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

9 April 1953

Report No. 690

(Quarterly)

Copy No. ____

INVESTIGATION OF LIQUID ROCKET PROPELLANTS



Contract N7onr-462

Task Order No. III

Project No. NR 220 023

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SECURITY INFORMATION

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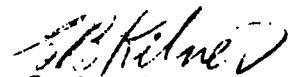
INVESTIGATION OF LIQUID ROCKET PROPELLANTS

Contract N7onr-462
Task Order III
Project NR 220 023

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No. of Pages: 38

Period Covered:

1 December 1952 through 28 February 1953

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AEROJET-GENERAL CORPORATION
Azusa, California

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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 1952 through 28 February 1953.

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I. INTRODUCTION

A. Contract N7onr-462, Task Order III, consists of several distinct phases, all of which have as the ultimate aim the improvement of rocket fuels and oxidizers. Studies of the manner of decomposition of monopropellants, determination of pertinent physical properties, alteration of undesirable physical properties, synthesis and characterization of new rocket propellants, calculations of theoretical performances of high-energy propellant combinations and evaluation of rocket propellants in a small test motor are all of continuing interest to this project. Results of this work have been published in a series of bi-monthly progress reports (Aerojet Reports 820-1 through 820-30), and more recently in the form of quarterly reports of which this is the second.

B. At present, efforts are being concentrated on the determination of the mechanism of the thermal decomposition of nitromethane at high pressures, synthesis and characterization of the new compound N-aminoethyl-enimine, and the alteration of the physical properties of hydrazine and dinitrogen tetroxide. A study of the ignition delay of triethyl trithiophosphite with nitric acid was also made during this report period. The planned testing of aviation gasoline with mixtures of liquid fluorine and oxygen has been delayed because of difficulties encountered with the re-machining of certain parts of the test installation.

II. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

A. INTRODUCTION

During this report period, the study of the thermal decomposition of nitromethane included experiments of 20, 31, and 45-min length at a temperature of 355°C. The effect of added nitric oxide upon the extent of decomposition and upon the decomposition products was investigated. The apparent order of the reaction is based upon the direct analysis of nitromethane remaining after an experiment, rather than upon total pressure change, which was used in most previous work. The pressure range under investigation, i.e., 80 to 360 psia, includes the highest pressure practicable with the present techniques. Previous work was at subatmospheric pressures, and indicated a deviation from true first-order decomposition, which has been confirmed by this work.

B. APPARENT ORDER OF THE REACTION

In this study, the kinetic experiments are conducted by determining polarographically the amount of nitromethane remaining within a sealed glass ampoule after it has been allowed to decompose for a given period of time at specified conditions of temperature and initial pressure. It has been previously reported (Reference 1) that when the results of decomposition tests at 355°C for 31 min were substituted into the integrated rate equations for various orders, the reaction appeared to be of an order higher than first with

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respect to nitromethane. Additional tests have now been made to verify the previous results. It was also determined that a correction factor had to be applied to all test results to account for the somewhat low values (approximately 4%) when ampoules containing known amounts of nitromethane were analyzed.* A plot of per cent decomposition vs initial pressure for the tests run at 355°C for 31 min is shown in Figure 1. The slope of the line was determined by the method of least squares.

1. If the reaction were of the first order, the extent of decomposition would be independent of initial pressure; since the data have a definite trend with pressure it becomes apparent that an order of higher magnitude is involved. Decomposition tests made for periods of 20 and 45 min at 355°C over a range of initial pressures again demonstrate that the order must be higher than first, the per cent decomposition being dependent upon the initial pressure. The results of these tests are shown in Figures 2 and 3.

2. To determine what order would best represent the course of the reaction, the data were substituted into the integrated rate equations for orders varying from one-half to two. It was found that the results were best represented by an order of 1.3 for the tests at 31 min. Values of the 1.3-order rate constants calculated from the data are given in Table II.

3. Previous investigators (References 2 and 3) found that a first-order law held at low pressures (200 to 400 mm) and at temperatures above 400°C. However, it was also noted by Taylor and Vesselovsky (Reference 2) that below 350°C the reaction deviated somewhat from a first-order law and assumed a higher order when the initial pressure was increased from 100 to 300 mm. By extrapolating the plot of Cottrell, Graham, and Reid for ($\log_{10} k$) vs ($1/T$) to 355°C (their lowest temperature is 380°C), and substituting the value of the first-order constant, k , thus obtained in a first-order equation, it is found that the per cent of decomposition at 300 mm pressure, for a 31-min reaction time, is 13.7%. If the present data are extrapolated from the lowest pressure studied (76 psia) to 5.7 psia or approximately 300 mm, a value of 18.4% decomposition is obtained. Considering the differences in orders and the extrapolations in temperatures and pressures, the agreement is good. The results obtained at high pressures in the present work are therefore consistent with those obtained at lower pressures.

