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NAVY DEPARTMENT
OFFICE OF NAVAL RESEARCH
WASHINGTON, D. C.

6 April 1954
Report No. 813
(Quarterly)
Copy No. 21

INVESTIGATION OF
LIQUID ROCKET
PROPELLANTS



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Contract N7onr-462

Task Order No. III

Project No. NR 220 023

Aerojet-General CORPORATION

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Written by:

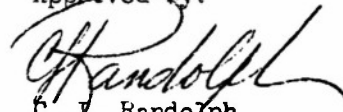
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CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order III, and covers the work done from 1 December 1953 to 26 February 1954.

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Report No. 813

I. INTRODUCTION

A. Investigations of the effect of additives on the thermal decomposition of nitromethane at 355°C and approximately 200 psia have shown that the addition of 15 mole percent of oxygen or of 19 mole percent of ethylene oxide has no significant effect on the decomposition rate. However, 0.35 mole percent of chromium acetylacetonate or a mixture of 0.35% chromium acetylacetonate and 19% ethylene oxide affects the rate of decomposition very significantly.

B. Preparation of N-aminoethylenimine and N-propargylethylenimine by new synthetic methods is promising.

C. Two experimental determinations of the heat of combustion of nitrosotrimethylhydrazine have resulted in values of 5954 cal/g and 6030 cal/g. These determinations were conducted in an open combustion tube on samples that were slightly orange; hence, the results are to be considered tentative.

D. The metathetical reaction of sodium acetylide with tetramethylammonium chloride in ether yielded a product that failed to give a positive test for chloride. Acid-base titrations indicated that the material may be primarily the desired tetramethylammonium acetylide.

E. A series of successful engine tests have been conducted with the unsym.-dimethylhydrazine and liquid oxygen system, and with the methylhydrazine and liquid oxygen system. A maximum specific impulse of 242 lb-sec/lb and a maximum characteristic velocity of 5600 ft/sec were recorded at a mixture ratio of 1.5 for the former system. For the latter system, a maximum specific impulse of 245 lb-sec/lb and a characteristic velocity of 5750 ft/sec were recorded at a mixture ratio of 1.3.

II. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

A. INTRODUCTION

1. During this report period the investigation of the effect of additives on the thermal decomposition of nitromethane at 355°C and at approximately 200 psia pressure was continued. This study is presently concerned with the action of additives on the rate of the decomposition, and on the distribution of the products formed. The reaction rate is determined by means of polarographic analyses for the undecomposed nitromethane, and the distribution of products is determined by means of mass-spectrometer analyses of similar samples.

2. Because of continued difficulties with the mass spectrometer (which necessitated repairs of certain components at the General Electric laboratories in Schenectady, New York), analyses could not be performed until just before the end of this report period, when the instrument was again in good working order. For this reason, the main emphasis was placed on a study of the effect of additives on the rate of decomposition.

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B. EXPERIMENTAL RESULTS

1. Several 5-min tests were made at 355°C with and without additives. The percent of nitromethane decomposed was determined by polarographic analysis. These data were combined with others obtained previously (Table I) and subjected to a statistical analysis based on the Student t-test, which involves the determination of the significance of the difference between sample means. This treatment of the data shows that 15 mole percent oxygen or 19 mole percent ethylene oxide has no significant effect on the rate of decomposition of nitromethane; on the other hand, both 0.35 mole percent chromium acetylacetonate (CAA), and a mixture of 0.35 mole percent CAA and 19 mole percent ethylene oxide affect the rate of the decomposition very significantly. There is, however, no significant difference in the extent to which the reaction is accelerated by CAA alone or by a mixture of CAA and ethylene oxide. Assuming that the sample means shown in Table I are close to the true means of the populations, it appears that the addition of CAA or of a mixture of CAA and ethylene oxide increases the rate of decomposition of nitromethane by a factor of 2.5 to 3.

2. It is known that under some conditions a small percentage of oxygen may have a different effect upon a reaction than a relatively large amount. Two tests were performed to determine whether a reduction in the amount of oxygen from 15 to 5 mole percent would affect the rate of decomposition of nitromethane. As shown in Table I, there appears to be no difference in the rates of thermal decomposition.

3. Mass spectrometer analyses were made on the products resulting from decomposition tests performed under the same conditions as the rate studies discussed in the previous section. The data appear to be in general agreement with those obtained previously (Reference 1), showing that the additives used tend to alter the product distribution during the decomposition in such a way as to form fewer endothermic intermediates and more of the exothermic end products. Because of the difficulties with the mass spectrometer, no product analyses will be presented at this time.

4. Ethylene oxide at approximately 200 psia was permitted to remain in the furnace for 5 min at 355°C in order to determine whether it decomposes itself when used as an additive. The decomposition was so slight that no products could be identified, but there may be trace amounts formed.

5. Methyl nitrite which is isomeric with nitromethane was prepared, and its mass spectrum was obtained in order to determine whether it may be formed during the thermal decomposition of nitromethane. Since its spectrum does not fit the product spectra, it may be assumed that it is not produced.

C. DISCUSSION

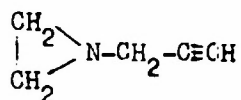
On the basis of the data presented here and in Reference 1, it appears that additives may act in at least two ways to improve operating conditions in a motor. An additive such as CAA may bring about satisfactory operation by increasing the rate of decomposition of nitromethane, whereas additives such as oxygen and ethylene oxide may accomplish the same objective by altering the product distribution in such a way as to increase the heat liberated. This thesis will be amplified in the next report when the results from the mass spectrometer analyses will be available.

III. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

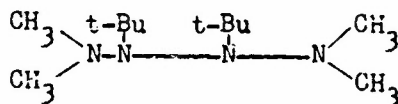
A. INTRODUCTION

1. Continued efforts toward the further methylation of methylhydrazines by the method of Leuckart have been unsuccessful. The catalytic reduction of methylene-unsym.-dimethylhydrazine and the reaction of trimethylhydrazine with formaldehyde have been further investigated. The initial steps in the synthesis of the following new compounds have been conducted during this report period:

a. N-Propargylethylenimine



b. N,N,N''',N'''-Tetramethyl-N,N'''-di-tert.-butyltetrazene



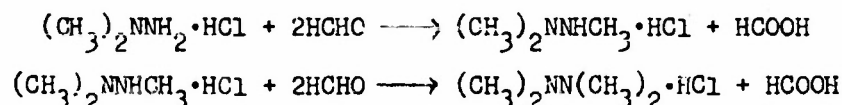
2. A new approach has been adopted for the preparation of N-aminoethylenimine, and involves the action of ammonia on N-chloroethylenimine. Small samples of sym.-tetramethyltetrazene and nitrosotrimethylhydrazine were synthesized, and the heat of combustion of the latter compound was determined.

B. PREPARATION OF TRIMETHYL AND TETRAMETHYLHYDRAZINE

1. Because of the known reaction of ammonium chloride and paraformaldehyde to yield trimethylamine in good yield (Reference 2), the analogous reaction of hydrazine and some of its methyl derivatives with

formaldehyde has been investigated. It was the purpose of investigations made during this report period to determine whether the more highly alkylated methylhydrazines could be obtained by this method, since the only known syntheses of tri- and tetramethylhydrazine require the expensive lithium aluminum hydride (Reference 3).

2. Preparation of tri- and tetramethylhydrazine was sought by further methylation of unsym.-dimethyl- and trimethylhydrazine through the action of formaldehyde on the hydrochlorides:



When unsym.-dimethylhydrazine hydrochloride (mp 83 to 84°C) and paraformaldehyde were heated together the mixture turned black on melting, and titration with potassium iodate indicated that nearly all of the reducing function had been destroyed. Similar results were obtained from the action of 40% formalin on aqueous unsym.-dimethylhydrazine hydrochloride, and on aqueous trimethylhydrazine hydrochloride. These results were similar to those obtained in the reaction of hydrazine hydrochloride with paraformaldehyde (Reference 3).

3. In an attempt to determine whether the methylation of hydrazine was possible without rupture of the N-N bond, a concentrated solution of hydrazine formate (prepared by neutralizing hydrazine hydrate with 87.5% formic acid) was treated over a period of 3 hr with one-half the stoichiometric amount of paraformaldehyde necessary for the formation of methylhydrazine. The solid paraformaldehyde was added gradually to the refluxing hydrazine formate solution. The reaction proceeded more smoothly than when the hydrochloride was employed, and at the end of the reaction period the mixture was yellow-orange. However, titration with potassium iodate indicated that about two-thirds of the reducing function had been destroyed. The main portion of the reaction mixture was added through a dropping funnel to an excess of hot aqueous potassium hydroxide, and the volatile components were flash-distilled. Solid potassium hydroxide was added to the distillate, and the oil which separated was dried over fresh potassium hydroxide. The yield of oil was about 10%, calculated as methylhydrazine, and based on the paraformaldehyde used. The oil was distilled at reduced pressure, and the fraction boiling at 40 to 45°C was collected as a colorless, mobile liquid. When an ethereal solution of the oil was mixed with ethereal picric acid, a mixture of picrates was obtained which could be fractionally crystallized from ethanol. The two picrates thus obtained melted at 179 to 182°C (dec), and 244°C. Only the lower-melting picrate reduced potassium iodate, but it is evident that no simple hydrazine had been isolated. (The melting point of methylhydrazine picrate is 163 to 164°C and that of unsym.-dimethylhydrazine picrate is 134 to 136°C.) As a result of the above series of experiments, it appears that the preparation of tri- and tetramethylhydrazines by the Leuckart reaction is not feasible.

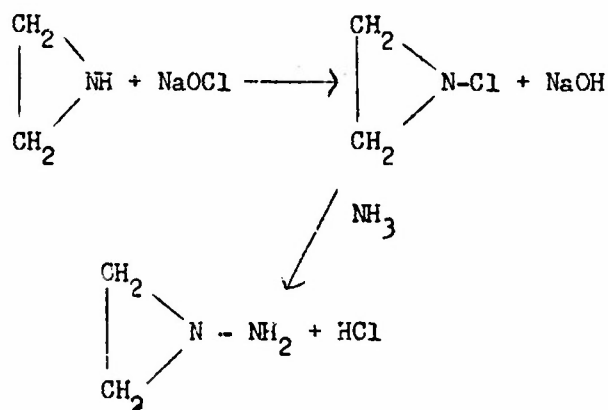
C. THE CATALYTIC REDUCTION OF METHYLENE-UNSYM.-DIMETHYLHYDRAZINE

1. The catalytic reduction of methylene-unsym.-dimethylhydrazine, $(CH_3)_2NN=CH_2$, represents a potentially inexpensive method for the preparation of trimethylhydrazine, since the required starting material is itself obtainable in high yield from the action of formalin on unsym.-dimethylhydrazine (References 3 and 4). Unsuccessful attempts to catalytically reduce the methylene compound with a 10% palladium on charcoal catalyst in water, and in ether were reported previously (Reference 1).

