

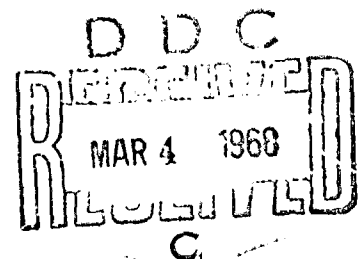
AD 665884

Preignition Products from Storable Propellants at Simulated High-Altitude Conditions

NOVEMBER 1967

Prepared by S. W. MAYER, D. TAYLOR, and L. SCHIELER
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Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California



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Air Force Report No.
SAMSO-TR-68-67

Aerospace Report No.
TR-0158(9210-02)-1

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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04695-67-C-0158.

This report, which documents research carried out from February 1966 through June 1967, was submitted for review and approval to Captain Keith S. Peyton, SMTAP, on 8 January 1968.

The authors wish to acknowledge valuable discussions with S. M. King, A. P. Maffei, and D. H. Jaeger. The mass spectra were obtained by P. Breisacher, and the DTA curves were determined by G. C. Denault and H. H. Takimoto. The assistance of V. M. Armstrong with the manuscript is also acknowledged.

Approved


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Aerodynamics and Propulsion
Research Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.


Keith S. Peyton, Captain, USAF
Project Officer

ABSTRACT

In view of the destructive ignitions that occur in hypergolic test firings of attitude-control motors under simulated high-altitude conditions, the preignition behavior of MMH, UDMH, A-50, and N_2H_4 with N_2O_4 was examined at low pressures and temperatures in the laboratory. At low NO_2 pressures and temperatures, such as those that would be encountered in combustion chambers during starts in space, the ignition of these fuels was significantly delayed. During the preignition period relatively involatile, reaction products were formed between NO_2 and the fuels. Infrared spectrophotometry, mass spectrometry, differential thermal analysis, and other techniques were used to examine these preignition residues. The IR absorption curves were consistent with the view that the major component in the MMH residue that could behave as an explosive monopropellant was MMH nitrate. IR spectra of the preignition residues formed with N_2H_4 or A-50 suggest that hydrazine nitrate (a potentially explosive monopropellant) was the major constituent of these residues. The preignition residues were strongly acid, as a result of their nitric acid content, and are a corrosion and a contamination threat to equipment on the exterior of flight vehicles. Mass spectrometric data indicate that unstable nitroamines are formed in the gas phase during the preignition period. DTA data show that most preignition residues had strongly exothermic peaks, suggesting potentially explosive behavior. The proportion of preignition residue formed was dependent on the mole ratio of NO_2 to fuel. Factors affecting the production of preignition residues are discussed, and methods of possibly decreasing that production are suggested for further investigation.

CONTENTS

FOREWORD.	ii
ABSTRACT	iii
I. INTRODUCTION	1
II. EXPERIMENTAL PROCEDURE.	5
A. Low-Temperature Reaction Chamber	5
B. Room-Temperature Reaction Chamber	9
C. Infrared Absorption Spectra of Preignition Residues . .	12
III. RESULTS AND DISCUSSION	13
A. Hypergolicity Tests at Low Temperatures and Low NO ₂ Pressures	13
B. Infrared Spectrophotometric Examination of Pre- ignition Residues	15
C. Mass Spectrometric Examination of -11°C Pre- ignition Products	24
D. Brief Tests of Residue Solubility and Volatility	26
E. Effect of NO ₂ Pressure on Ignition and on Residue Production at 23°C.	29
F. DTA and IR Spectra of Residues Produced in Room-Temperature Chamber	35
REFERENCES.	39

TABLE

1. Effect of NO ₂ Pressure and Mole Ratio on Ignition and on Residue Production at 23°C	31
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FIGURES

1(a).	Low-Temperature Reaction Chamber.	6
1(b).	Diagram of Manifold	8
2.	Room-Temperature Reaction Chamber	10
3.	IR Absorption Spectrum of the Hydrazine-NO ₂ Preignition Residue	16
4.	Hydrazine Nitrate IR Spectrum	16
5.	MMH Preignition Residue Produced at -11°C by Reactions with NO ₂ Vapor.	18
6.	IR Spectrum of MMH-NO ₂ Flow-Reaction Fog Condensation (Thiokol Corp., Ref. 2)	18
7.	IR Spectrum of MMH-HNO ₃ Salt	20
8.	UDMH Preignition Residue Produced at -11°C by Reaction with NO ₂ Vapor	20
9.	A-50 Preignition Residue Produced at -11°C by Reaction with NO ₂ Vapor	22
10.	Differential Thermal Analysis Curves for Residues from MMH and A-50 (The A-50 curve has been lowered by one division along the ΔT axis.).	36

I. INTRODUCTION

When rocket motors using MMH-N₂O₄ propellants are fired in pulse-mode tests under simulated high-altitude conditions, the motors can be destroyed by explosions in the combustion chamber and manifold region.^{1,2} Because of the seriousness of this problem as related to destruction of attitude-control engines for the Apollo vehicles in orbit, the causes of these severe hard-starts have been under investigation by several organizations,¹⁻⁴ but the problem is not yet well understood.⁵ It has been observed^{1,2} that the pulse-firings of these motors at high-altitude conditions that are capable of generating destructive pressure spikes are accompanied by an accumulation of viscous products in the combustion chamber. These products have also been formed by MMH-N₂O₄ propellants fired in a low-pressure environment and have an explosive power² approximately equivalent to TNT. It is thought^{1,3} that destructive overpressures do not occur unless such a condensed phase is present in the motor. Consequently, these residues are being investigated as a possible cause of the severe pressure spikes found in the testing of attitude-control engines.

Since hypergolic propellants generally exhibit severe spikes only in a low-pressure environment characteristic of high altitudes, consideration of the causes of the spikes has been centered on the phenomena that would occur when the initial combustion-chamber pressure is less than 10 mm Hg. When liquid N₂O₄, which has a vapor pressure of 730 mm at 20°C, is injected into

a combustion chamber at high-altitude conditions, rapid vaporization occurs with consequent rapid cooling. Combustion chamber measurements at Marquardt Corporation¹ have shown that the temperature in the chamber can quickly drop to -11.2°C (the triple-point temperature of N_2O_4), at which solid N_2O_4 exists in equilibrium with liquid and vapor phase N_2O_4 . At this temperature, N_2H_4 (hydrazine) and A-50 (50% UDMH-50% N_2H_4) freeze, and the frozen fuels may be slow to ignite, leading to prolonged ignition delays. Although MMH and UDMH do not freeze at -11.2°C , their ignition by N_2O_4 may be retarded at this temperature. Such delays could lead to excess quantities of condensed phase in the combustion chamber prior to ignition.

This important temperature region near -11°C , and extending from -20°C to 0°C , has been overlooked in previous laboratory work on the ignition behavior of hydrazine and its derivatives with N_2O_4 . Much of that previous research, as a matter of fact, has involved the N_2O_4 combustion of hydrazine at conditions that correspond to booster-engine ignitions at sea level, rather than attitude-control engines for orbiting vehicles. In the laboratory studies described herein, preignition product formation by MMH with N_2O_4 was examined at -11°C and in the 0°C to -18°C range. Additionally, the products formed with UDMH, hydrazine, and A-50 were investigated since the quantity or explosibility of the products from these fuels might differ from those of the MMH residue. During the later phases of these laboratory investigations, the production of preignition products from these fuels at a temperature of 21°C was examined, in view of the fact that specifications on the attitude-control engine of particular interest were changed so

that the propellants and the chamber were to be maintained at a temperature of not less than 21°C before firing. For safety reasons, the quantity of fuel used in each experiment was limited to 0.15 ml.

This report is considered an interim progress report since, although substantial progress has been made, it is evident that further investigations would be worthwhile.

II. EXPERIMENTAL PROCEDURE

A. LOW-TEMPERATURE REACTION CHAMBER

In order to examine the reaction of NO_2 with fuels at low temperatures near the -11.2°C triple-point temperature of NO_2 , the reactions were carried out inside a glass-jacketed chamber shown in Fig. 1(a). The refrigerant pumped through the jacket was methanol that was cooled in a 10-gal insulated tank to the selected temperature by a thermostatically controlled mechanical refrigerator. In order to prevent the deposition of an opaque coating of frozen water from the atmosphere onto the exterior of the cold jacket, dry nitrogen was circulated within a cylindrical chamber of transparent acrylic plastic around the jacket. This plastic chamber also served as an additional safety shield against detonation of the hydrazine-type fuel. Since a high-explosive laboratory was not available, the apparatus was located inside a hood in a general purpose laboratory. In this initial series of experiments, the quantity of fuel used for each reactivity test was limited to 0.05 ml for safety reasons in view of the possibility of detonation. The drop of fuel was held in a 2-mm loop of 28-gauge stainless steel wire. After the fuel loop was placed in the chamber, clear plastic safety shields were stationed between the apparatus and the experimenter. The stopcocks on the apparatus were manipulated by long rods fitting through small holes in the plastic sheets. No detonations occurred during the course of the experiments, even though hydrazine and A-50 were solid at some test temperatures.