4. The data for the 45-min decomposition tests follow very closely a 1.3-order law, although a somewhat higher order would also fit. The test results of the 20-min decomposition experiments seem to be somewhat better represented by a 1.5-order law than by a 1.3-order law. Since the number of test results on the 20- and 45-min runs is relatively limited, additional tests will be necessary to determine whether these differences are real.

* The test results with packed ampoules were also corrected and are shown in Table I.

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5. It is also planned to conduct further tests at different time intervals in order to obtain curves relating the extent of decomposition to time. This will make it possible to use the differential method for determining the order of the reaction, which is considered to be more sensitive than the method of integration. A further advantage of this method is that the initial rate of the reaction is obtained immediately by extrapolation. This initial rate is independent of the influence of the reaction products on the disappearance of nitromethane.

C. EFFECT OF ADDED NITRIC OXIDE

During the last report period it was shown that nitric oxide is found in the partially decomposed nitromethane samples, but not in those completely decomposed. Because nitric oxide is a known chain inhibitor there exists the possibility that it disappears by reacting with free-radical chain carriers. If this were so, the addition of a small amount of nitric oxide might affect the rate of decomposition of nitromethane. It was reported previously (Reference 3) that at subatmospheric pressures the addition of nitric oxide did not affect the reaction significantly, when it was studied by the manometric method. Decomposition tests were carried out with added nitric oxide in order to determine whether the same behavior is followed at the considerably higher pressures employed in this investigation and whether a direct analysis of the amount of nitromethane reacted would reveal any effect of nitric oxide. The results are shown in Table III and Figure 1. It is seen that, at a concentration of 1%, nitric oxide does not affect the decomposition of nitromethane. Mass-spectrometer analyses were made to determine whether the addition of a small amount of nitric oxide affected the products of the reaction (Section D,2). The conclusions to be drawn from the experiments with added nitric oxide are discussed in Section E.

D. PRODUCTS OF THE REACTION

1. Analytical Procedures

a. It had been observed that mass peaks corresponding to certain nitromethane decomposition products were found in the spectrograms of stock nitromethane. These peaks could not be removed from the spectrograms by repeated purification of the nitromethane, but were found to decrease in successive runs of the same nitromethane standard sample. Analysis of the same sample on different days always showed a higher concentration of these extraneous peaks in the first run. Conditioning the mass-spectrometer tube by flushing it with butene overnight reduced the relative heights of the peaks and stabilized their distribution. A considerably larger reduction in the relative heights and distribution of these extraneous peaks was accomplished by the installation of a new filament for the electron gun, but they were not removed completely. From this evidence it was assumed that the occurrence of these peaks in spectrograms of pure nitromethane was largely the result of secondary processes in the mass-spectrometer ion source, and was not an indication of impurities in the sample. Since, for pure nitromethane, the magnitude and distribution of these peaks is fixed for any

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particular electron gun and focusing arrangement in the ion source, the apparent composition of partially decomposed nitromethane can be corrected for this effect.

b. The distribution of reaction products previously reported (Reference 1) was determined by the simultaneous analysis of all the constituents in the mass-spectrometer. Although this method was fairly satisfactory, it was believed that the accuracy of both the qualitative and quantitative analyses could be improved by separating the sample into several fractions and analyzing each fraction.

(1) The fractionation of the samples was carried out in a vacuum system which consists of an ampoule breaker, a trap, a Toepler pump, and an expansion volume equipped with a manometer (Figure 4). The sample could be introduced directly into the mass spectrometer expansion volume via a three-way stopcock.

(2) The following procedure was used for the analyses of samples 76 and 92. The system was evacuated with the ampoule in place. Stopcocks J and K were closed, the trap D was cooled with liquid nitrogen, and the ampoule was broken. After temperature equilibrium was established, stopcock J was opened, the non-condensable gases were pumped by means of the Toepler pump into the expansion volume C, and the pressure was noted. The sample was introduced into the mass-spectrometer expansion volume and analyzed. Stopcock J was closed, the system was evacuated, and a new coolant was placed around the trap. Temperatures of -196, -150, -110, -78, and -40°C were used in the fractionation just described.

(3) By fractionating the sample in this manner it was possible to obtain unambiguous results for methane, which, when present in small concentration, was completely masked by the ion fragments of nitromethane, nitrogen, carbon dioxide, etc. The analysis for the complete sample was obtained by combining the results of all fractions.