2. When absolute ethanol was used as the solvent, three products were obtained. The first of these precipitated when ether was added to the ethanol solution, after removal of the catalyst. This material is a white crystalline solid melting at higher than $300^\circ C$; it is soluble in water to give a neutral solution; it is insoluble in ether; and its acid solution does not reduce potassium iodate. Two other components were isolated as their picrates by the distillation into ethereal picric acid of various fractions of the ethanol-ether solution remaining after separation of the first product. The picrates were fractionally crystallized from ethanol and their melting points were 190 to $191^\circ C$ and 210 to $212^\circ C$. Neither of these compounds reduced potassium iodate solution, and attempts to prepare trimethylhydrazine by this method were therefore discontinued.

D. N-AMINOETHYLENIMINE

1. Previous efforts to synthesize N-aminoethylenimine were only partially successful (Reference 5). A new synthesis, involving the reaction of N-chloroethylenimine and ammonia, is therefore proposed as a possible method of preparation:

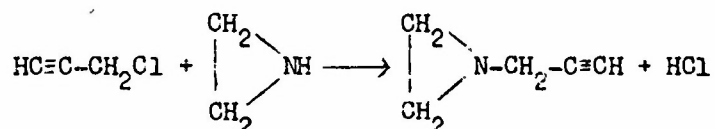


In order to remove the hydrochloric acid, and thus prevent opening of the ring, triethylamine or sodium hydroxide must be added in the second reaction.

2. When ethylenimine at -10°C was added to an aqueous solution of sodium hypochlorite (also at -10°C) the temperature quickly rose to $+5^{\circ}\text{C}$ and an oil separated. The characterization of this product is in progress. The reaction of N-chloroethylenimine with ammonia will be conducted in aqueous solution in the presence of sodium hydroxide, and in liquid ammonia in the presence of sodium hydroxide or triethylamine during the next report period.

E. N-PROPARGYLETHYLENIMINE

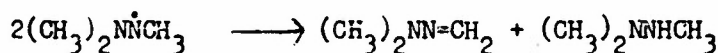
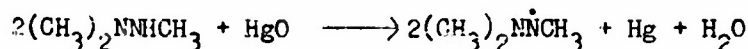
Although N-aminoethylenimine is the only ethylenimine derivative considered previously in this program for use as a high-energy propellant, other derivatives with high-energy-content substituents should also be of value. One such material would be N-propargylethylenimine. The preparation of N-propargylethylenimine was attempted by the action of propargyl chloride on ethylenimine:



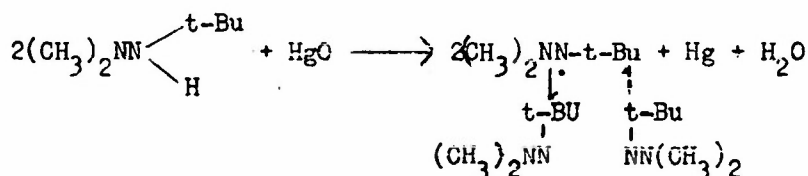
Propargyl chloride was prepared from the alcohol and thionyl chloride in the presence of pyridine (Reference 6). The chloride, after redistillation, boiled at 63 to 64°C (lit 65°C). The ethylenimine used was redistilled from solid sodium hydroxide, and the fraction boiling at 55 to 56°C was collected (lit bp 56°C). Anhydrous triethylamine was used in this reaction to remove the hydrochloric acid formed, in order to avoid polymerization of the ethylenimine and propargylethylenimine (Reference 7). Both ethylenimine and propargylethylenimine should be weaker bases than triethylamine (References 7 and 8), so that if the reaction were run in a non-polar solvent only triethylamine hydrochloride should precipitate. When equimolar amounts of propargyl chloride, ethylenimine, and triethylamine were refluxed in a tenfold volume of anhydrous benzene only polymerization of the ethylenimine was observed. Accordingly, the reaction was run in a twofold volume of absolute ether at room temperature. Although a white solid precipitated, the reaction under these conditions is very slow. After the mixture was permitted to stand for three weeks, approximately 65% of the expected amount of solid was obtained. An analysis of the solid and isolation of the N-propargylethylenimine from the ether solution are in progress.

F. N,N,N',N'-TETRAMETHYL-N',N'-DI-TERT-BUTYL-TETRAZANE

1. Former attempts to oxidize trimethylhydrazine to hexamethyl-tetrazane with mercuric oxide or lead dioxide did not yield the desired product (Reference 1). The most plausible side reaction appears to be the stabilization of the free radical first formed by expulsion of a hydrogen atom:

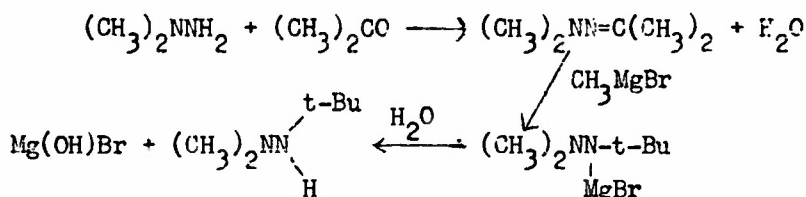


The postulated stabilization of the free radical initially formed in this manner is supported by the work of Klages (Reference 4). The oxidation of N,N-dimethyl-N'-tert.-butylhydrazine, on the other hand, would be a unique reaction in which the initially formed free radical could not be stabilized in the above manner



Also, because of steric hindrance the radicals formed might exist as such in solution, instead of combining to form the tetrazane. Because of its bearing on the problem of the synthesis of tetrazanes, some study of this oxidation reaction appeared justified.