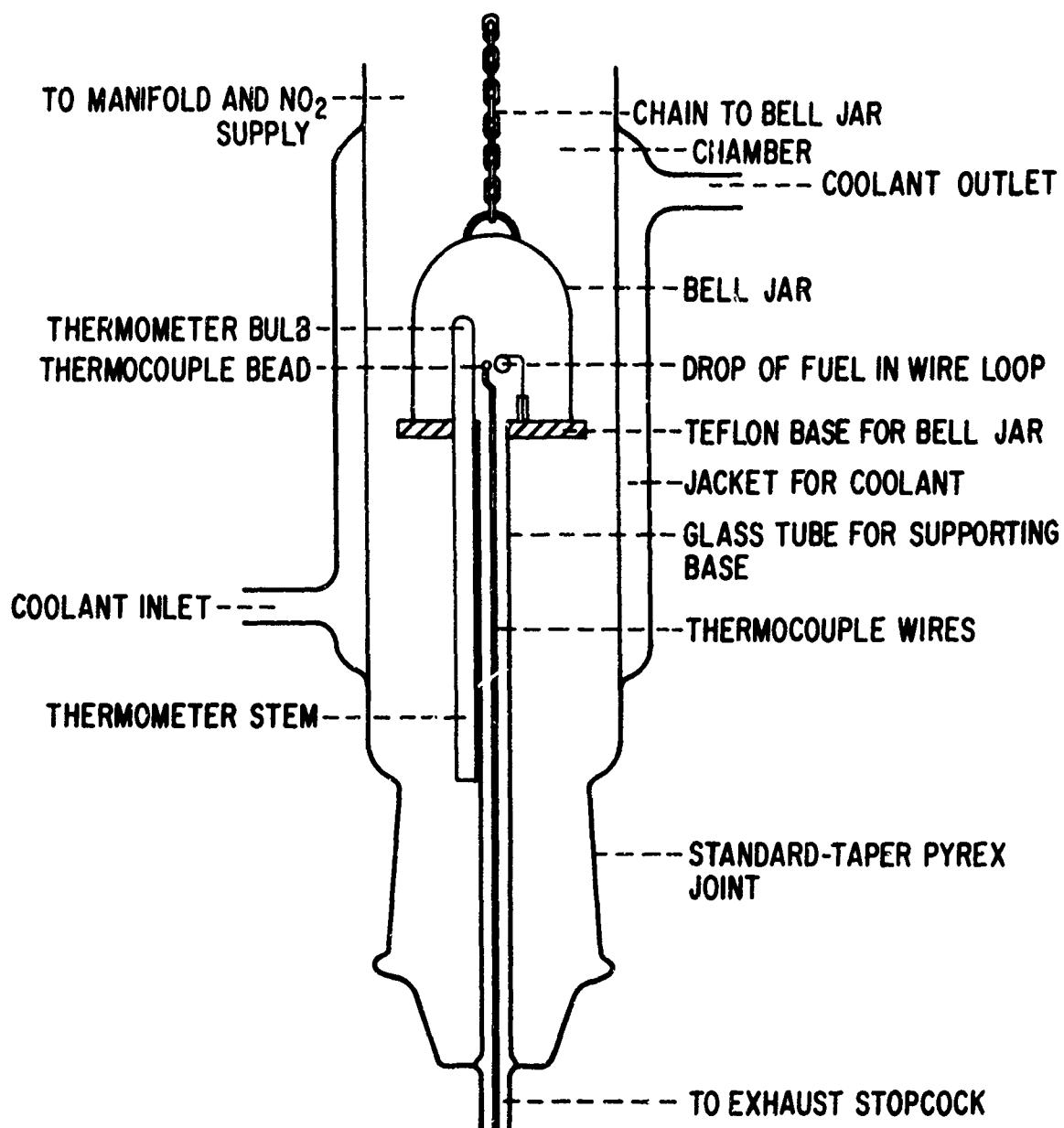


Fig. 1(a). Low-Temperature Reaction Chamber

As shown in Fig. 1(b), the chamber was attached to a vacuum system manifold and to a reservoir of NO_2 .^{*} The vapor pressure of the NO_2 admitted to the manifold was measured by a manometer. The manometer was filled with a stable organic fluorochloro fluid for the lower pressure ranges; mercury was used for pressures from 100 mm to 800 mm.

The experimental procedure is described as follows. In a dry box with an inert atmosphere of dry nitrogen, a drop of MMH, hydrazine, A-50, or UDMH fuel was placed in the wire-loop single-drop holder [Fig. 1(b)] mounted in the base of the jacketed chamber. The drop was covered with the 1-1/4-in. bell jar [Fig. 1(a)], which was fitted snugly to its base with a fluorocarbon grease. The bell jar protected the drop from a reaction with air, moisture, or NO_2 during the prereaction steps. The drop holder was moved from the dry box and inserted into the bottom of the jacketed chamber through the greased standard-taper ground joint. Jacketed chamber, manifold, manometer, and NO_2 reservoir were then evacuated to about 1μ . The NO_2 vapor pressure in the reservoir was negligible during this step since the reservoir was cooled with a Dewar flask of liquid nitrogen. Methanol coolant was passed through the chamber jacket to bring it to the desired temperature, as shown by the 20-gauge copper-constantan thermocouple sealed into the base of the chamber and the small thermometer sealed into the base of the bell jar. At the same time, the NO_2 in the reservoir was

^{*}For convenience, the formula NO_2 is used in this report instead of the cumbersome phrase "the NO_2 - N_2O_4 equilibrium mixture," since it is so well known that NO_2 dimerizes to a considerable extent to form N_2O_4 .

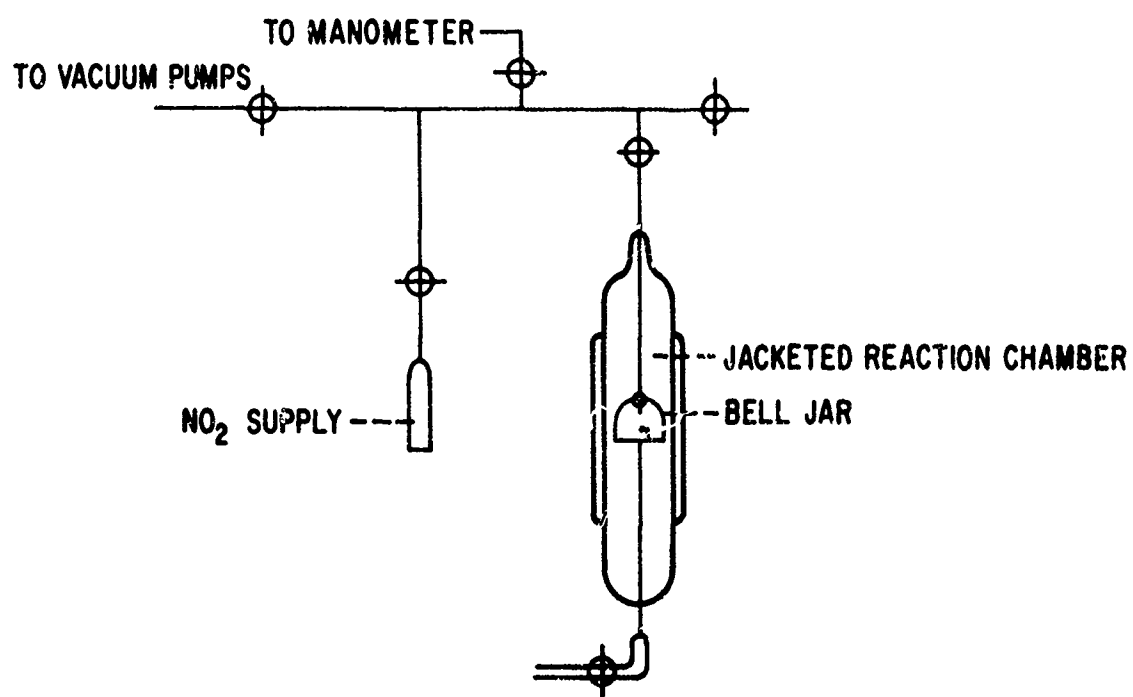


Fig. 1(b). Diagram of Manifold.

warmed and allowed to flow into the chamber (the drop of fuel was still covered by the small bell jar) until the desired pressure and temperature were attained. At least 20 min were required to attain pressure and temperature equilibrium. Then the bell jar was raised** from its base to permit the NO_2 to react with the drop of (solid or liquid) fuel.

Samples of preignition residue for IR and other tests were prepared by using a procedure similar to that described, except that the fuel was contained in a 1-ml microbeaker rather than suspended in the wire loop. The beaker rested on a Teflon base [Fig. 1(a)] under the bell jar. The quantity of fuel placed in the beaker (in the dry-box atmosphere) was 0.05 ml. A significant quantity of yellow, viscous preignition residue was always obtained in the microbeaker after the NO_2 was reacted with the fuel in the low-temperature chamber.

B. ROOM-TEMPERATURE REACTION CHAMBER

A recent change to the specification for the attitude-control motor of particular interest that required the temperature of the propellant and chamber walls to be above 21°C made it desirable to investigate preignition product formation in this temperature range, i.e., near room temperature. It was, therefore, unnecessary to have a cooling jacket around the reaction chamber. A chamber (Fig. 2) and reaction procedure were devised that made it feasible to measure accurately the initial weight of fuel used and the

**Raising of the bell jar was accomplished by remote control; an electric motor lifted a gold chain attached to the top of the bell jar.