2. Results

a. The distribution of reaction products in two samples analyzed in this manner is given in Table IV. The agreement between the two analyses is fair. In Run 76, 1% NO had been added to the nitromethane; it is evident from Table IV that its effect on the distribution of reaction products is within the experimental error of the determinations. The data for each run are self-consistent; this is evident from an inspection of the material balance in Table IV. The ratios C:N:O:H in nitromethane are 1:1:2:3, and the same atomic ratios should hold for the products. The fact that these ratios hold quite well for both samples is additional evidence that the method of fractionating samples prior to analysis is capable of giving better results than had previously been obtained.

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b. In addition to the major decomposition products listed in Table IV, other materials which have been identified only tentatively, have been found in trace amounts. There is some evidence that very small amounts of ethylene, formaldehyde, and possibly cyanogen (C_2N_2) are present. Another material also seems to be present which has its major peaks at masses 52 and 54, and may have its parent peak at mass 70. The peaks, however, are too small to be measured accurately, and no identification can yet be made.

c. In order to increase the amount of information obtainable from each decomposition run, the residual gases were collected from ampoules that were broken for polarographic analyses. The samples thus obtained consisted of materials which were volatile at $-78^\circ C$, and were analyzed without further fractionation. They consisted of N_2O , NO , N_2 , CO_2 , CO , and CH_4 . Any small amounts of HCN , CH_3CN , or CH_3NO_2 were disregarded in the calculations. Their presence in the samples indicated that condensation had not been complete in the trap, but had no bearing on the relative amounts of the various materials which were volatile at $-78^\circ C$. The amounts of nitromethane found corresponded to approximately 0.5% of the total that was analyzed polarographically, and hence were well within the error of the polarographic analysis. The results of the analyses of samples obtained in this manner are tabulated in Tables V through VIII. Table V consists of data for three 20-min decomposition runs. The agreement between results on the two samples which decomposed at similar initial pressures is very good; the results on the third sample, No. 85, which was run at almost twice as great an initial pressure, deviate considerably from the others. A fairly large air correction had to be applied to the data for Run No. 85 which might result in abnormally high values for both nitrogen and carbon monoxide, and correspondingly lower values for the other components. It is probable, however, that at least part of the decrease in the observed NO concentration is real and caused by the difference in initial pressure, inasmuch as similar pressure dependence was also observed in the 31-min runs.

d. Table VI lists the results for four 31-min runs. Two runs performed previously are included in this table; they were analyzed without fractionation and CH_4 and N_2O were not detectable. For ease in the comparison of these values, the data for the recent tests have been recalculated to exclude CH_4 and N_2O , and are given in parentheses after those actually found. Again the agreement is very good for samples with approximately the same initial pressure; the NO concentration drops significantly on going from a lower to a higher initial pressure. The analysis of Run 32 is in complete disagreement with the others. Since this was the first decomposition sample to be analyzed, it is possible that initial difficulties with the experimental technique are to blame; however, there is no definite proof for this supposition and the data cannot be excluded until more test results are available.

e. Table VII includes two 31-min runs in which 1% NO was added to the nitromethane. Two 45-min runs are listed in Table VIII.

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3. Discussion

It can be seen from the data that the agreement between runs made at similar initial pressures and carried out for the same length of time is good. The validity of the data is further supported by the fact that the results obtained from the samples in which only the products which were volatile at -78°C were analyzed agree well with those from samples for which complete analyses were carried out. The data in Tables V and VI indicate that the concentration of NO, relative to the concentration of other materials which were volatile at -78°C , depends on the initial nitromethane pressure. Since Cottrell et al. (Reference 3) found that the NO concentration decreased with increasing per cent decomposition of nitromethane, it was of interest to determine whether the data obtained in this study corroborated their findings. Table IX correlates all of the Aerojet data on runs at similar initial pressures. It can be seen from this tabulation that the relative NO concentration depends on the duration of the decomposition run. This is particularly evident from a comparison of the data for the 31- and 45-min runs. Further work is planned to confirm and extend these observations.

E. MECHANISM

1. Introduction

As shown by the diversity and number of the products, and the non-integral order of the thermal decomposition of nitromethane, the overall reaction is extremely complex. It is therefore of interest to discuss some of the reactions that may be important in the process, to evaluate the evidence for these reactions as it is presented by this and previous investigations, and to suggest experiments that will clarify the mechanism further.