2. An attempt was made to synthesize N,N-dimethyl-N'-tert.-butylhydrazine by the following sequence of reactions:



The acetone unsym.-dimethylhydrazone was prepared by refluxing a mixture of one mole of unsym.-dimethylhydrazine, five moles of dry acetone, and five moles of absolute methanol over 300 g of Drierite for several hours. The Drierite* was used in two 150-g portions, the first portion being removed (by decantation of the solution) before the addition of the second. The mixture was fractionated through a 30-cm column packed with Berl saddles, and the fraction boiling at 93 to 94°C was collected as the pure hydrazone. The yield was only approximately 20% of the theoretical amount, partly because of the large amount of Drierite employed. The structure of the hydrazone was proved by the following experiments:

* Although Drierite is an excellent dehydrating agent, it absorbs only about six weight percent of water.

Hydrolysis of the acetone unsym.-dimethylhydrazine followed by treatment with ethereal picric acid gave unsym.-dimethylhydrazine picrate, mp 137 to 139°C. The mixed melting point of this compound with an authentic sample of unsym.-dimethylhydrazine picrate (mp 134 to 136°C) was 134 to 137°C. The acetone was identified by reaction with 2,4-dinitrophenylhydrazine to yield acetone 2,4-dinitrophenylhydrazone, mp 124 to 126°C (lit. mp 126°C).

3. The reaction of acetone unsym.-dimethylhydrazine with methyl magnesium bromide will be considered during the next report period. In this connection, it is of interest that tert.-butylhydrazine has been prepared in an analogous manner by the action of methyl magnesium bromide on dimethylketazone (Reference 4).

G. TETRAMETHYLTETRAZENE AND NITROSOTRIMETHYLHYDRAZINE

1. Small samples of tetramethyltetrazene and nitrosotrimethylhydrazine were prepared for a determination of their heats of combustion. The former compound was obtained by the oxidation of unsym.-dimethylhydrazine in ether with mercuric oxide (Reference 9), and the latter from the nitrosation of trimethylhydrazine (Reference 5).

2. Two experimental determinations of the heat of combustion of nitrosotrimethylhydrazine in the Parr oxygen bomb, have resulted in values of 5954 cal/g and 6030 cal/g. These determinations were conducted in an open combustion tube on samples that were slightly orange; hence, the results are to be considered tentative. A heat of combustion of this compound calculated according to the method of Kharasch (Reference 10), considering the compound to be a tetra-substituted hydrazine, yielded a value of 5940 cal/g.

IV. STUDY OF THE FEASIBILITY OF EMPLOYING ACETYLIDE SALTS AS PROPELLANT COMPONENTS

A. INTRODUCTION

Several methods are being studied for the preparation of non-metallic acetylide salts for use as rocket propellant components. The desired product from all of the following reactions is tetramethylammonium acetylide.

1. Reaction of tetramethylammonium chloride with sodium acetylide in liquid ammonia or ether solution.

2. Reaction of tetramethylammonium free radical with acetylene in liquid ammonia.

3. Reaction of tetramethylammonium triphenyl methide with acetylene.

4. Reaction of trimethylammonium methyllide with acetylene.

B. REACTIONS IN LIQUID AMMONIA

1. The study of the direct precipitation of tetramethylammonium acetylide from a solution of tetramethylammonium chloride and sodium acetylide in anhydrous liquid ammonia at -33°C was continued. The procedure for addition of components was modified in the following manner: Acetylene was bubbled into a clear, agitated solution of 2.06 g tetramethylammonium chloride in approximately 300 ml of ammonia. Simultaneously, under an atmosphere of nitrogen, 0.50 g of metallic sodium was added in small pieces at a rate such that the solution was never colored to a great extent by the dissolving sodium. After addition of the sodium, the solution was refluxed at -33°C for 1-1/2 hr. A gelatinous precipitate which had formed during the reaction was removed by filtration, and the last traces of ammonia were removed under reduced pressure. The extremely small amount of product permitted only cursory examination, consisting of a chloride analysis and an acid-base titration. On the basis of these two analyses, it appears that some tetramethylammonium acetylide may have been present. It was hoped that better solubility relationships would exist at 25°C and that the reaction could be carried out in a pressure vessel, but the solubility of tetramethylammonium chloride at 25°C was found to be 0.452 g/100 ml of solution, which is only half the solubility at -33°C . It is therefore anticipated that emphasis in further work on the metathetical reaction will be placed on solvents other than liquid ammonia.

2. The possibility of producing tetramethylammonium acetylide from tetramethylammonium free radical and acetylene was considered. Only one analogous reaction, the reaction of tetraethylammonium free radical with acetylene in liquid ammonia at -33°C (Reference 11), has been found in the literature. Though discoloration was noted, the product obtained did not appear to be the acetylide salt. An attempt was made to prepare the tetramethylammonium free radical by treating a solution of lithium in liquid ammonia with a solution of tetramethylammonium chloride in liquid ammonia at -33°C (Reference 12). Decoloration of the lithium solution was observed. After filtration, the addition of acetylene produced a cloudy solution, but no solid could be collected. The literature reports (Reference 13) the free radical to be colored at -80°C , and colorless and more unstable at -33°C . If further work on this method is done, it should be carried out at -80°C .