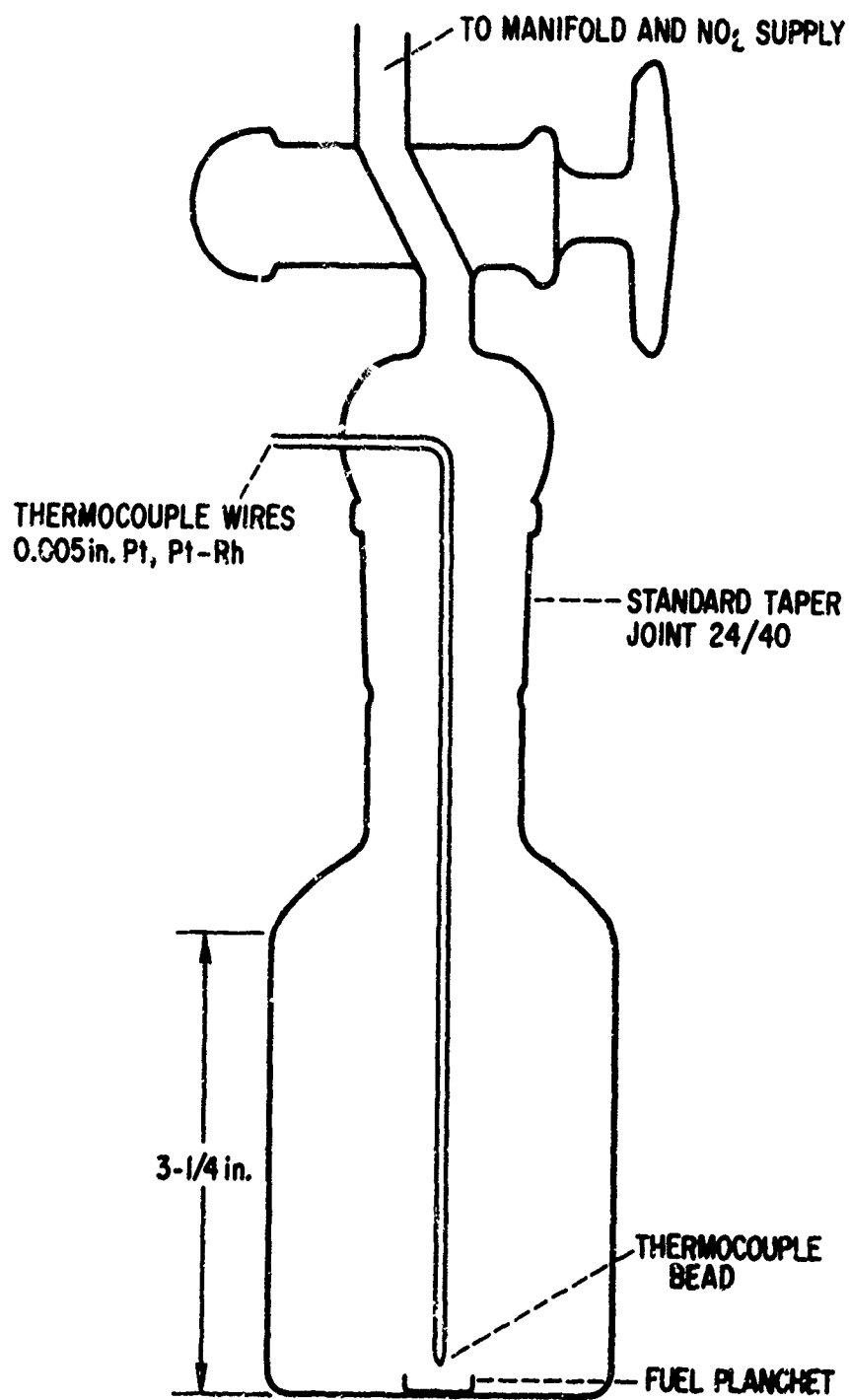


Fig. 2. Room-Temperature Reaction Chamber.

weight of preignition residue collected in the fuel planchet or on the walls of the reaction chamber. Also, a corrosion-resistant micro (0.005-in. wire) thermocouple bead was positioned 3 ± 1 mm above the layer of fuel in the planchet so that the flame temperature could be detected. The thermocouple was composed of a platinum-10% rhodium in platinum couple. The fuel planchet was a shallow, cylindrical pyrex dish 8 mm in diam and 2 mm in height. For safety reasons, the quantity of fuel in each experiment was limited to less than 140 mg. The previously mentioned precautions were continued with regard to: remote control, plastic shielding, and protection of fuel and NO_2 from the atmosphere.

The experimental procedure for preignition and combustion studies in the room-temperature chamber was as follows. A known volume of liquid fuel was injected into the fuel planchet, using a hypodermic syringe. A stream of dry nitrogen was passed through the chamber and manifold to prevent atmospheric contamination. The chamber was attached to the manifold with a greased standard-taper ground joint. Dewars containing liquid nitrogen were used to freeze the fuel in the planchet and the NO_2 in the reservoir. The chamber, reservoir, manometer, and manifold were then evacuated to 1μ . The stopcock between the manifold and the chamber was closed. Fuel and NO_2 vapor (at a selected pressure) separated by that stopcock were allowed to reach the characteristic room temperature of the laboratory ($23 \pm 1^\circ\text{C}$). Reaction between the fuel and NO_2 was initiated by the remote-control opening of the stopcock separating them. The temperature of the

reaction flame was automatically recorded on a self-balancing rapid-response potentiometer. The weight of residue in the planchet and on the walls of the reaction chamber was then readily obtained since their tare weights had been determined.

C. INFRARED ABSORPTION SPECTRA OF
PREIGNITION RESIDUES

A preliminary test showed that the preignition residues were strongly acid from the HNO_3 formed during the course of the reaction; consequently the residues badly corroded the NaCl 1-in. discs ordinarily used as sample holders for viscous materials. Good IR spectra could be obtained from the preignition residues, however, if thin, IR transparent discs were used as sample holders. These discs, pressed from KBr powder at 5000 lb, were about 1-mm thick and 12-mm wide. Two discs were used for each sample; the preignition residue was sandwiched between the discs since that procedure gave the sharpest spectra. A Perkin-Elmer Model 21 IR spectrophotometer was used to record the absorption spectra.

III. RESULTS AND DISCUSSION

A. HYPERGOLICITY TESTS AT LOW TEMPERATURES AND LOW NO₂ PRESSURES

It was emphasized in Section I that the temperature region near the triple-point temperature of NO₂, -11.2°C, was of special interest in high-altitude starts of hypergolic bipropellant attitude-control motors. Consequently, this initial series of tests was centered around -11°C, particularly since laboratory tests of hypergolicity had hitherto neglected this significant temperature region. The experimental procedure for reacting a single drop of fuel, held in a wire loop, with NO₂ vapor at selected low temperatures and pressures has been described in Section II. The most striking finding in this series of tests was that none of the fuels, MMH, A-50, hydrazine or UDMH, were hypergolic at -11°C with NO₂ in the low NO₂ pressure range (to 110 mm Hg) that is characteristic of high-altitude starts. No ignition and no flame occurred under these low-temperature conditions, whether the fuel was solid or liquid. Instead, a flameless reaction with NO₂ took place at the surface of the drop, leading to effervescence at the surface as gaseous reaction products escaped. The flameless reaction was considerably slower with solid drops of hydrazine and A-50 (melting points of 1.4°C and -8°C, respectively), but when the heat from the reaction melted the surface of the solid drop, the rate of reaction increased. In these cases, the drop would continue to react for 5 min or more. The reactivity of MMH

and UDMH (melting points of -52.4°C and -57.2°C , respectively) was greater and increased when additional NO_2 vapor was added to the reaction chamber, but no flame or high reaction temperature was observed even with these more volatile, unfrozen fuels at -11°C below 110 mm NO_2 .

Consequently, at the NO_2 triple-point temperature and at the low pressure involved in high-altitude starts, the ignition delay could be significantly longer than the 3 msec characteristic of room temperature and atmospheric pressures.⁷ For attitude-control motor firing pulses as short as 15 msec, such increased ignition delays could have relatively large effects in producing abnormal ignition behavior. In addition to testing the reactivity of solid hydrazine with NO_2 at -11°C , it was tested at -3.4 , -5.8 , -8.8 , -12.5 , -13.0 , and -17.3°C . Hypergolic ignition did not occur at any of these temperatures. The flameless (i.e., preignition) reaction that took place apparently became slower at lower temperatures. For example, at -17.3°C , the drop of hydrazine was not fully consumed after 30 min of reaction in 110 mm of NO_2 . In a test of liquid hydrazine at 2.8°C , the drop did not ignite in NO_2 , but was consumed by reaction in less than 10 min.

When vigorous, flameless reaction occurred between NO_2 and MMH, UDMH, A-50, or hydrazine, relatively large quantities of yellow clouds of fog were produced. This characteristic of NO_2 reactions with the vapors of hydrazine has also been observed by other investigators.² A viscous condensed phase from the fog collected on the glass walls of the reaction vessel. It has been suggested that such a condensate may accumulate on combustion

chamber walls in attitude-control motors and may participate in producing pressure spikes.² During the described series of low-temperature reactivity tests, it was observed that in addition to the clouds of fog produced, an oily residue of preignition product remained on the loop of wire that had been holding the drop of MMH or other fuel during the course of the reaction. Since the preignition residue frequently appeared to represent 20% to 40% of the initial volume of the drop of fuel, it could be a significant factor in the behavior of attitude-control motors on orbiting vehicles. An investigation of the properties of the residues was therefore begun.