2. Free-Radical Mechanisms

a. Taylor and Vesselovsky (Reference 2) assumed a split of an N-O bond for the first step of the reaction:



It was later pointed out by Cottrell et al. (Reference 3) that this step is unlikely from the standpoint of energy, as a minimum energy of 70 kcal would be required to break the N-O bond. They proposed that the first step in the reaction is a split of the C-N bond because the fission of this bond requires an energy of only 52 kcal:



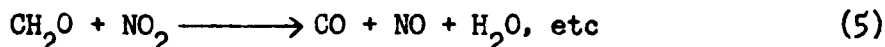
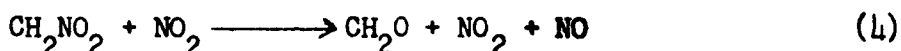
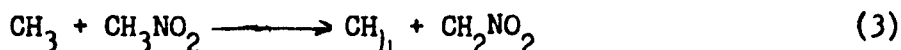
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Fréjacques (Reference 4), using a different value for the heat of formation of nitromethane (-17.6 kcal), arrived at a value of 57.8 kcal for the heat of reaction of Equation (2). Cottrell's heat of formation of nitromethane (-12.2 kcal) is perhaps the more accurate. It agrees with the value accepted for the tables of thermodynamic constants of the Bureau of Standards for 1952. Even if the higher value is taken, fission of the C-N bond appears to be more likely as the first step than fission of an N-O bond.

b. On the basis of pressure measurements, Taylor determined an overall activation energy of 61 kcal, Cottrell 53.6 kcal, and Aerojet (Reference 5) 53 kcal. Fréjacques, studying the reaction at much lower pressures, found activation energies varying from 40 to 46 kcal as the initial pressure was varied from 4 to 30 mm Hg. Hillenbrand and Kilpatrick (Reference 6), studying the reaction in the flow system in the presence of a large excess of nitrogen, found an activation energy of 50 kcal on the basis of nitromethane analyses. Except for the somewhat high value of Taylor and the low values of Fréjacques, the activation energies seem to be between 50 and 53 kcal. The low activation energies of Fréjacques may be connected with the low pressures he employed. He also states that the reaction was heterogeneous to the extent of 6 to 10%, which may account in part for his values. The high value of activation energy obtained by Taylor is difficult to explain. If the activation energy is between 50 and 53 kcal, a non-chain-radical mechanism involving initial fission of the C-N bond (53 kcal) appears to be reasonable. Cottrell lists several reactions which he considers probable and which follow such a course:



c. If the higher value for the energy necessary to split the C-N bond (57 kcal) as proposed by Fréjacques is the correct one, the occurrence of a chain reaction would be indicated. It becomes important, therefore, to determine whether free-radical chains are involved. One method frequently used in the determination of chains is the addition of small amounts of nitric oxide or propylene, which are chain inhibitors. Previous investigators (Reference 3) had studied the influence of added nitric oxide at subatmospheric pressures of nitromethane, employing the manometric method. They found no inhibition. The effect of propylene under similar conditions was investigated in this laboratory (Reference 5); no appreciable inhibition could be detected. The results obtained in the present investigation with high pressure, by actual analysis of the per cent nitromethane decomposed

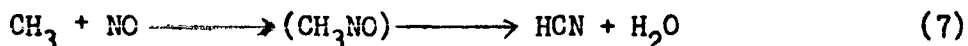
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with and without added nitric oxide (Section II,C) again show that no inhibition occurs. The conclusions to be drawn from this behavior, however, are not unequivocal. It has been found in a number of studies of thermal decomposition (Reference 7) that the extent of inhibition can be increased only to a limiting value by increasing the concentration of inhibitor, and that further addition is ineffective. In some cases, notably those of acetaldehyde and acetone, the rate of decomposition is first decreased and then accelerated as the concentration of the nitric oxide is increased. It is quite possible, therefore, that there is actually a chain reaction during the decomposition of nitromethane, but that the amount of nitric oxide formed during the decomposition is sufficient to cause maximum inhibition. Further addition would therefore be ineffective. Fréjacques, in his work at very low pressures, reported a slight inhibition with small concentrations of nitric oxide and an acceleration of the rate as its concentration was increased, just as with acetaldehyde.

d. In this investigation it is planned also to study the effect of larger concentrations of nitric oxide, in order to ascertain whether larger amounts will increase the rate in the case of high nitromethane pressures, and to determine how the products will be affected. Kuchler and Theile (Reference 8) obtained evidence for the formation of hydrogen cyanide by the reaction of methyl radicals and nitric oxide:

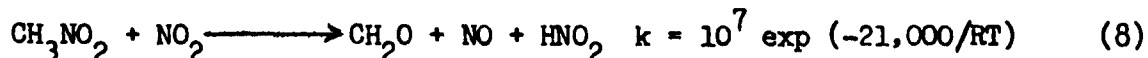


If the addition of large amounts of nitric oxide to nitromethane should therefore result in the production of more hydrogen cyanide, evidence would be provided for the occurrence of the above reaction.