C. REACTION OF SODIUM ACETYLIDE WITH TETRAMETHYLAMMONIUM CHLORIDE
IN ETHER

The reaction of tetramethylammonium chloride with sodium acetylide in ether solution at room temperature was carried out at $(\text{CH}_3)_4\text{NCl}/\text{NaC}\equiv\text{CH}$ molar ratio of 3.4/1. This reaction was considered as a result of an analogous reaction (Reference 14) in which tetramethylammonium chloride was

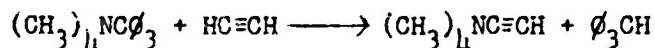
permitted to react with sodium triphenyl methide in ether, with subsequent extraction of the reaction product, tetramethylammonium triphenyl methide, with anhydrous pyridine. The tetramethylammonium chloride--sodium acetylide solution was shaken for 24 hr, after which the solid residue was washed repeatedly by decantation. Prior to pyridine extraction the solubility of sodium chloride and tetramethylammonium chloride in boiling pyridine was measured, and both salts were found to be insoluble. A pyridine extraction was then carried out, followed by addition of ether, which resulted in the precipitation of a very small quantity of white solid. Titration of this material for chloride ion gave negative results. Acid-base titration indicated that the material may be primarily tetramethylammonium acetylide. Further study of the reaction is planned.

D. ATTEMPT TO PREPARE N-METHYL PYRIDINIUM ACETYLIDE

Another quaternary ammonium acetylide under consideration was N-methyl pyridinium acetylide. In order to test a possible method for preparing this compound, N-methyl pyridinium iodide was permitted to react with sodium acetylide in ether solution. After the residue was washed with ether, pyridine was added; the entire mixture turned black. The more promising aspects of other methods for the preparation of tetramethylammonium acetylide (to be described below) have not allowed time for further work on this pyridinium compound.

E. REACTION OF TETRAMETHYLAMMONIUM TRIPHENYL METHIDE WITH ACETYLENE

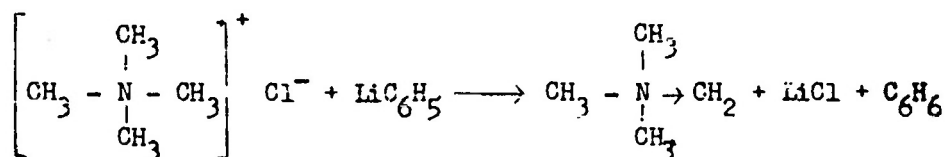
Another method under consideration for the preparation of tetramethylammonium acetylide was conceived as a result of a reported study of the synthesis of tetramethylammonium triphenyl methide (Reference 14) and the relative acidities of triphenyl methane and acetylene (Reference 15). The greater acidity of acetylene suggested that the acetylide ion might replace the triphenyl methide ion if acetylene was bubbled into a solution of tetramethylammonium triphenyl methide:



In order to prepare tetramethylammonium triphenyl methide, triphenyl chloromethane (recrystallized from petroleum ether) was permitted to react with 2% sodium amalgam in dry ether solution to form sodium triphenyl methide. Reaction of this ether-soluble compound with tetramethylammonium chloride caused a decoloration of the sodium triphenyl methide solution and the deposition of a dark precipitate on the surface of the unreacted tetramethylammonium chloride. After repeated washing of the precipitate with ether, dry pyridine was added, producing a dark-red solution which was filtered under nitrogen. The solution of tetramethylammonium triphenyl methide in pyridine thus prepared will be treated with dry acetylene gas as the next step in the procedure.

F. REACTION OF TRIMETHYLAMMONIUM METHYLID WITH ACETYLENE

It has been shown (Reference 16) that the reaction of tetramethylammonium chloride with phenyl lithium proceeds as follows:



The compound produced, trimethylammonium methylid, has a great affinity for a proton, and the possibility that it will react with acetylene to produce tetramethylammonium acetylide is being studied. In preparation for this reaction, phenyl lithium was prepared by reaction of lithium metal with bromobenzene in ether solution. Treatment of the phenyl lithium solution with tetramethylammonium chloride will be followed by washing of the residue with ether and extraction of the methylid with tetrahydrofuran. Acetylene will then be bubbled through the methylid solution in an attempt to produce the tetramethylammonium acetylide.

V. ENGINE TEST PROGRAM

A. UNSYM.-DIMETHYLHYDRAZINE AND LIQUID OXYGEN

1. A total of 13 successful tests were made in evaluating the performance of the unsym.-dimethylhydrazine and liquid oxygen propellant system. The 100-lb-thrust rocket motor used for previous testing on this contract was used for this series (D-55-LF) and that reported below. A maximum specific impulse of 242 lb-sec/lb and a maximum characteristic velocity of 5600 ft/sec was recorded at a mixture ratio of 1.5.

2. Curves of the experimental performance parameters are presented along with the calculated theoretical values in Figure 1. It can be seen that the specific impulse (corrected for heat loss to the coolant) averaged 90% of theoretical, calculated on the basis of shifting equilibrium.

B. METHYLHYDRAZINE AND LIQUID OXYGEN

1. A total of 22 tests were made in evaluating the performance of methylhydrazine and liquid oxygen (Series D-61-LF). A maximum specific impulse of 245 lb-sec/lb and a characteristic velocity of 5750 ft/sec were recorded at a mixture ratio of 1.3. Performance data (Figure 2) indicate that the experimental specific impulse is 90% of theoretical, calculated on the basis of shifting equilibrium.