B. INFRARED SPECTROPHOTOMETRIC EXAMINATION OF PREIGNITION RESIDUES

The IR absorption spectrum is shown in Fig. 3 for the preignition residue prepared at -11°C (as described in Section II) by the flameless reaction of 50 μl hydrazine with 20 mm of NO_2 vapor. Comparison of this spectrum with the IR spectrum (Fig. 4) of hydrazine nitrate shows that the characteristic IR absorption peaks of hydrazine nitrate can be found at corresponding wavelengths in the spectrum of the hydrazine- NO_2 preignition residue. The relative absorbance and shape of some peaks in the residue differ from those of pure hydrazine nitrate, in agreement with the expectation that the residue would contain small amounts of other possible reaction products (e.g., H_2O , CO_2 , NH_4NO_3 , H_2NNO_2) plus some unburned N_2H_4 .

Hydrazine nitrate for IR spectrum determination was prepared in accordance with the following method. Fifty milligrams of hydrazine were dissolved in 5.0 ml of distilled water in a 50-ml flask. An equimolar quantity

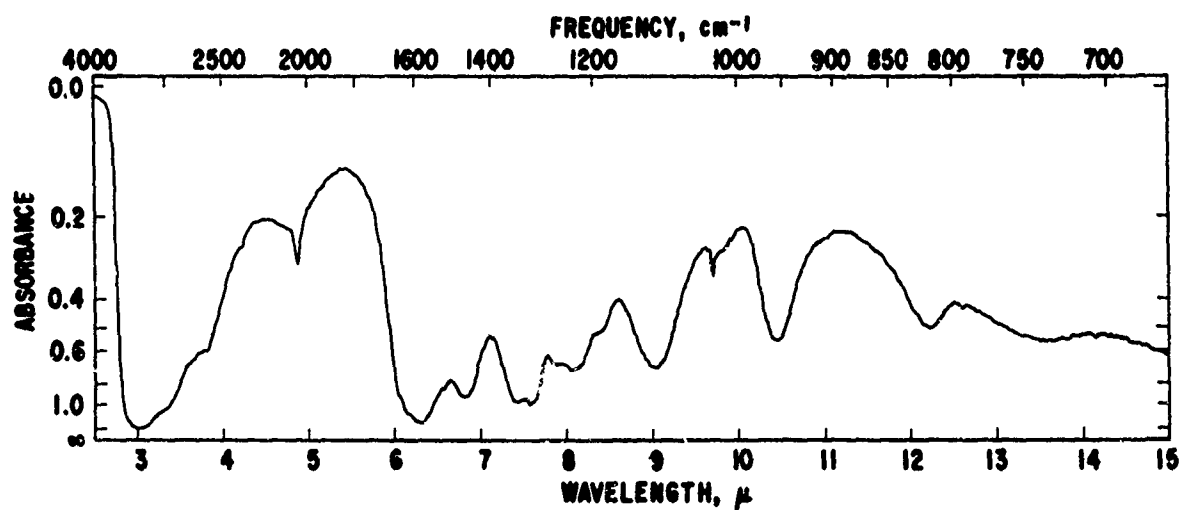


Fig. 3. IR Absorption Spectrum of the Hydrazine-NO₂ Preignition Residue.

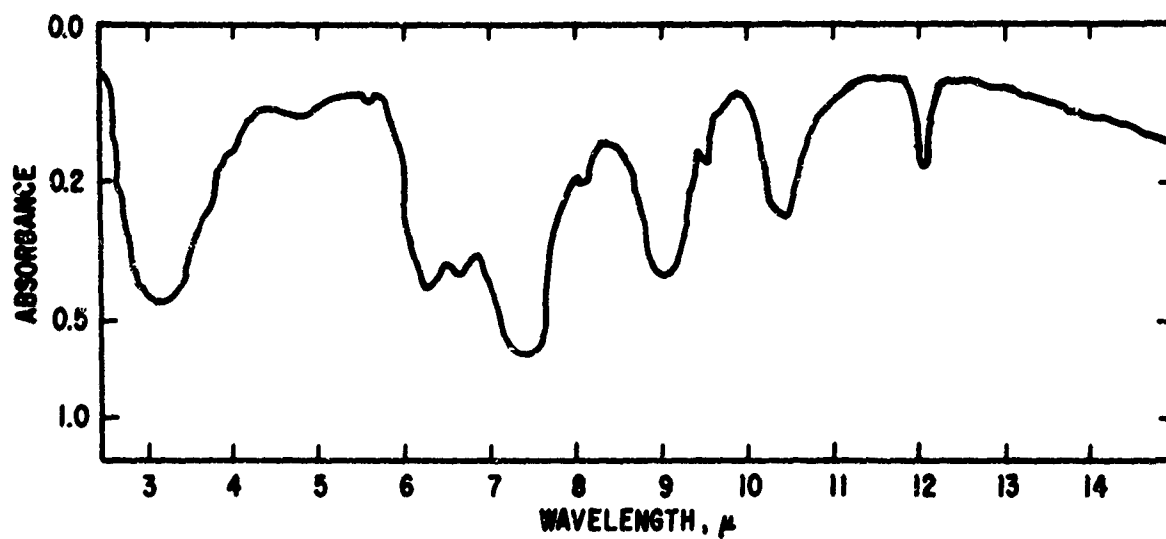
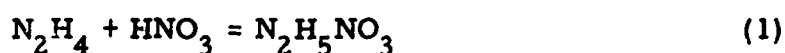


Fig. 4. Hydrazine Nitrate IR Spectrum.

of standardized 0.5 M HNO_3 was transferred from a burette to 10.0 ml of distilled water. The HNO_3 solution was washed into the flask containing the hydrazine to prepare hydrazine nitrate (the mononitrate salt):



The water was evaporated from the solution under vacuum, leaving the white solid, hydrazine nitrate. An IR spectrum of this solid agreed with that reported elsewhere.⁶ Hydrazine nitrate is known to be a hazardous explosive and can detonate in layers as thin as 0.05 in.⁴

In Fig. 5, the IR spectrum is presented for the preignition residue formed at -11°C by the flameless reaction of 50 μl of liquid MMH with NO_2 at a pressure of 30 mm. Figure 6 contains the IR spectrum reported² by the Reaction Motors Division of Thiokol Corporation for the condensed "fog" formed by the nonignition flow reaction (initially at room temperature) of MMH vapor at 3 mm with NO_2 vapor at 5 mm. Most of the IR absorption peaks (Fig. 5 and Fig. 6) occur at about equal wavelengths. This is of particular interest as it indicates that preignition residues formed from MMH may be rather similar to each other even when formed under quite different temperature and vapor pressure conditions, within the temperature ranges involved in this work and in the Reaction Motors Division vapor phase flow-reactor. Furthermore, with the Trauzl block and drop test equipment available at their location, Reaction Motors Division was able to show that the MMH preignition residue was comparable to TNT in detonation sensitivity and explosive power.

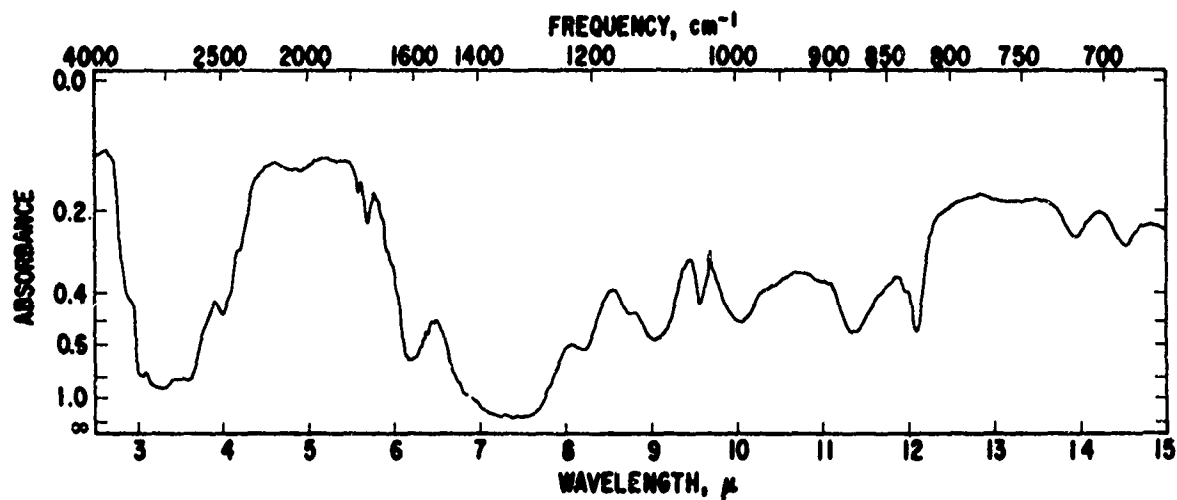


Fig. 5. MMH Preignition Residue Produced at -11°C by Reactions With NO_2 Vapor.