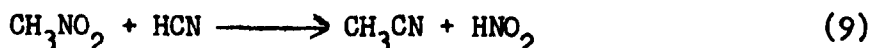
3. Molecular Mechanisms

a. In addition to the above considerations, it should be pointed out that a molecular mechanism may also be operative, or what is perhaps more likely, that a molecular mechanism may occur in addition to a free-radical mechanism. If the activation energies of the two modes of reaction were similar, one would obtain approximately the same activation energy regardless of whether either one or both mechanisms are operative.

b. For example, it has been shown that nitrogen dioxide reacts with nitromethane as follows (Reference 9):



Another possibility is that nitromethane reacts with hydrogen cyanide:



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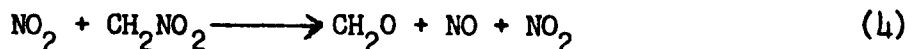
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Both hydrogen cyanide and acetonitrile are products of the decomposition of nitromethane. Nitrous acid cannot be identified; however, it is very unstable even at room temperature, as shown by the work of Wayne and Yost (Reference 10), who studied the reverse reaction. As it is known also that aromatic nitro compounds react with hydrogen cyanide in a manner analogous to reaction (9), one may perhaps expect that aliphatic nitro compounds would react in a similar manner at the temperatures employed in this investigation. On the basis of data on bond strength the reaction appears to be endothermic by less than 10 kcal, and can therefore, not be ruled out on the basis of the observed activation energy. It is planned to study the effect of the addition of hydrogen cyanide to nitromethane. If reaction (9) is important, an increase in the rate of disappearance of nitromethane should be observed and more acetonitrile should be found. Also, a comparison of the variation of apparent order of the reaction as a function of extent of decomposition may offer some evidence with respect to the occurrence of this or similar reactions.

c. In regard to the question of whether the decomposition of nitromethane takes place at least partly by a non-radical mechanism, the work of Hillenbrand and Kilpatrick (Reference 6) should be examined. In that investigation the reaction was studied in a flow system in the presence of large amounts of nitrogen used as a carrier gas. It was found that considerable quantities of formaldehyde are formed, which decrease to a limiting value as the reaction proceeds. In previous static experiments, however, no formaldehyde could be detected. In the present study also, not more than a trace of formaldehyde was found. In order to account for the differences, Hillenbrand suggests that since their experiments were carried out at higher temperatures, the rate of decomposition of nitromethane is in part determined by an intramolecular rearrangement that leads to the formation of formaldehyde, and that it increases in importance at the higher temperatures. There are alternative explanations, however, which do not involve an intramolecular rearrangement of nitromethane. One is that under the conditions of the static experiments the rate of decomposition of formaldehyde is greater than in the case of the flow experiments. Another is that formaldehyde can also be formed by a direct rearrangement of the radical CH_2NO_2 , as follows:



This reaction would involve somewhat more rearrangement than



if the latter reaction is assumed to take place through an activated complex (Reference 3). It appears likely that in the presence of a large excess of nitrogen, reaction (10) is favored, as the number of collisions with reactive molecules such as nitromethane and its products would be diminished. During collisions with nitrogen molecules the radical would either remain intact or undergo reaction (10). This explanation is in accord with the relatively high stability toward dissociation of the radical CH_2NO_2 as compared with that of

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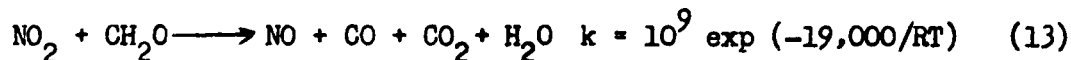
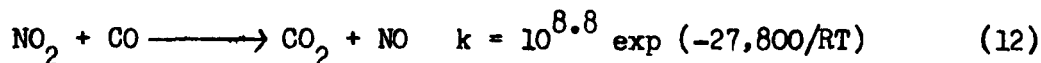
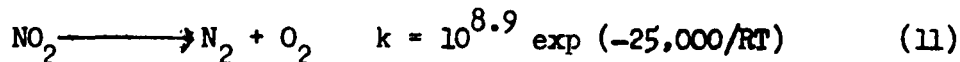
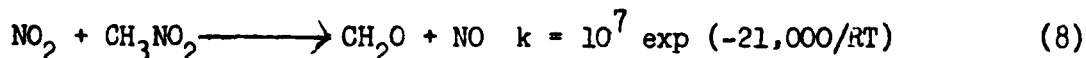
CH_3NO_2 . Thus, the radical CH_2NO_2 will be stabilized because of the possibility of resonating forms involving a $\text{C}=\text{N}$ bond, which would be unimportant in nitromethane. The radical should in fact be more stable than nitromethane itself, although, being a radical, it would of course be more reactive than nitromethane. One would therefore expect that in the presence of reactive molecules it would react before undergoing decomposition according to (10). The relatively high stability of the radical has another important consequence. It may be one reason that the thermal decomposition of nitromethane seems not to be a chain reaction, or at least not one involving long chains. If this radical were relatively unstable it could decompose to CH_2 and NO_2 and continue the chain. It would then be comparable to the acetyl radical, CH_3CO , which is very unstable. Whenever the latter is formed, as in the thermal decomposition of acetaldehyde, it decomposes to CH_3 and CO , and continues the chain.