C. INJECTOR

The injector consisted of five pairs of 2:1 oxidizer-fuel streams. The resultant stream from the impingement of the fuel and oxidizer streams was axial to the walls of the thrust chamber at all mixture ratios; a schematic of the injector is shown in Figure 3. Orifices were chosen so that both fuel and oxidizer velocities would be 50 ft/sec at optimum mixture ratio for the unsym.-dimethylhydrazine and liquid oxygen propellant system. This selection allowed for a wide variation in propellant combinations and range of mixture ratios while maintaining adequate velocities for good mixing. Combustion was smooth and stable in both test series except at the lowest mixture ratio. The flame was normally quite sharp, and an unusual semi-opaque blue in color; this is ascribed to CN spectral emission bands.

REFERENCES

1. Aerojet Report No. 779, 13 January 1954 (Confidential).
2. R. Adams and C. S. Marvel, Organic Synthesis, Vol I, Wiley, p. 531.
3. J. B. Class et al., J. Am. Chem. Soc., 75, 2937 (1953).
4. F. Klages et al., Ann., 547, 1 (1941).
5. Aerojet Report No. 717, 9 July 1953 (Confidential).
6. A. I. Vogel, Practical Organic Chemistry, p. 273, Longmans, Green, N. Y., 1948.
7. H. Bestian et al., Ann., 566, 210 (1950).
8. K. N. Campbell et al., J. Org. Chem., 17, 1141 (1952).
9. J. Renouf, Ber., 13, 2173 (1880).
10. M. S. Kharasch, J. Research Nat. Bur. Standards, 2, 359-430 (1929).
11. H. H. Schlubach, Ber., 53B, 1689-93 (1920).
12. F. C. Whitmore, Organic Chemistry, D. Van Nostrand Co., Inc. (1937).
13. H. H. Schlubach and F. Ballauf, Ber., 54B, 2811-25. (1921).
14. W. Schlenk, Ber., 49, 607 (1916).
15. G. B. Conant and C. W. Wheland, J. Am. Chem. Soc., 54, 1212 (1932).
16. G. Wittig and M. H. Wetterling, Ann., 557, 193-201 (1947).

TABLE I

THERMAL DECOMPOSITION OF NITROMETHANE

Effect of Additives on Rate of Decomposition

Temperature 355°C

Duration 5 min

Run No.	Initial Pressure of Nitromethane psia	Additive, mole %	Percent Decomposed
118	227	—	6.0
144	227	—	7.8
177	227	—	3.4
196	244	—	5.4
218	233	—	3.8
			Mean 5.1
130	188	13.5% Oxygen	3.2
155	182	13.5% Oxygen	5.8
178	232	14.7% Oxygen	1.2
193	250	16.1% Oxygen	5.8
229	225	16.0% Oxygen	8.3
			Mean 4.9
194	268	6.6% Oxygen	2.5
195	242	4.5% Oxygen	6.6
190	244	17.0% Ethylene Oxide	8.0
192	245	17.9% Ethylene Oxide	5.5
212	248	19.6% Ethylene Oxide	5.4
213	246	19.6% Ethylene Oxide	4.4
220	240	18.9% Ethylene Oxide	5.3
			Mean 5.7
200	246	0.36% CAA*	12.1
201	224	0.41% CAA	7.4
216	244	0.36% CAA	10.5
217	242	0.34% CAA	11.7
219	250	0.36% CAA	14.8
221	238	0.33% CAA	14.4
222	229	0.35% CAA	11.1
223	236	0.37% CAA	13.8
224	223	0.35% CAA	20.4
			Mean 12.9

* Chromium acetyl acetonate (weight % = mole % x 5.13)

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TABLE I (cont.)

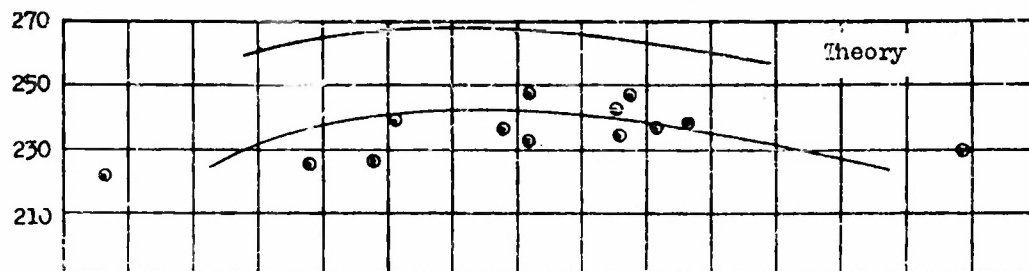
<u>Run No.</u>	<u>Initial Pressure of Nitromethane psia</u>	<u>Additive, mole %</u>	<u>Percent Decomposed</u>
197	243	0.34% CAA + 19.4% Ethylene Oxide	14.0
202	248	0.31% CAA + 18.6% Ethylene Oxide	8.2
203	244	0.33% CAA + 19.8% Ethylene Oxide	14.1
214	263	0.33% CAA + 19.4% Ethylene Oxide	17.4
215	244	0.35% CAA + 19.1% Ethylene Oxide	14.8
225	242	0.33% CAA + 19.1% Ethylene Oxide	17.0
226	232	0.34% CAA + 19.1% Ethylene Oxide	22.0
227	221	0.41% CAA + 19.6% Ethylene Oxide	16.1
228	231	0.38% CAA + 19.4% Ethylene Oxide	12.2
		Mean	15.0

