on the variable speed motor was found at which the highest temperature was observed; any change in the stirring speed would lower the equilibrated temperature. For these experiments the analysis and temperature reported correspond to that stirring speed at which the temperature was maximum. The analyses completely neglect the quantities of any condensed phase products such as water and ammonium nitrate. No attempt was made to determine these species.

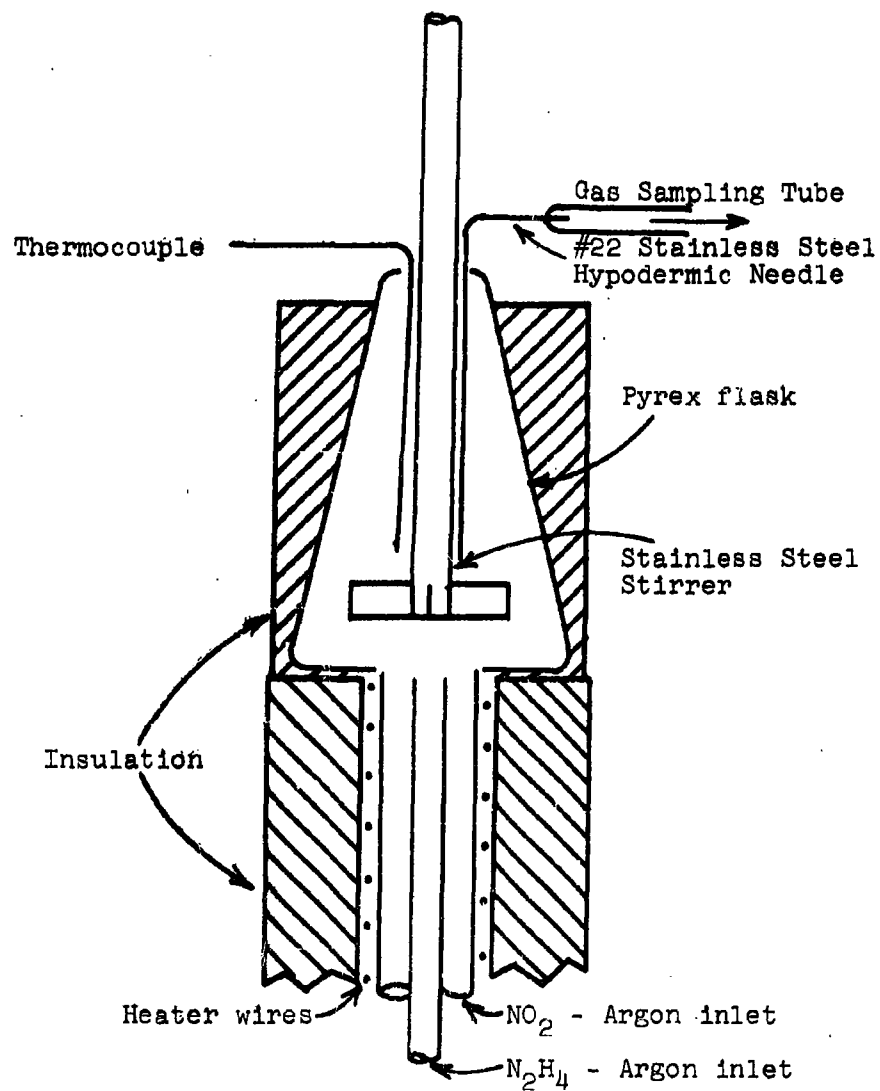


Figure 4: Stirred Reactor for Hydrazine-Nitrogen
Tetroxide Ignition Studies

Table 4. GAS PRODUCT ANALYSIS AND EQUILIBRIUM TEMPERATURE
RISES FOR ARGON-DILUTED HYDRAZINE-NITROGEN DIOXIDE
STIRRED REACTIONS

Mole % of Each Reactant	2.0	3.0	3.0	3.5	4.0	4.0	4.5	5.0	6.0
Temperature Rise, °C	109	238	237	315	468	542	606	737	843
Mole % Products									
N ₂ O	0.70	0.24	0.22	0.16	0.29	0.16	0.10	0.23	0.24
N ₂	1.68	3.79	4.13	5.15	6.06	6.92	(a)	7.98	8.75
NH ₃	(b)	0.25	(b)	0.68	0.23	0.72	(a)	(b)	(b)
NO	1.66	3.93	3.78	3.79	4.39	2.80	(a)	3.16	4.73
H ₂	0.022	0.11	0.10	0.21	0.44	0.91	(a)	0.95	0.61

(a) Product analysis prevented by air leak into samples.