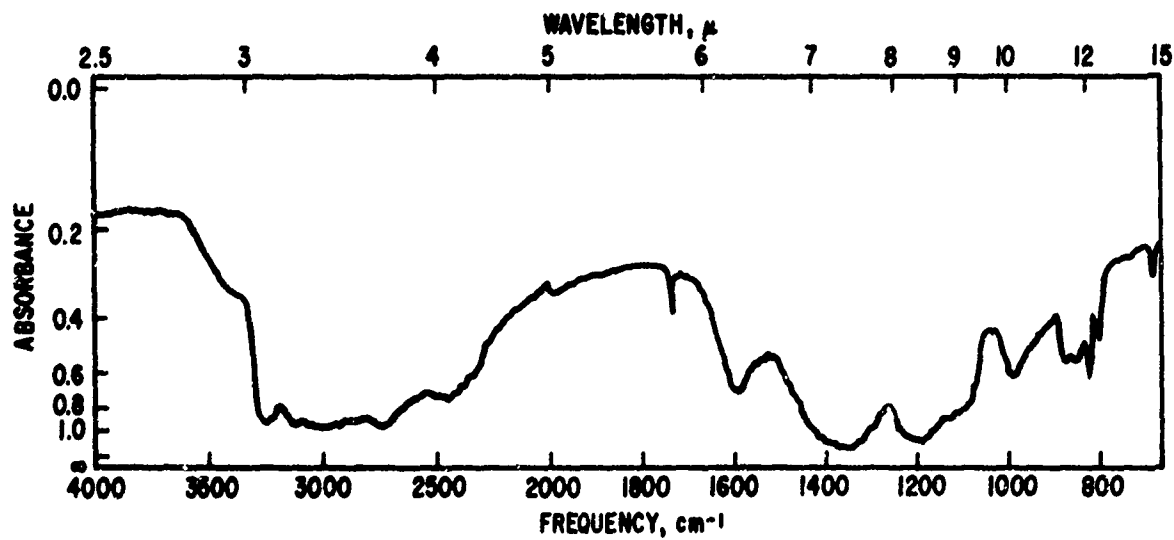


Fig. 6. IR Spectrum of MMH- NO_2 Flow-Reaction Fog Condensation (Thiokol Corp., Ref. 2).

In order to investigate the difficult problem of chemically identifying the major constituent of the MMH preignition product at -11°C , MMH mononitrate was prepared by a dilute aqueous neutralization procedure analogous to that previously described for the preparation of hydrazine nitrate. The infrared absorption spectrum of this preparation of MMH nitrate is given in Fig. 7. Comparison of Fig. 5 with Fig. 7 shows generally good agreement with respect to absorption peak wavelengths, although the relative heights and shapes of the peaks show some differences. Consequently, although the spectra indicate that the major constituent of the MMH preignition residue is MMH nitrate, they also suggest that appreciable amounts of other reaction products (e.g., H_2O , CO_2 , nitrates, and nitroamines) and MMH may be present in the preignition residue. The MMH nitrate would be expected to constitute the major source of explosive power in the residue, but the sensitivity of the residue to shock could be augmented or decreased by relatively minor quantities of other reaction products present in the residue.

MMH nitrate, like other nitrate salts, has a very low vapor pressure, as indicated by the mass spectrometer and weight loss measurements described in later sections of this report. The low vapor pressure allows this monopropellant to accumulate from several successive propellant pulses in the combustion chambers of attitude-control motors. The shock sensitivity² of MMH nitrate suggests that the accumulated preignition residue can be detonated by a vapor-phase-ignition pressure spike.^{1,3} Detonation of accumulated MMH nitrate, augmented by the vapor-phase pressure spike, could rupture the rocket motors unless the motors are strengthened to resist these powerful shocks.

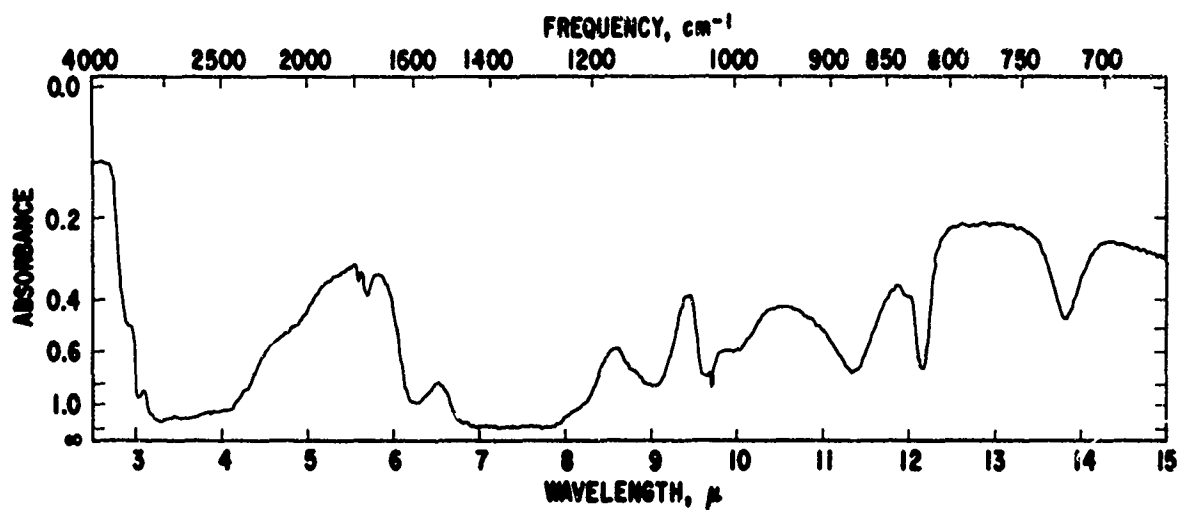


Fig. 7. IR Spectrum of MMH-HNO₃ Salt.

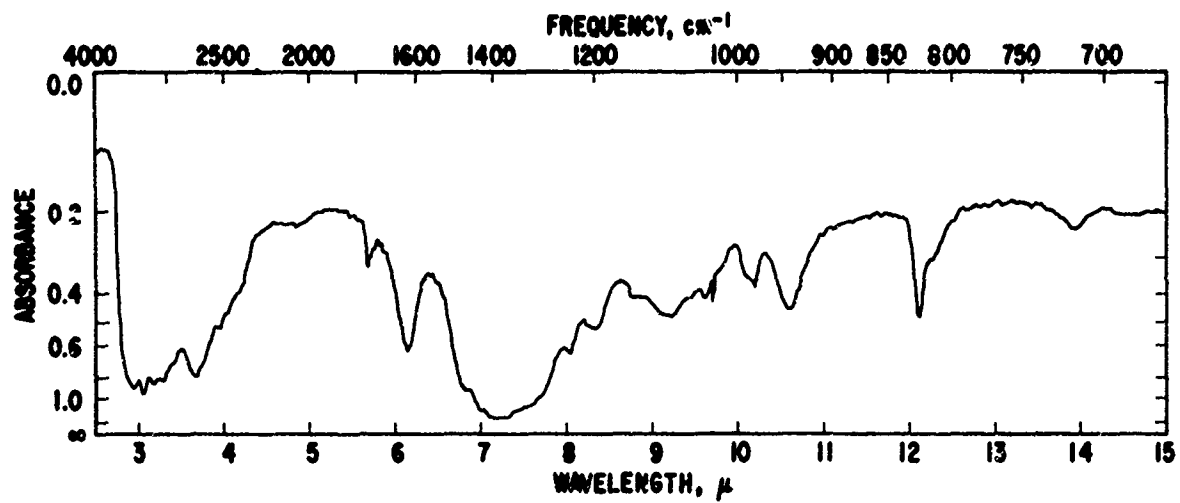


Fig. 8. UDMH Preignition Residue Produced at -11°C by Reaction With NO₂ Vapor.

The infrared absorption spectrum is shown in Fig. 8 for the preignition residue from the -11°C reaction of $50\text{ }\mu\text{l}$ of UDMH with NO_2 vapor at 30 mm. This spectrum is in good agreement with that obtained² at the Reaction Motors Division of Thiokol Corporation for the condensate formed from the flameless flow reaction initiated at room temperature between UDMH vapor at 5 mm and NO_2 vapor at 5 mm. Accordingly, as in the case of the MMH-NO_2 preignition residue, the major features of the UDMH-NO_2 residue may not be highly dependent on temperature in the -11°C to 25°C temperature range. When an attempt was made to prepare UDMH nitrate by the neutralization procedure corresponding to that used for preparing $\text{N}_2\text{H}_5\text{NO}_3$ and MMH mononitrate, it was observed that the residue from the water-evaporation step was unstable at 25°C since the dried residue decomposed with the evolution of heat. Attempts will be made to prepare UDMH nitrate at lower temperatures.

Should this apparent instability of UDMH nitrate at 25°C be confirmed, it may have valuable practical applications. It suggests that if UDMH were used as the fuel UDMH nitrate formed as a preignition product would decompose because of its instability when the firing pulse raises the temperature of the combustion chamber to 25°C or above. Under such circumstances, the UDMH nitrate would decompose during each firing pulse, rather than accumulate from pulse to pulse as MMH nitrate can because of its relative stability. Data from test firings of attitude-control motors with UDMH could be used effectively to investigate the possible advantages of UDMH at high-altitude conditions. Furthermore, if the instability of the nitrates increases from

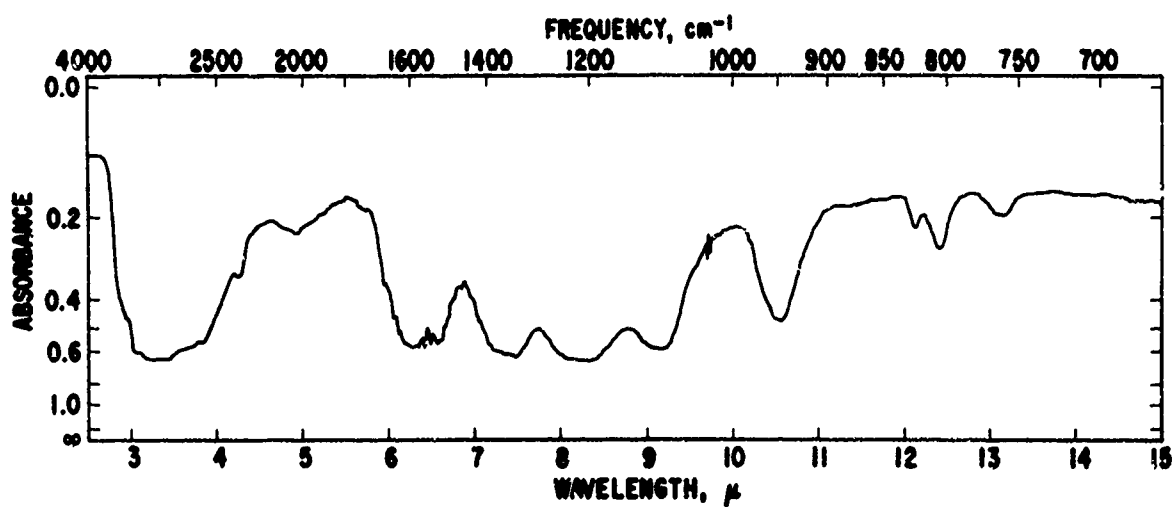


Fig. 9. A-5 Preignition Residue Produced at -11°C by Reaction With NO_2 Vapor.

monomethylhydrazine to dimethylhydrazine, it is possible that trimethylhydrazine (which was considered as a fuel a decade ago) might offer advantages also, in terms of forming a nitrate that would not accumulate in the combustion chamber during successive pulses.