Table I
Sheet 2 of 2

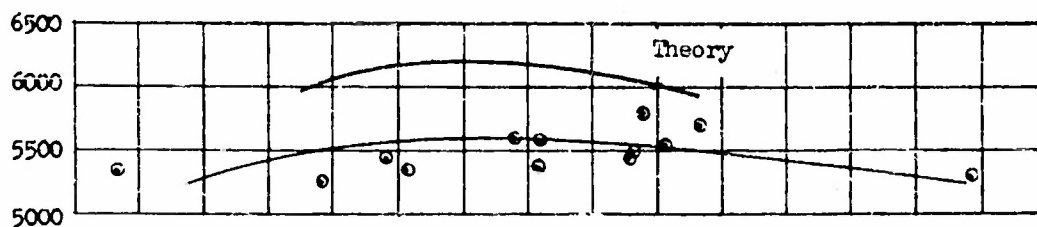
PERFORMANCE VS. MIXTURE RATIO
unsym.-Dimethylhydrazine and Liquid Oxygen
 (Data Corrected for Heat Transfer)

C-3547 HS:em 3-10-54

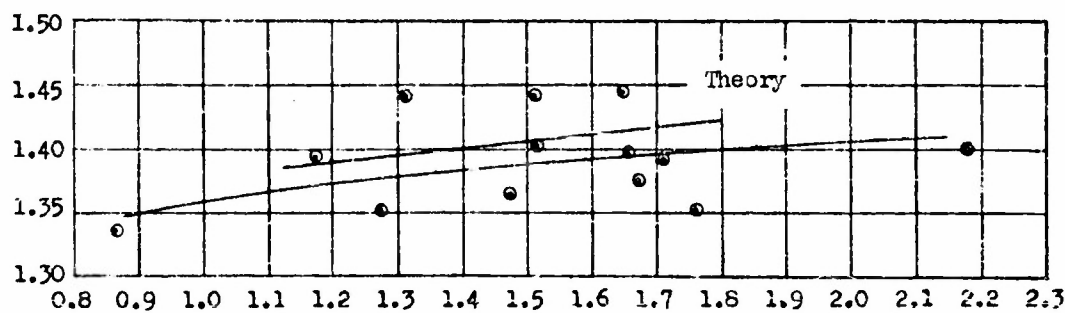
SPECIFIC IMPULSE
 lb-sec/lb



CHARACTERISTIC VELOCITY
 ft/sec



THRUST COEFFICIENT



MIXTURE RATIO, w_{ox}/w_f

Figure 1

PERFORMANCE VS. MIXTURE RATIO
 Diethylhydrazine and Liquid Oxygen
 (Data Corrected for Heat Transfer)