(b) No NH₃ present.

The nonflame reaction continued at reactant concentrations below 5 mole %. At 5 mole % a very dim flame was observed, and at 6% reactants the flame appeared to fill the entire reactor. Product analysis indicates that at 6% reactants the reaction is not yet complete according to the reaction



This is supported by the measured temperature rise of 737°C for the 5% reactant experiment, compared to the calculated temperature rise of 1244°C for complete reaction. Thus the actual value represents an efficiency of only 60%. The maximum change of temperature with reactant concentration was found to occur between 3.5 and 4.0% of reactants. At about 3.8% reactants the indicated temperature from the thermocouple constantly fluctuated between two extremes. In one case the fluctuation was rapid between 438°C and 597°C (these temperatures include a preheat of 85°C). This behavior indicates a change in reaction mechanism. That is, at 3.8% reactants, or at about 440°C, a new reaction is just at the threshold of asserting itself in the overall reaction mechanism.

The data of Table 4 can be more realistically presented by calculating the per cent of total gas phase nitrogen appearing in each of the gaseous products. Data so calculated more clearly represent the approach to the complete reaction. Consider, for example, a product mixture which contains equal quantities of nitrogen and nitrous oxide. As far as the complete reaction is concerned, where all nitrogen atoms appear as nitrogen gas, the reaction is 67% complete. The results of these calculations are illustrated in Figure 5 where the mole per cent of product gases based on their nitrogen atom content is plotted against the per cent of each reactant in the argon-diluted streams. In addition the equilibrium temperature rise is illustrated for each experiment.

The data are not completely consistent, but the trend with increasing reactant concentration is readily apparent:

1. The proportion of nitrogen and hydrogen gas to the remaining gaseous products increases with temperature or concentration.
2. The proportion of nitrous oxide decreases with temperature to a low constant value.