4. Discussion of Certain Decomposition Products

a. Nitrogen Dioxide

(1) If the primary decomposition occurs by fission of the $\text{C}-\text{N}$ bond as postulated in Paragraph E,2,a, one might expect to find nitrogen dioxide among the products. The fact that it was not found in this investigation is not evidence against this primary step, as the discussion below will show.

(2) Both Cottrell and Hillenbrand report very small amounts of nitrogen dioxide. In this investigation no nitrogen dioxide could be detected. Because the carbon-to-nitrogen ratio of the products was found to be close to that of nitromethane (Section C,2), it is not probable that appreciable amounts of nitrogen dioxide could have remained undetected. In any event, the amount of nitrogen dioxide appears to be small. An examination of the reactions by which nitrogen dioxide can be removed may explain this situation (References 9, 11, 12, 13 and 14):



Reaction (13) becomes explosive above 180°C . All the above reactions have relatively low activation energies, but in the presence of formaldehyde, nitrogen dioxide would probably be removed mainly by reaction (13).

b. Nitric Oxide

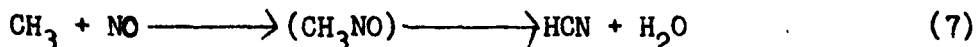
(1) The mass-spectrometer analyses of the products indicate that the concentration of nitric oxide is dependent on both the

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II Kinetic Study of the Thermal Decomposition of Nitromethane, E (cont.)

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reaction time and the initial pressure of nitromethane (Section C,2). The dependence on time is to be expected, as nitric oxide is not found among the final products of the reaction (Reference 1). Since the thermal decomposition of nitromethane at high pressures appears to follow a 1.3-order law, identical time intervals for different initial pressures represent different percentages of decomposition. This may account for some of the dependence on pressure, but does not seem to be the only cause, as the percentage decomposed increases by less than 10% from the lowest to the highest nitromethane pressure studied (Figure 1), whereas the nitric oxide concentration varies by approximately 50%. It is difficult to say at present whether the rate of formation or the rate of decomposition of nitric oxide is pressure-dependent. Because nitric oxide disappears during the course of the reaction, it becomes important to examine the ways in which it may be removed. The reaction



has already been discussed (Section E,2,c). The following reaction may also take place:



It is not certain what the products would be. The formation of nitrous oxide is one possibility, but nitrogen, oxygen, and formaldehyde would perhaps be more likely products. The thermal decomposition of nitric oxide itself is less likely. This is shown by an extrapolation of the data of Wise and French (Reference 15) to the lower temperatures employed in this investigation. The calculated amount of decomposition occurring at 355°C is very slight. As a check on the calculations, a small amount of nitric oxide in an ampoule was allowed to remain in the furnace for 31 min at 355°C and was subsequently analyzed in the mass-spectrometer. No decomposition could be detected. However, the possibility is not excluded that nitric oxide is removed by reaction with O and N atoms supplied by other reactions, as it has been postulated that nitric oxide decomposes by a chain mechanism involving these atoms (References 15 and 16).

(2) Behrens (Reference 17) has shown that nitric oxide reacts with C_2 and CH in flames as follows:



He suggests that when nitric oxide reacts with other radicals, one of the products may also be carbon monoxide. It is possible that some of the nitric oxide formed during the decomposition of nitromethane disappears by a reaction that results in the formation of carbon monoxide. The data obtained in the present study do not exclude such a reaction. As was discussed previously, the addition of relatively large amounts of nitric oxide (10 to 15%) to nitromethane may further clarify the reactions which it undergoes.

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II Kinetic Study of the Thermal Decomposition
of Nitromethane, E (cont.)

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c. Methane

In this study it has been found that methane is one of the minor products of the decomposition. Only 0.04 mole of methane is formed for one mole of nitromethane decomposed. The reaction scheme of Cottrell, Graham, and Reid (reactions 2 to 6) requires the production of 0.5 mole of methane, but these investigators find only 0.3 mole per mole of nitromethane. They ascribe this deficiency to possible polymerization reactions. In the high-pressure experiments the difference is too large to be the result of the formation of polymers. Methane itself does not decompose thermally at 355°C. Harnsberger (Reference 9) found that methane and nitrogen dioxide react to give nitromethane. It is not likely that methane would disappear by this reaction, as the concentration of nitrogen dioxide is very low. One way for methyl radicals to disappear without forming methane or ethane is for them to take part in a mechanism leading to the production of acetonitrile, CH_3CN . The amount would not be sufficient, however, to account for all the methyl radicals. It is thought possible that the relatively large amounts of carbon dioxide found in this investigation may be connected with the low yield of methane.