The infrared absorption spectrum of the preignition residue formed at -11°C by the reaction of 50 μl of A-50 in 30 mm of N_2O_4 vapor is shown in Fig. 9. So far as is known, this is the first IR spectrum obtained for the residue derived from A-50 fuel. As will be shown later, when the differential thermal analysis results are described, this residue exhibits strongly exothermic behavior, which suggests considerable explosive power. The wavelengths of the peaks in the IR spectrum (Fig. 9) show a similarity to those in Fig. 3 for the preignition product formed from hydrazine. Inasmuch as hydrazine is much less volatile than UDMH (the vapor pressures of hydrazine and UDMH at 20°C are 20 mm Hg and 120 mm Hg, respectively), it is perhaps not unreasonable that the composition of the residue should appear to depend on the 50% hydrazine in A-50 more than the 50% UDMH in A-50. The explosive character of hydrazine nitrate⁴ is consistent with the strongly exothermic behavior of the A-50 residue shown during differential thermal analysis.

Additional IR studies are in progress. Because of its structure and properties, nitrosodimethylamine might be expected to be a constituent of the UDMH- NO_2 preignition residue. Examination of its IR spectrum shows that, although the wavelengths of some of its absorption peaks are in fairly good agreement with those of the UDMH residue, not all the major peaks

found in the residue are present in the IR spectrum of nitrosodimethylamine. It is therefore probable that there are other constituents in the UDMH residue. It is hoped that additional investigations of the UDMH residue and UDMH nitrate will clarify this problem.

C. MASS SPECTROMETRIC EXAMINATION OF -11°C
PREIGNITION PRODUCTS

1. GAS-PHASE PREIGNITION PRODUCTS

Fifty microliters of MMH in a 1-ml microbeaker were allowed to react flamelessly with 30 mm of NO_2 vapor at -11°C in the low-temperature chamber [Fig. 1(a)]. The gas-phase reaction products were then collected in a U-tube cooled by liquid nitrogen. The U-tube was transferred to the inlet system of a Bendix time-of-flight mass spectrometer, liquid nitrogen was removed from around the U-tube, and the mass spectrum of the volatile species was determined. The low molecular-weight region of the spectrum had mass peak patterns corresponding to all the anticipated reaction products and un-consumed reactants: H_2O , CO , CO_2 , NH_2 , NH_3 , NO , NO_2 , CH_3 , and CH_2 . In addition there were mass peaks of larger mass corresponding to the cracking patterns of nitro-substituted volatile products such as nitromethane (H_3CNO_2), nitramide (H_2NNO_2), and monomethylnitramide (H_3CHNNO_2). These nitro compounds can act as monopropellants with possible detonation because the oxygen in the nitro group readily oxidizes the hydrogen and carbon atoms within the molecule. The consequent, strongly exothermic formation of H_2O , CO , or CO_2 can produce a shock wave since intramolecular reactions proceed with great rapidity, independent of intermolecular collision frequency limitations.

A similar sampling of the gas-phase preignition products of the UDMH reaction with NO_2 was examined in the mass spectrometer, and a new mass peak, corresponding to mononitrodimethylamine [$\text{O}_2\text{NN}(\text{CH}_3)_2$], was observed. If the mass spectrometer again becomes available for these studies, it is planned to make a full examination of the gas-phase reaction products of NO_2 with hydrazine, A-50, MMH, and UDMH.

2. RESIDUAL PREIGNITION PRODUCTS

Volatile preignition products of the -11°C flameless reaction were removed from the reaction chamber by flowing dry helium gas through the chamber for 15 min. The residual preignition product was then transferred in a microbeaker to the inlet system of the Bendix TOF mass spectrometer. The mass spectrum of the UDMH- NO_2 residue had mass peaks that indicated the presence of nitrosodimethylamine [$\text{ONN}(\text{CH}_3)_2$] and nitrosomonomethylamine (ONNHCH_3) fragmentation products. The mass spectrum of the MMH- NO_2 residue showed a peak corresponding to nitrosomonomethylamine. There was no clearcut evidence of a peak corresponding to the nitrate salt of MMH. The absence of such a peak suggests that the volatility of the nitrate salt is so low that the Bendix mass spectrometer is not sensitive enough to detect the nitrate salt in the vapor phase. Employing a more recently developed commercial mass spectrometer, such as the quadrupole type (which is several orders of magnitude more sensitive) is therefore suggested. The quadrupole mass spectrometer could also be used to determine the now unknown, but potentially highly significant, steps involved in the processes of hypergolic combustion (for propellants of importance in space and ballistic programs).

D. BRIEF TESTS OF RESIDUE SOLUBILITY AND VOLATILITY

The preignition residues prepared in these experiments have the appearance of yellow viscous oils or greases. Nevertheless, a brief series of tests of solubilities showed that the preignition residues were readily soluble in water. This solubility is consistent with the deduction from IR spectra data that nitrates are major constituents of the MMH, hydrazine, and A-50 residues inasmuch as water is a good solvent for inorganic and organic nitrate salts. The hydrazine-based fuels and NO_2 are also water-soluble. Consequently, unreacted propellant present in preignition deposits in the combustion chamber would also be soluble in water. The residues were soluble in the partially polar solvent, chloroform, but were not completely soluble in carbon tetrachloride, which is a nonpolar solvent. Nitrosodimethylamine, though classified as a yellow oil, is water-soluble. It would, therefore, be consistent with the observed water solubility and IR spectrum of the UDMH preignition residue to state that nitrosodimethylamine could be present in this residue.

The problem of the low volatility of preignition residues in high vacuums may be of considerable practical importance since the volatility of the material deposited in the combustion chamber will affect the tendency of the residue to accumulate. If this material has a sufficiently low volatility in vacuum, the residue formed by each pulse of propellant in the attitude-control motor could accumulate until enough residue is present to be dangerous in terms of destructive ignition spikes. Because of the potential significance of

the low volatility of the residues, many tests of volatility by determining the residue weight loss in typical laboratory vacuum equipment were made over measured time intervals. These tests can be summarized by stating that, with a variation depending on the conditions of preparing the residues, only 20% to 50% of the weight of the residue volatilized in the first 24 hr. At least 2 days were required for essentially complete evaporation of the residues in laboratory vacuums of the order of 1μ at room temperature. Since, in some operational modes of attitude-control motors, there may be more than ten propellant pulses per minute, these tests suggest that the volatility of the residues is low enough that they can accumulate from pulse to pulse, particularly when the interval between each pulse is less than 1 min or even when it is less than 1 hr. If, however, the pulse duration is long enough so that the chamber walls are heated to a few hundred degrees (e.g., 300°C), it is probable that the volatility of the residues would greatly increase and that they consequently would not accumulate. Moreover, the residue will become thermally unstable if the propellant feed pulse is long enough to heat them to $\sim 300^{\circ}\text{C}$, and, as indicated by the differential thermal analysis tests to be described in a later section, the residue will decompose exothermically to increase the specific impulse. With firing pulses of adequate duration, the residue would be largely decomposed during each pulse and could not collect from pulse to pulse until potentially dangerous quantities of residue are present in the motor. If suitable ultrahigh vacuum equipment becomes available, the volatility of the residues formed in motors that

use hypergolic propellants should be determined at simulated temperature and vacuum conditions comparable to those encountered in the motors of orbiting vehicles.