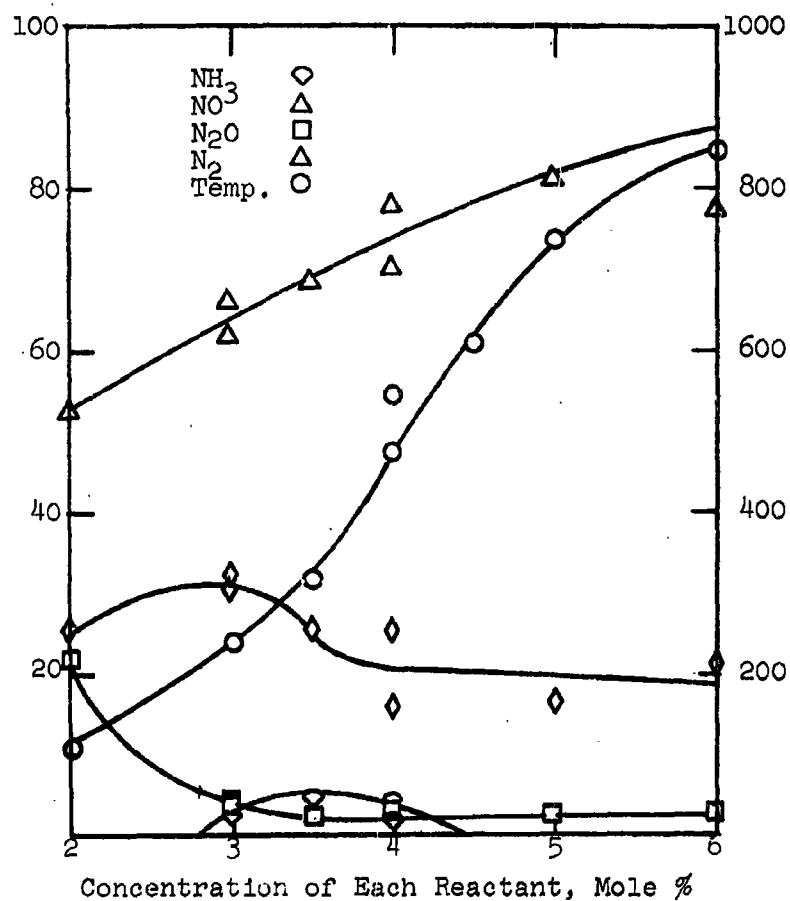


Figure 5. Equilibrium Temperature Rise and Product Distribution as a Function of Reactant Concentration in the Stirred Reactor

3. The proportion of nitric oxide first increases and then decreases with temperature.
4. The quantity of ammonia increases to a maximum and then decreases.
5. The major gaseous products above 3% reactants are nitrogen and nitric oxide.

5. CONCLUSIONS AND RECOMMENDATIONS

The pattern of combustion product distribution and reactant temperatures furnished by the stirred reactor investigations suggests that the over-all reaction mechanism is complex. To appreciate this fully, potential competing reactions are listed in Table 5, along with their heats of reaction at 25°C.

In the following paragraphs the information available on the individual reactions is discussed, with the objective of explaining which would be important in the over-all reaction. The temperature at which the reaction rate becomes sufficiently rapid that an appreciable fraction of the reactants would be used up in one second was considered the critical property. These temperatures, listed in Table 5, are those above which the reactions are rapid enough to play a part in the ignition process.

Reaction N-1 Initially the only oxidizers present are nitrogen dioxide and nitrogen tetroxide. They are in dynamic equilibrium, with about 50% of the latter dissociated at room temperature and pressure (Ref. 3). At 75°C the dissociation of nitrogen tetroxide is 95%, and this percentage increases steeply with temperature. Therefore, as the reactions occur and heat the gas as high as 140°C (Ref. 4), nitrogen tetroxide converts almost quantitatively to nitrogen dioxide. Since ignition occurs only at much higher temperatures, one can rule out nitrogen tetroxide reactions as its cause.

Reaction N-2 The initial reaction between nitrogen dioxide and hydrazine to yield nitrous oxide, ammonium nitrate, and a considerable amount of heat is definitely known to occur at room temperature even when the partial pressure of the reactants is less than 0.01 atmosphere.