C-3545 HS:em 3-10-54

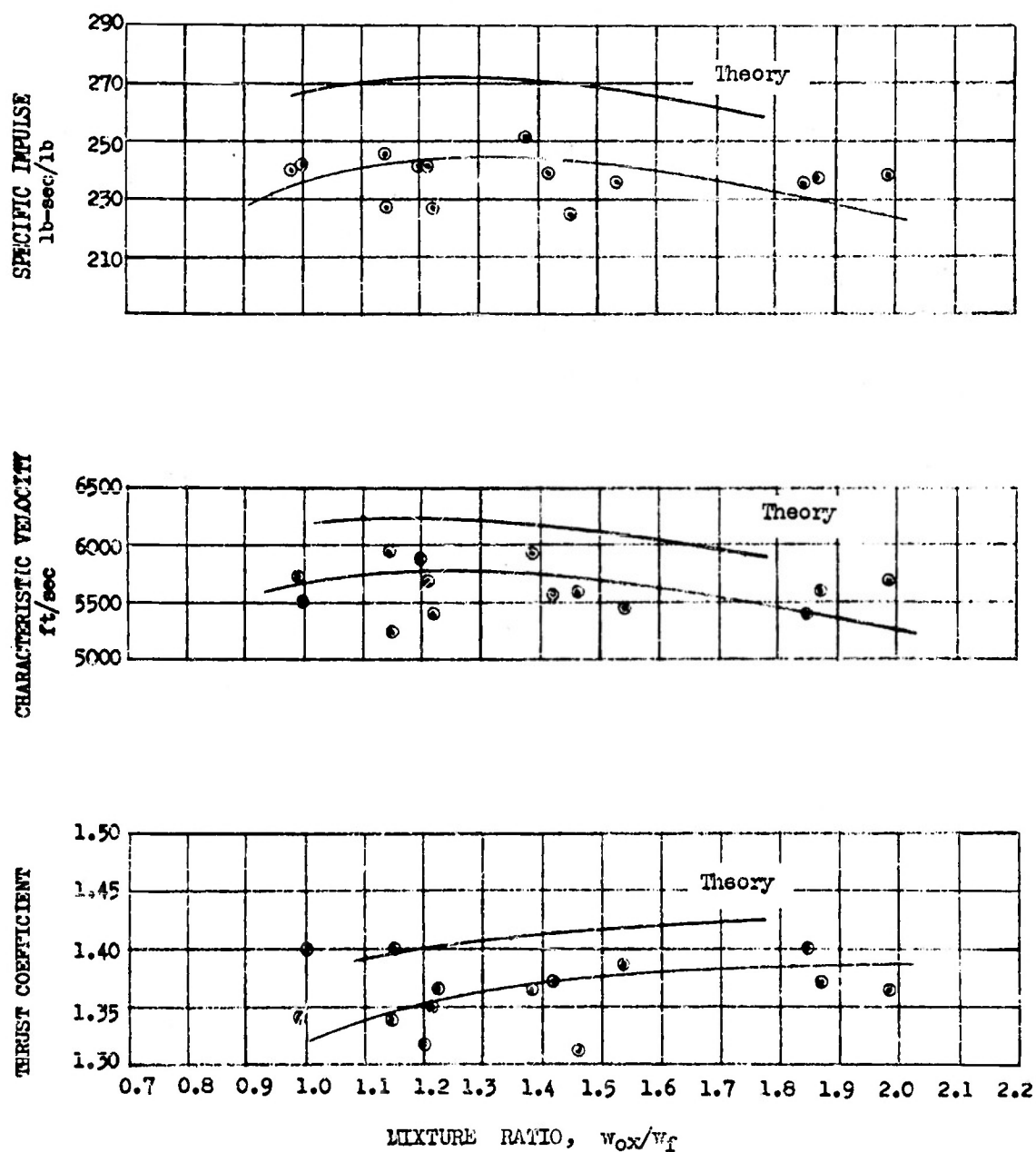


Figure 2

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INJECTOR CONFIGURATION
TEST SERIES D-55-LF & D-61-LF

C-3546 ES:em 3-10-54

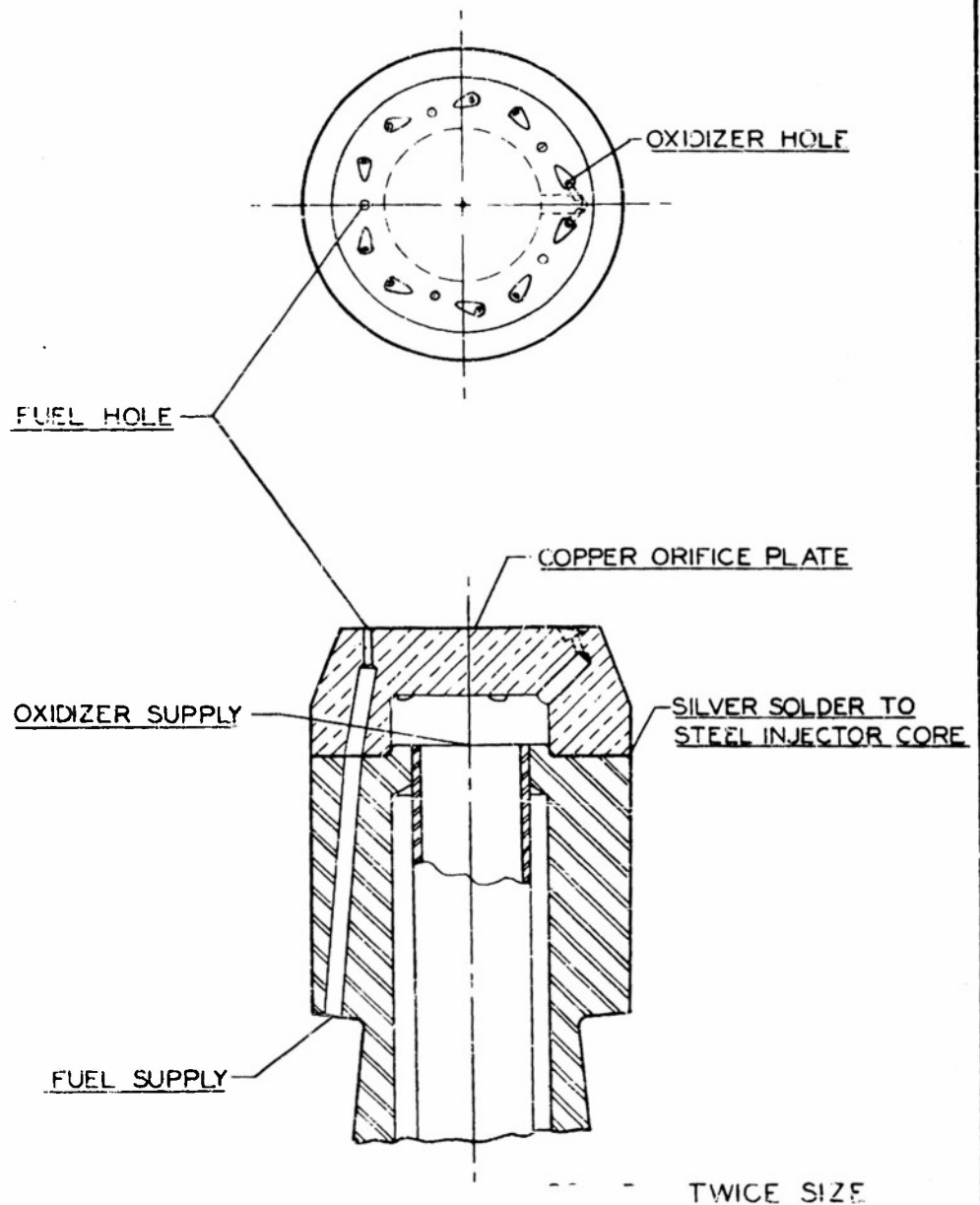


Figure 3