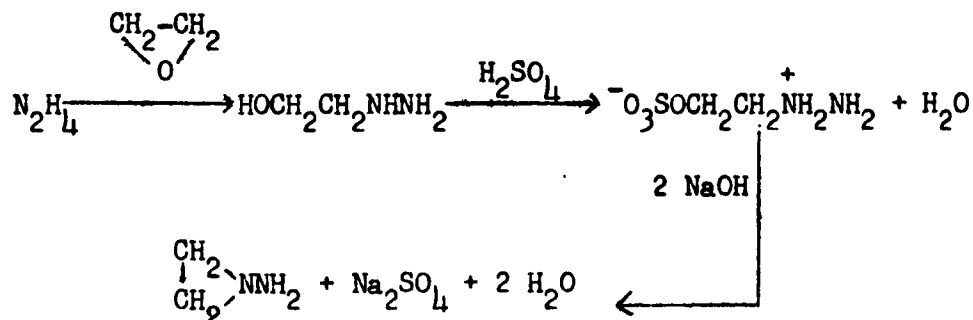
III. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

A. INTRODUCTION

Work on the preparation of new rocket propellants has been concerned with the preparation and characterization of the new fuel N-amino-ethylenimine. The importance of this compound as a rocket fuel lies in the fact that its estimated specific impulse with oxygen surpasses that of hydrazine, and that its freezing point appears to be sufficiently low that it can be used without an additive.

B. METHODS OF PREPARATION OF N-AMINOETHYLENEMINE

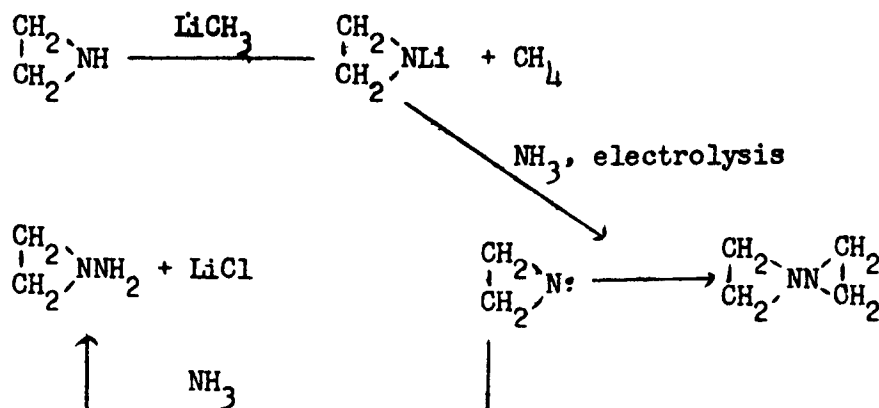
1. The dehydration of ethanolhydrazine with sulfuric acid has been given primary consideration as an economical and convenient method for the preparation of N-aminoethylenimine:



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III Research on the Preparation of New Rocket Propellants Report No. 690
B (cont.)

2. A further possible method for the preparation of N-aminoethylenimine is based on the fact that ethylenimine forms an N-lithium derivative which might be electrolyzed in liquid ammonia:



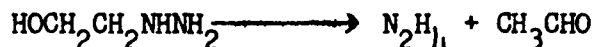
The synthesis of nitroethylenimine by the action of ethyl nitrite on ethylenimine in ethanol solution, with subsequent reduction, also exists as a possible method of preparation. Work has been started on this latter reaction, but results are not yet available.

C. PURITY OF SYNTHESIZED N-AMINOETHYLENIMINE

1. It has been determined that the product obtained from the dehydration of ethanolhydrazine contains materials other than N-aminoethylenimine. This is indicated by the following analysis of the product after it had been distilled twice at 100 mm and a middle cut obtained:

	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>Total</u>
Found	42.01 41.93	10.65 10.71	42.10 42.22	94.76 94.86
Calculated for C ₂ H ₆ N ₂	41.36	10.41	48.23	100.00

If the low nitrogen analysis is attributed to the presence of oxygen, a reasonable source of the impurity is the decomposition of ethanolhydrazine during some stage of the synthesis:



If the quantity of acetaldehyde present in the derived N-aminoethylenimine is about twice that of the hydrazine, the carbon and hydrogen contents are not appreciably affected, in conformance with the above analytical results.