Table 5. KNOWN AND POSSIBLE SUB-REACTIONS IN THE
HYDRAZINE-NITROGEN TETROXIDE REACTION

No.	Reaction (All substances are taken as gases unless otherwise noted)*	Heat of Reaction at 25°C, Kcal per g mol of First Reactant in Equation
N-1	$\text{N}_2\text{O}_4 \xrightleftharpoons{140^\circ} 2 \text{NO}_2$	+ 13.9
N-2	$\text{N}_2\text{H}_4 \text{ (liq.)} + 2\text{NO}_2 \xrightleftharpoons{25^\circ} \text{N}_2\text{O} + \text{NH}_4\text{NO}_3 \text{ (sol.)}$	- 95.8
N-3	$\text{NH}_4\text{NO}_3 \text{ (solid)} \xrightarrow{400^\circ} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	- 8.6
N-4	$\text{N}_2\text{H}_4 \text{ (liquid)} \xrightarrow{600^\circ} \text{NH}_3 + 1/2 \text{N}_2 + 1/2 \text{H}_2$	- 23.0
N-5	$\text{NO}_2 \xrightarrow{920^\circ} \text{NO} + 1/2 \text{O}_2$	+ 13.5
N-6	$\text{NO} \xrightarrow{1350^\circ} 1/2 \text{N}_2 + 1/2 \text{O}_2$	- 21.5
N-7	$\text{N}_2\text{O} \xrightarrow{1100^\circ} \text{N}_2 + 1/2 \text{O}_2$	- 19.6
N-8	$\text{N}_2\text{H}_4 \text{ (liq.)} + 2\text{N}_2\text{O} \xrightarrow{760^\circ} 3\text{N}_2 + 2\text{H}_2\text{O}$	-166.8
N-9	$\text{NH}_3 + 3/2 \text{N}_2\text{O} \xrightarrow{950^\circ} 2\text{N}_2 + 3/2 \text{H}_2\text{O}$	-105.1
N-10	$\text{H}_2 + \text{N}_2\text{O} \xrightarrow{750^\circ} \text{N}_2 + \text{H}_2\text{O}$	- 77.4
N-11	$\text{NH}_3 + 5/2 \text{NO}_2 \longrightarrow 7/2 \text{NO} + 3/2 \text{H}_2\text{O}$	- 15.4
N-12	$\text{H}_2 + \text{NO}_2 \xrightarrow{\sim 500^\circ} \text{NO} + \text{H}_2\text{O}$	- 44.3
N-13	$\text{N}_2\text{H}_4 \text{ (liq.)} + 2\text{NO} \longrightarrow 2 \text{N}_2 + 2\text{H}_2\text{O}$	-170.6
N-14	$\text{NH}_3 + 3/2 \text{NO} \longrightarrow 5/4 \text{N}_2 + 3/2 \text{H}_2\text{O}$	-108.0
N-15	$\text{H}_2 + \text{NO} \xrightarrow{>1500^\circ} 1/2 \text{N}_2 + \text{H}_2\text{O}$	- 79.3
N-16	$\text{N}_2\text{H}_4 \text{ (liquid)} + \text{O}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$	-127.7
N-17	$\text{NH}_3 + 3/4 \text{O}_2 \xrightarrow{650^\circ} 1/2 \text{N}_2 + 3/2 \text{H}_2\text{O}$	- 75.8
N-18	$\text{H}_2 + 1/2 \text{O}_2 \xrightarrow{575^\circ} \text{H}_2\text{O}$	- 57.8

* All temperatures in degrees centigrade.

Reactions N-3 and N-4 Reaction N-3, the thermal decomposition of ammonium nitrate, and reaction N-4, the thermal decomposition of hydrazine, are known to occur below the over-all ignition temperature and are almost certainly involved in the ignition processes. Extrapolation of published data (Ref. 5) shows that Reaction N-3 will go to 99% completion in one second at 410°C. Data on Reaction N-4 (Ref. 6) indicate that this reaction should go to 99% completion in one second at 598°C. Since Reactions N-2, -3, and -4 are all exothermic, they raise the temperature considerably.

Reactions N-5, N-6 and N-7 As the temperature rises, other thermal decomposition reactions of the oxidizers become possible, as indicated by sub-reactions N-5, -6 and -7 in Table 5. One must also consider the possibility of the disappearance of each of the nitrogen oxides by thermal decomposition.

Reaction N-5 From a consideration of thermodynamics the thermal decomposition of nitrogen dioxide to nitric oxide and oxygen (Reaction N-5) is nearly quantitative at 600°C (Ref. 7). Kinetically this second order reaction only goes to 64% completion in one second at this temperature with a partial pressure of nitrogen dioxide of 0.10 atmosphere; at 920°C, Reaction N-5 is 99% complete in one second (Ref. 8).

Reaction N-6 Nitric oxide, formed by the decomposition of nitrogen dioxide, is thermally very stable. The thermal decomposition of nitric oxide (Reaction N-6) goes only to 13% completion in one second for a gas sample at 1347°C, containing 0.10 atmosphere partial pressure nitric oxide (Ref. 9). This reaction is zero-order at temperatures below 1100°C, second order in the 1400-1800°C range, and both mechanisms are involved in the 1100-1400°C range (Ref. 10). Potter and Waymouth (Ref. 11) state that even at 2400°K thermal decomposition of nitric oxide is so slow that the reaction is unlikely to contribute to a flame front.

Reaction N-7 Nitrous oxide is also very stable thermally; at temperature of 971°C, 99% of the nitrous oxide initially present at 0.10 atmosphere partial pressure would decompose in ten seconds and at 1110°C, 99% conversion would be obtained in one second (Ref. 12).

Reactions N-8 and N-18 The sub-reactions suspected to occur in the preignition period could produce several fuels and oxidizers not initially present, the fuels being ammonia and hydrogen, and the oxidizers being nitric oxide, nitrous oxide and oxygen. These possibilities are expressed in sub-reactions N-8 through N-18 in Table 5.