In general, when an amine is neutralized by HNO_3 a nitrate salt of very low volatility is formed. A familiar example is the neutralization with HNO_3 of the highly volatile amine NH_3 to produce the salt ammonium nitrate, which has an extremely low vapor pressure at room temperature. (At high temperatures, NH_4NO_3 develops high vapor pressures, and it is believed to be detonatable.) The decrease in volatility of MMH (which has a vapor pressure of 45 mm Hg at 20°C) when it is converted into the preignition residue can probably be attributed to the formation of the nitrate salt by a neutralization with HNO_3 , similar to that shown for hydrazine in Eq. (1). To produce the nitrate salt of MMH, or hydrazine, in the combustion chamber, it is necessary to form HNO_3 also. Nitric acid can be produced in the combustion chamber by reaction of NO_2 with H_2O , present as a combustion product, in accordance with



Two molecules of HNO_3 are produced per molecule of H_2O combustion product. Reaction (2) has one highly unusual, but potentially significant, characteristic. The rate constant for the formation of HNO_3 by reaction (2) has been shown⁸ to increase as the temperature decreases below 30°C . The production of HNO_3 is accordingly favored by the low temperatures that are characteristic of preignition conditions in high-altitude pulse firings of

attitude-control motors. Reaction (2) is reported⁸ to be heterogeneous in character. Consequently, the fog and smoke produced in the preignition reaction of hypergolic propellants could facilitate the formation of HNO_3 by providing a large surface area for catalyzing reaction (2). The HNO_3 could form part of this fog, but the acid HNO_3 would tend to neutralize such basic amine fuels as MMH via



to produce a fog containing MMH nitrate. As discussed, the nitrate salt probably has a relatively very low vapor pressure, and the fog containing it could accumulate on the combustion chamber walls. This preignition residue is found to be strongly acid, probably because the weakly basic amines do not completely neutralize the strongly acidic HNO_3 . It is probable that some of this acidic, poorly volatile fog escapes through the engine throat and nozzle to the space environment near the orbiting vehicle. This acidic fog can collect as a contaminating, potentially corrosive film on the spacecraft exterior where it may have damaging effects on sensors and on other hardware. Globules of coalesced preignition product could also be expelled from the attitude-control motors and could be the "mysterious" bright droplets observed in sunlight by astronauts.

E. EFFECT OF NO_2 PRESSURE ON IGNITION AND
ON RESIDUE PRODUCTION AT 23°C

Specifications have recently been established for the attitude-control motor involved in the program of particular interest in these studies that

require the temperature of the combustion chamber and the propellants to be above 21°C before firing. For this reason, a series of measurements has been begun to examine the influence of NO_2 pressure at room temperature on the attainment of ignition and on the quantity and nature of residue production for specific fuels. (Because of the relative priority of other important problems, this series of measurements was interrupted after the tests summarized in Table 1, but it is hoped that the series will be resumed.)

The room-temperature chamber described in the Experimental Procedures section was used. The corrosion-resistant, 0.010-in. platinum, platinum-10% rhodium thermocouple bead was positioned 3 mm above the layer of liquid fuel in the shallow fuel planchet. The flame temperature listed in Table 1 is the temperature reached by the thermocouple during the course of the reaction of the NO_2 vapor with the fuel. In tests where no flame was observed (e.g., when the thermocouple temperature reached only 70°C) this temperature would better be described as a reaction temperature rather than a flame temperature. The mole ratio of NO_2 to fuel as listed in Table 1 corresponds to the total number of moles of NO_2 in the reaction chamber, with each mole of N_2O_4 in the equilibrium mixture equivalent to two moles of NO_2 . In Table 1, the weight of planchet residue corresponds to the weight of reaction product found in the fuel planchet at the completion of the reaction, after 5 min of pumping at a vacuum of 20μ to remove relatively volatile materials. The total residue in the chamber corresponds to the weight of reaction product found in the planchet and on the walls of the

Table 1. Effect of NO₂ Pressure and Mole Ratio on Ignition and on Residue Production at 23°C

Fuel	Weight of Fuel, mg	Pressure ^a of NO ₂ , mm Hg	Mole Ratio, NO ₂ /Fuel	Planchet Residue, mg	Total Residue, mg	Flame Temp., °C	Number of Tests
MMH	131	656	4.6	2 ± 1	46 ± 5	920 ± 80	3
MMH	131	420	2.8	7 ± 1	63 ± 2	630 ± 30	2
MMH	131	228	1.4	41 ± 6	85 ± 8	190 ± 100	4
MMH	87	316	3.1	1	45	950	1
MMH	44	138	2.4	12	77	70	1
N ₂ H ₄	100	324	2.0	2	35	>1040	1
N ₂ H ₄	50	130	1.4	0	13	1240	1

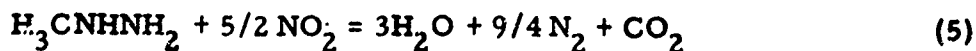
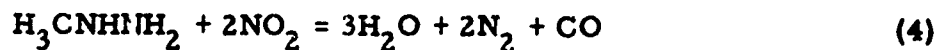
^aThis is the pressure of the NO₂-N₂O₄ equilibrium mixture. The mole ratio of NO₂ to fuel is corrected for the presence of N₂O₄ in the equilibrium mixture since one N₂O₄ molecule is equivalent to two NO₂ molecules in computing the mole ratio of NO₂ to fuel.

reaction chamber at the completion of the reaction, after the 5 min of pumping at 20 μ. The residue on the walls of the reaction chamber was produced by the deposition of the fog formed by reaction of NO₂ with these fuels.

In tests where the thermocouple temperature was 600°C or higher, ignition took place; no ignition was observed in the tests where the reaction temperature did not reach 600°C. When the thermocouple bead reached or surpassed this temperature, the weight of residue in the fuel planchet did not exceed 5% of the initial weight of fuel used for the test. Apparently, most of

the residue in the planchet was decomposed and removed when the temperature in its vicinity exceeded 600°C for the 10- to 20-sec duration of these flames. In those tests for which the temperature of the thermocouple was 600°C, the weight of residue in the planchet decreased correspondingly. For those tests in which ignition did not occur, the weight of this residue was equivalent to about 30% of the initial weight of the fuel. In the test of 44 mg of MMH reacting with 138 mm of NO₂-N₂O₄ mixture, the total residue in the chamber and planchet was found to be 77 mg. This 33-mg increase in weight arose from the NO₂ that reacted with the MMH (e.g., in the formation of nitrate salt). It can be noted throughout Table 1 that the total residue consistently exceeds the residue remaining in the planchet. This excess arises from the previously mentioned reaction fog deposited on the chamber walls. A deduction of practical interest is that the weight of residue collected on the walls of the combustion chambers of rocket motors can be reduced by arranging firing conditions so that the walls are heated to several hundred degrees in order to decompose and remove the preignition residue.

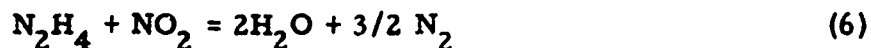
Although NO₂ can react with MMH via several chemical pathways, the stoichiometry for the most exothermic reactions is probably given by



A mixture ratio of 2.2 moles NO₂ to 1.0 mole MMH provides near-maximum specific impulse for N₂O₄-MMH booster propellants at typical chamber

pressures. From Table 1, it can be seen that when the mixture ratio was decreased to 1.4 for MMH, the "flame" temperature decreased and the planchet residue increased sharply. In attitude-control motors it may be anticipated, therefore, that poor mixing in the combustion chamber which reduces the effective mixture ratio to 1.4 would lower the specific impulse and increase the formation of preignition residue. It would be highly important to ensure that satisfactory mixing of NO_2 and fuel occurs within the combustion chamber, particularly in view of the large pressure gradient between injector and throat when, as in orbiting vehicles, the throat and chamber are exposed to the vacuum of space. If mixing is not essentially complete in time to allow for high combustion efficiency, the quantity of preignition products formed can be expected to increase substantially, with a relatively large decrease in specific impulse because of losses in gas mass in addition to lowered enthalpy and mean temperature.

Inasmuch as the MMH molecule has a CH_2 group not present in the hydrazine molecule, the mole ratio of NO_2 to N_2H_4 required for hydrazine reaction stoichiometry drops to 1.0 as shown by the equation



Consequently, it is not unexpected that ignition accompanied by minimal planchet residue was observed for the two hydrazine tests listed in Table 1 at mole ratios of 2.0 and 1.4. In the latter test, a flame temperature of 1240°C was attained although the pressure of the NO_2 vapor was only 130 mm.

In contrast, MMH at a mixture ratio of 2.4, but at a NO_2 vapor pressure of 138 mm, did not ignite. Instead, a reaction temperature of only 70°F was reached and a very high proportion of preignition residue was formed. It is hoped that this series of tests will be resumed when the pressure of other problems permits and that the behavior of the practical fuels in important NO_2 pressure ranges can be further investigated. If the desirability of providing the higher NO_2 pressures in the combustion chamber is confirmed,² it would appear that decreasing throat cross section or increasing propellant injection rates might be required for attitude-control motors operating at high altitudes.

The mode of operation of the attitude-control motors can be expected to have an important effect on the extent of formation of preignition products. Oxidizer leads probably⁵ reduce the occurrence of explosive pressure spikes. This can be explained on the basis of the evidence in Table 1, indicating that a high mole ratio of NO_2 to fuel favors vigorous combustion and reduces production of the residues. A fuel lead would, on the other hand, provide a low ratio of oxidizer to fuel during the preignition period and would augment the production of preignition residue. During tail-off of the fuel pulse, an excess of fuel would also entail the risk of increasing the production of preignition residue that can be detonated by subsequent firing pulses. These experiments, although incomplete as of now, suggest that production of preignition residues would be minimized by maintaining a sufficient ratio of NO_2 to fuel during the tail-off and preignition periods. Leakage of fuel from the

injector into the chamber could, of course, have a harmful effect in terms of favoring the accumulation of preignition residues in the chamber. As pointed out earlier in this report, the reduction of propellant pulses to very short times such as 10 or 15 msec can also tend to degrade effective specific impulse and to increase the proportion of preignition residue production because the intrinsic ignition delay time (about 3 msec⁷) then becomes significant relative to propellant pulse length. Testing attitude-control motors for effect of the aforementioned variables is clearly desirable.