Reaction N-8 No data for reaction of nitrous oxide with hydrazine were found, so attempts were made to measure the autoignition temperature of this reaction with the standard ASTM apparatus. The procedure of dropping hydrazine into nitrous oxide-argon atmospheres was tried but was not successful. At elevated temperatures, sudden vaporization of hydrazine created a local high concentration which burned, but whether ignition began in the flask or in the air was not apparent. A droplet of hydrazine in air will spontaneously ignite at temperatures as low as 270°C (Ref. 2). Therefore experiments were carried out in which a continuous gas stream containing argon, nitrous oxide, and vaporized hydrazine was passed into the spontaneous ignition apparatus. The mixtures tried contained 0.5, 1.0, and 2.0 times the stoichiometric amounts of hydrazine with 4 and 8% nitrous oxide. Also an undiluted mixture, 23% hydrazine, 77% nitrous oxide, was tried. None of these mixtures ignited even at temperatures as high as 760°C (the upper temperature limit of the apparatus). At this high temperature, hydrazine thermally decomposes rather rapidly to ammonia, nitrogen and hydrogen. This strongly suggests that at these concentrations neither ammonia nor hydrogen are reactive toward nitrous oxide below 760°C . At other concentrations, as indicated below, nitrous oxide and hydrogen will react at this temperature.

Reactions N-9 and N-10 Concerning the reaction of ammonia and nitrous oxide, Destriau and Laffitte reported that one part ammonia mixed with six parts of nitrous oxide at a combined partial pressure of 100 mm ignited at a temperature of 950°C (Ref. 13). A mixture of 30 mm of nitrous oxide plus 10 mm of hydrogen ignited when heated to 750°C (Ref. 14).

Reactions N-11 and N-12 Two additional possible sub-reactions of nitrogen dioxide should be considered, one with ammonia and the other with hydrogen. No published data was found for the former system. For the

system nitrogen dioxide-hydrogen, Ashmore and Levitt (Ref. 15) reported that these gases ignite above 500°C, and that this reaction is inhibited by the presence of nitric oxide, oxygen and nitrogen and inert gases, but is slightly accelerated by the presence of water vapor. Oxygen, the most effective inhibitor, reduces the initial rate of reaction about 50% when present at 0.5 atmospheres partial pressure.

Reactions N-13, N-14 and N-15 Though nitric oxide may potentially react with hydrazine, ammonia and hydrogen, data on the first reaction are not yet available. The reaction of hydrogen with nitric oxide (Reaction N-15) is very hard to initiate as evidenced by the fact that nitric oxide is stable in nitrogen dioxide-hydrogen flames at temperatures as high as 1500°C (Ref. 16, 17). Reaction N-14 between ammonia and nitric oxide, is only somewhat less difficult to initiate (Ref. 18). Heating ammonia to about 2000°C causes decomposition, forming NH and NH₂ radicals. These radicals then react with nitric oxide, but the nitric oxide is not completely consumed unless ammonia, and thus NH and NH₂, is present in excess. These last two sub-reactions can almost certainly be ruled out as contributing to ignition of hydrazine-nitrogen dioxide.

Reactions N-16, N-17 and N-18 Oxygen, a good oxidizer, reacts with hydrazine, ammonia and hydrogen at relatively low temperatures. The ignition temperature of hydrazine in air has already been stated to be only 270°C (see Reaction 8), which is 300°C below its decomposition temperature. The minimum ignition temperatures of hydrogen and ammonia in air are 575°C and 650°C respectively (Ref. 19). Thus, although these reactions were considered, they probably do not play a role in hydrazine ignition in NO₂*, because there is no oxygen present.

Figure 6 diagrams the possible reaction sequences discussed above. The results of the stirred reactor studies can now be interpreted in light of Table 5 and Figure 6. Ignition occurred at a temperature greater than 690°C and less than 817°C. These temperatures correspond to the sums of the temperature rise and preheat temperatures for experiments at 4.5% and 5.0% of both reactants, or the concentrations just before and after spontaneous ignition occurred.