F. DTA AND IR SPECTRA OF RESIDUES PRODUCED
IN ROOM-TEMPERATURE CHAMBER

Differential thermal analysis (DTA) is valuable² in characterizing thermally unstable and explosive materials since it indicates the temperatures at which exothermic reactions or explosions occur and the magnitudes of the heat evolved from the material investigated. Endothermic segments of the DTA curve can arise from the melting or vaporization processes. In order to obtain samples of preignition residues for these DTA studies, MMH, A-50, or UDMH were reacted with NO₂ vapor in the room-temperature chamber at NO₂ pressures that did not produce ignition. Commercially available equipment was used to determine the DTA curves. Figure 10 contains the DTA curves (at a heating rate of 30°C per min) for the residues from MMH and A-50 fuels. For MMH, an exothermic peak began soon after 100°C was reached. The peak attained its maximum height at about 130°C, after which exothermicity was exhibited in a sharp but smaller peak at about 145°C and a broad peak near 235°C. By the time 275°C was reached, the curve had

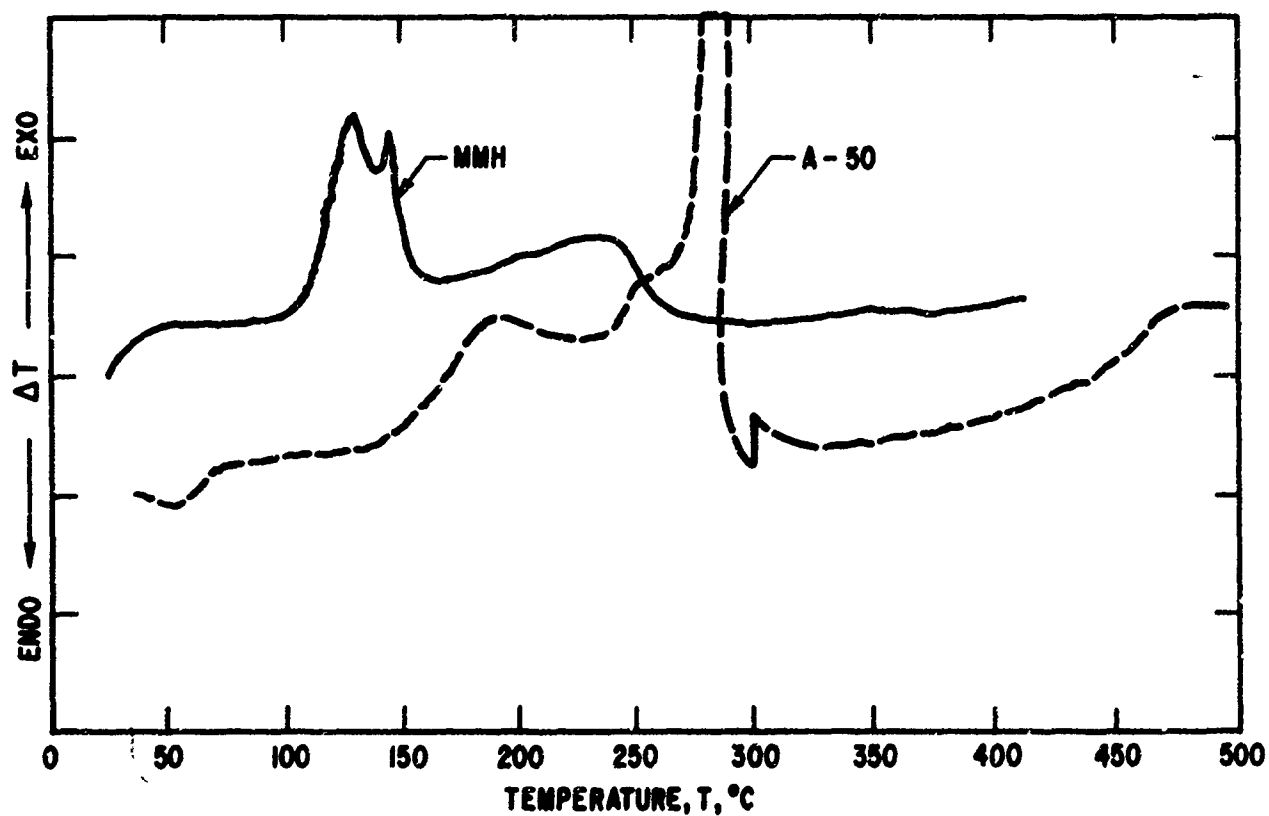


Fig. 10. Differential Thermal Analysis Curves for Residues From MMH and A-50 (The A-50 curve has been lowered by one division along the ΔT axis.).

dropped back to its level at temperatures below 100°C . This tail-off of exothermicity before 275°C suggests that the accumulation of possibly explosive preignition product from pulse to pulse could be prevented if the preignition product could be heated by each pulse so that its temperature remained above 275°C for several seconds. Additional experimental studies are needed to determine DTA curves at the maximum heating rate so as to simulate more closely heating rates encountered by preignition residues in combustion chambers.

The DTA curve (Fig. 10) obtained with the sample of A-50 residue showed a relatively small exothermic rise beginning near 60°C and a larger rise beginning at about 135°C that reached a rather broad peak near 190°C . Then a strong, sharp rise developed at 270°C and went off scale. A change of vertical scale factor from 2°C/in. to 5°C/in. returned the curve to the scale, and near 300°C the scale factor was restored to 2°C/in. No further peaks were observed until $\sim 475^{\circ}\text{C}$. This latter exothermicity could correspond to the combustion in air of the products from the previous peaks since the DTA curve was determined in air. It is probably desirable to run additional tests in an inert atmosphere or in vacuum.

Unfortunately, DTA curves obtained for the UDMH preignition residue have not been consistent, and additional tests will be needed to determine whether the UDMH residue prepared at 23°C does in fact have much less explosive character than the MMH or A-50 residues. The first DTA curve for the UDMH residue indicated a thermal instability exothermicity less than 10%

that of the MMH or A-50 residues. Some of the subsequent DTA curves agreed with the first DTA curve, but others showed considerably more exothermicity than the first curve. Obviously, the variables affecting the exothermicity shown by the DTA curve for UDMH residue need further clarification and control. The DTA measurements should be supplemented by drop, block, or gap tests for explosibility.

Infrared absorption curves were determined for MMH and UDMH combustion residues formed in the room-temperature chamber when the NO_2 pressure was great enough to produce ignition and flame temperatures higher than 600°C . Although the temperatures of the flames 3 mm above the residue remained higher than 600°C for at least 10 sec, the IR spectra were in good agreement with those previously described for the MMH and UDMH preignition residue produced at -11°C . This result is somewhat surprising and suggests that the effect of elevated temperatures on decomposing the residues should be directly determined.

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UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1 ORIGINATING ACTIVITY (Corporate author) Aerospace Corporation El Segundo, California		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3 REPORT TITLE PREIGNITION PRODUCTS FROM STORABLE PROPELLANTS AT SIMULATED HIGH-ALTITUDE CONDITIONS		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5 AUTHOR(S) (Last name, first name, initial) Mayer, Stanley W., Taylor, David, and Schieler, Leroy		
6 REPORT DATE November 1967	7a. TOTAL NO. OF PAGES 44	7b. NO. OF REFS 8
8a. CONTRACT OR GRANT NO. F04695-67-C-0158	9a. ORIGINATOR'S REPORT NUMBER(S) TR-0158(9210-02)-1	
b. PROJECT NO. c. d.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) SAMSO-TR-68-67	
10 AVAILABILITY/LIMITATION NOTICES This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Space and Missile Systems Air Force Systems Command Los Angeles, California
13 ABSTRACT In view of the destructive ignitions that occur in hypergolic test firings of attitude-control motors under simulated high-altitude conditions, the preignition behavior of MMH, UDMH, A-50, and N_2H_4 with N_2O_4 was examined at low pressures and temperatures in the laboratory. At low NO_2 pressures and temperatures, such as those that would be encountered in combustion chambers during starts in space, the ignition of these fuels was significantly delayed. During the preignition period relatively involatile, reaction products were formed between NO_2 and the fuels. Infrared spectrophotometry, mass spectrometry, differential thermal analysis, and other techniques were used to examine these preignition residues. The IR absorption curves were consistent with the view that the major component in the MMH residue that could behave as an explosive monopropellant was MMH nitrate. IR spectra of the preignition residues formed with N_2H_4 or A-50 suggest that hydrazine nitrate (a potentially explosive monopropellant) was the major constituent of these residues. The preignition residues were strongly acid, as a result of their nitric acid content, and are a corrosion and a contamination threat to equipment on the exterior of flight vehicles. Mass spectrometric data indicate the unstable nitroamines are formed in the gas phase during the preignition period. DTA data show that most preignition residues had strongly exothermic peaks, suggesting potentially explosive behavior. The proportion of preignition residue formed was dependent on the mole ratio of NO_2 to fuel. Factors affecting the production of preignition residues are discussed, and methods of possibly decreasing that production are suggested for further investigation.		

DD FORM 1673
(FACSIMILE)

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Security Classification

KEY WORDS

Attitude-Control Motors
Attitude-Control Propulsion
Hydrazine
Hypergolic Ignition
Monomethylhydrazine
Nitrogen Tetroxide
Reaction Intermediates
Safety
Sensor Damage
Storable Propellants
Unsymmetrical Dimethylhydrazine

Abstract (Continued)