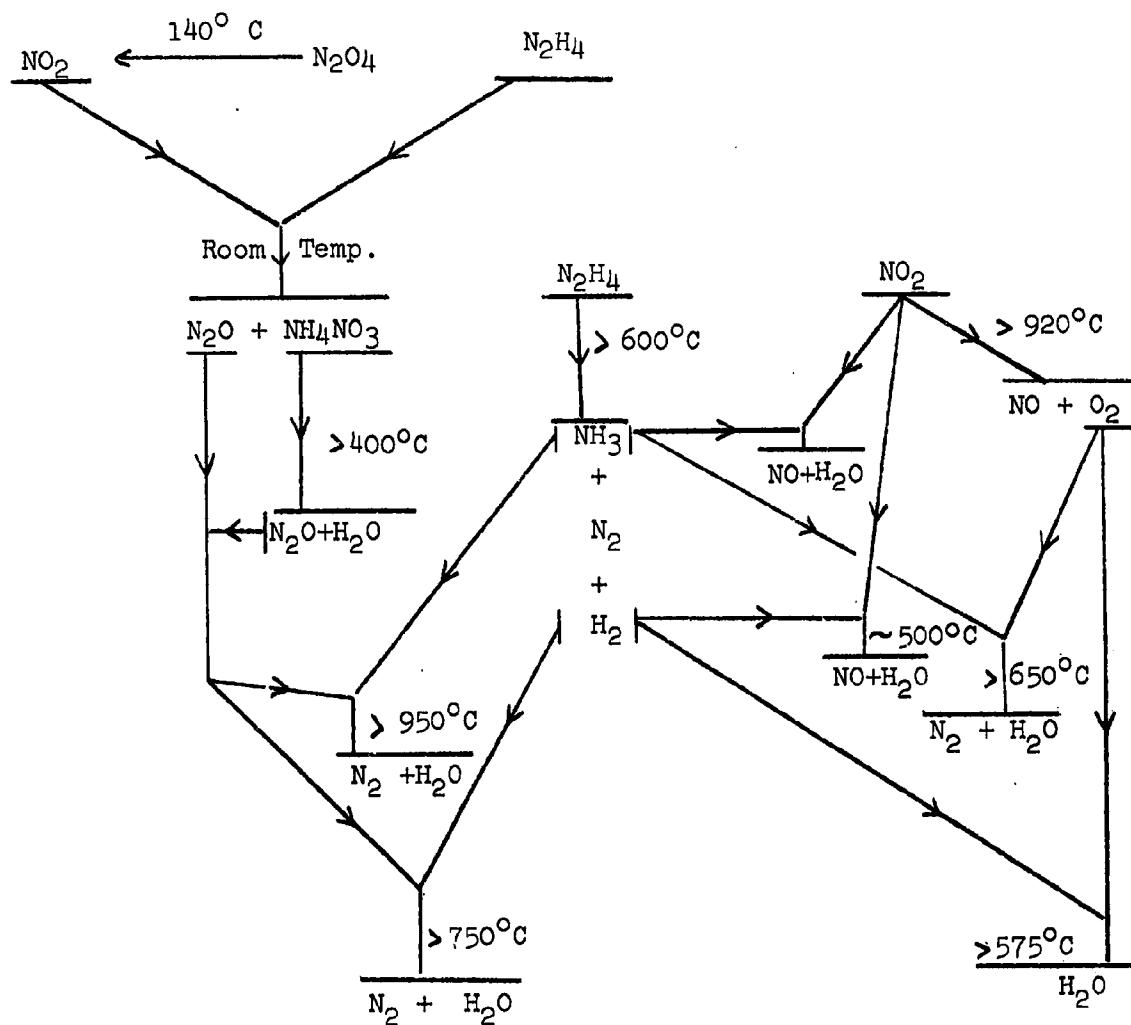
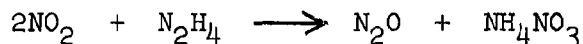


Figure 6. Possible Reaction Sequences in Hydrazine-Nitrogen Tetroxide Flame Reaction

The species present just before the ignition temperature is reached are nitrous oxide, nitrogen, nitric oxide, hydrogen and water, since at 400°C all the ammonium nitrate would have decomposed. These products are all stable toward decomposition up to at least 1100°C where nitrous oxide decomposition to $N_2 + 1/2 O_2$ is 99% complete in one second. From the analysis of the products at 2% reactants, and from earlier investigations of preignition reaction at lower concentrations it seems likely that the initiating reaction is Reaction N-2



That this equation does not completely account for the reaction at low reactant concentrations is evident due to the presence of large quantities of nitric oxide and nitrogen in the 2% investigation, and the sudden decrease in nitrous oxide concentration at 3 mole per cent reactants. In this concentration region both nitric oxide and nitrogen have increased at the expense of nitrous oxide, while copious quantities of ammonium nitrate are still observed as white particulate smoke issuing from the reactor. In this region, therefore, the initial reaction between nitrogen dioxide and hydrazine must be producing nitric oxide and nitrogen as well as nitrous oxide and ammonium nitrate. This is presented as a mechanism for nitric oxide and nitrogen formation since none of the sub-reactions presented in Table 5 will account for nitrogen and nitric oxide at temperatures in the order of 200 to 300°C. The initiating reaction above 2% reactants is therefore considered to result from molecular interaction of nitrogen dioxide and hydrazine as a type of Lewis acid-base reaction with the formation of ammonium nitrate, nitrogen, nitric oxide and nitrous oxide. The relative concentration of nitrous oxide from the initial reaction then drops off at the higher temperatures encountered at 3 mole % reactants. Consideration of the temperatures required for depletion of nitrous oxide by Reactions N-7, N-8, N-9, and N-10 emphasizes the fact that as the reaction temperature is increased the initiating reaction yields a product distribution with very little nitrous oxide, since this oxide cannot react by any sub-reaction considered.

When one calculates the heat given off by Reaction N-2, a temperature rise of approximately 100°C per 1% increase in reactant concentration is predicted. The experimental values at 2% and 3% fall far short of this since one would expect temperature rises of 200 and 300°C rather than 109

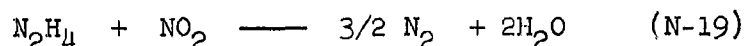
and 236°C. Any change in the product distribution where the concentration of nitric oxide and nitrogen is increased at the expense of nitrous oxide or ammonium nitrate would tend to decrease the expected temperature since the heats of reaction would be lower. The experimental temperatures and the gas compositions therefore are in rough agreement.

As mentioned earlier, an apparent change in reaction mechanism occurs at 3.8 mole % reactants where the largest rate of temperature rise with increased composition occurs. This was observed experimentally as a temperature fluctuation between about 440°C and 600°C as the reactor was warming up. This fluctuation is equivalent to temperature rises between 355°C and 520°C. Unfortunately no traumatic change in the over-all gas composition is apparent at this point. This temperature region is where the exothermic decomposition of ammonium nitrate would occur. Since, at this temperature, nitrous oxide cannot be removed by Reactions N-7, N-8, N-9 or N-10, and no increase in nitrous oxide concentration is observed, it is concluded that ammonium nitrate must decompose to a mixture of water, nitrogen and nitric oxide, or even water, nitrogen and oxygen. This decomposition path is more exothermic than that of Reaction N-3 and might furnish the thermal energy necessary for initiation of reactions such as N-4, N-11 and N-12, the exothermic decomposition of hydrazine and reaction of nitrogen dioxide with the resultant hydrogen and ammonia to form water, nitric oxide and nitrogen. If ammonium nitrate is present as a vapor, the exothermic nature of N-3 would be further enhanced.

The nonflame reaction is therefore pictured to be a thermal reaction mechanism, originally initiated by the molecular collision of nitrogen dioxide and hydrazine molecules. As the concentrations of reactants are increased, the mechanism of reaction changes since more exothermic heat is available for initiation of further sub-reactions. This trend increases until at 5 mole % reactants the mixture becomes hypergolic.

The inhibition of a thermal reaction mechanism of this type is virtually impossible since there exists no pre-reaction zone during which critical concentrations of free radicals must build up in order to establish a self-supporting free radical chain mechanism as is the case for hydrogen-oxygen reactions. In this case small quantities of inhibitors, which remove the free radicals from the reactant stream before the flame front, are extremely effective in moderating the reaction. In the

case of nitrogen dioxide-hydrazine, the formation of nitrous oxide and ammonium nitrate as the initiating reaction predominant at high dilutions results in a heat of reaction which is about 2/3 of the heat of reaction based on one mole of hydrazine for the over-all desired result:



In view of this, and the failure to find any highly successful inhibitors out of 55 candidates tested, it seems improbable that effective inhibitors exist for the nitrogen tetroxide-hydrazine reaction.

Preliminary plans have been completed for construction of a low pressure burner similar to that designed by Wolfhard and coworkers (Ref. 20). This burner (Figure 7) will permit flame studies of premixed gas systems which cannot be investigated at atmospheric pressure due to hypergolic tendencies, preignition solid adduct formation, or burner clogging by solid reaction products. Although the burner is primarily intended for other reacting systems, it should be ideal for the study of nitrogen tetroxide-hydrazine flames. Spectroscopic studies of the flame in the region before the flame front should afford valuable information concerning the existence of free radicals in the preflame region. In addition, the five vaporized additives which appeared to have some influence on the composition ignition limit of NO_2^* -hydrazine mixtures can be tested as to their ability to inhibit the premixed flame velocity of the system.

It is recommended that the research outlined above be conducted in hope that the reaction mechanism and the possibility of inhibition be further defined.

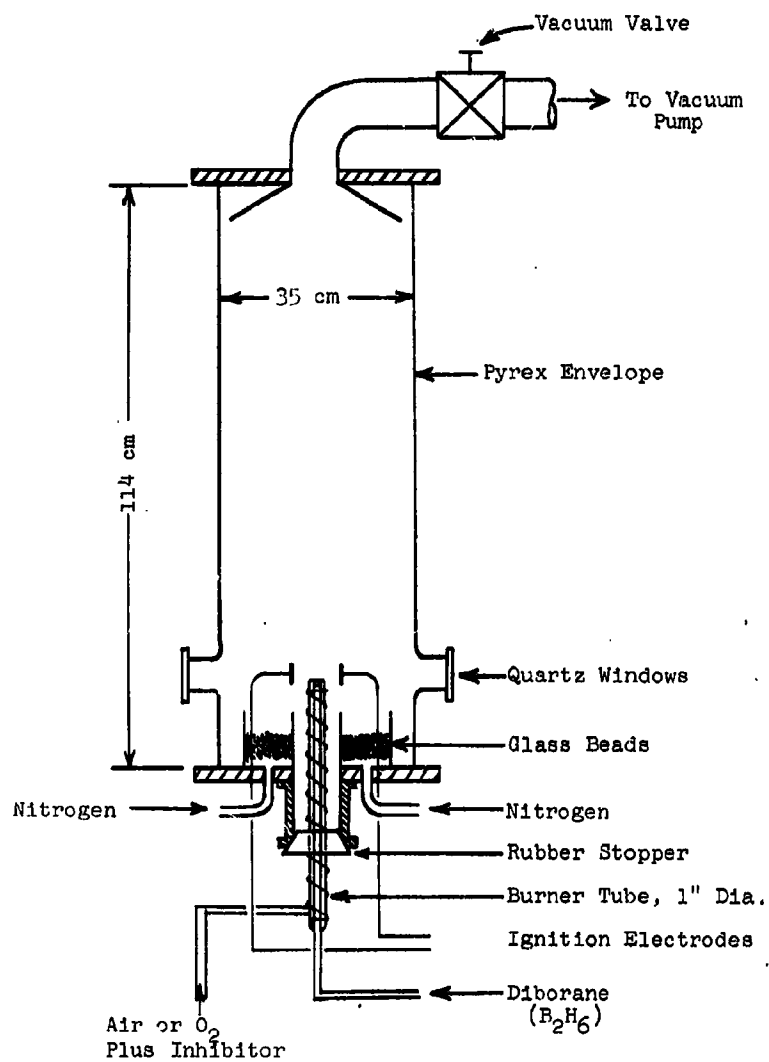


Figure 7. Low Pressure Burner, after Wolfhard (Ref.20)

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