2. The presence of hydrazine in the analyzed product was confirmed by treating an aqueous solution of the product with sulfuric acid. The slightly soluble hydrazine sulfate, N₂H₄·H₂SO₄, was obtained. On treating

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III Research on the Preparation of New Rocket Propellants,
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the filtrate with 2,4-dinitrophenylhydrazine, acetaldehyde 2,4-dinitrophenylhydrazone was obtained. The hydrazone sulfate recrystallized from water had a melting point of 250 to 251°C (lit. 254°C). The hydrazone was recrystallized three times from 95% ethanol, once from 60% ethanol, and once from benzene, and melted at 158 to 159°C (lit. 164°C). The discrepancy in melting point noted here is attributed to the fact that this compound strongly occludes impurities, and can only be obtained in pure condition when pure acetaldehyde is used in preparing the hydrazone, and when the carbonyl compound is present in excess (Reference 18).

3. In order to determine in which step decomposition occurs, samples of ethanolhydrazine and the crude ester derived from it were treated with 2,4-dinitrophenylhydrazine. If the impurity is assumed to consist entirely of acetaldehyde, it was found that the ethanolhydrazine contained 1.26% acetaldehyde; on redistillation of the aldehyde content was reduced to 0.54%. The sulfuric acid ester (prepared from the redistilled ethanolhydrazine) contained only 0.24%. The extent to which acetaldehyde and hydrazine are present in the final product has not been precisely determined, but it appears that these materials occur to the extent of several per cent. Consequently, appreciable decomposition must occur in the conversion of the ester to the desired product. This was confirmed by decomposing a sample of the ester of low aldehyde content. The crude reaction product gave a heavy precipitate with 2,4-dinitrophenylhydrazine after removal of basic materials with sulfuric acid.

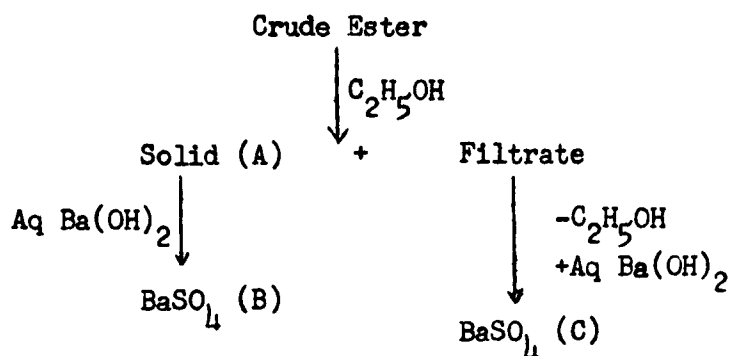
4. One source of difficulty in obtaining pure N-aminoethylenimine from ethanolhydrazine has been the inability to obtain the sulfuric acid ester in pure form; heretofore (Reference 1) the crude, glassy ester has been used directly in the subsequent reaction. It was realized that the use of an impure ester might well afford the impure product obtained and, accordingly, a renewed effort was made to obtain the ester in pure condition. It was found that this could be accomplished by thorough digestion of the crude ester with absolute ethanol. A sample of the crude product was placed under ethanol, porcelain marbles were introduced, and the mixture was stirred vigorously for two days. The yellow color was transferred to the ethanol, and a crystalline white solid remained, mp 65 to 130°C. This was further digested with boiling methanol for two hours. The residue, when recrystallized twice from an ethanol-water mixture, gave a product melting at 123 to 124°C. Its aqueous solution was slightly acidic to litmus, and gave no precipitate with barium chloride; an acid solution liberated iodine from potassium iodate. There are the properties to be expected of the desired ester, $^{-}O_3SOCH_2CH_2^{+} - NH_2NH_2$. Absolute ether was added to the methanol extract and afforded a compound which, after two recrystallizations from ethanol, gave a melting point of 72 to 74°C. This was shown to be ethanolhydrazine sulfate by mixed-melting-point determinations (at three compositions) with the pure compound, prepared by mixing ethanolic solutions of sulfuric acid and ethanolhydrazine at room temperature. On recrystallizing twice from absolute methanol the pure compound was obtained, mp 73 to 74°C.

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C (cont.)

5. The isolation of the pure ester in this manner made possible a direct analysis of the crude ester for $\text{O}_3\text{SOCH}_2\text{CH}_2\text{NH}_2\text{NH}_2^+$, the salt $(\text{HOCH}_2\text{CH}_2\text{NH}_2\text{NH}_2)(\text{HSO}_4)^-$, and unreacted H_2SO_4 . The analysis is based on the use of barium hydroxide solution, as indicated in the following diagram:



The solid A affords the weight of ester plus salt (i.e., ethanolhydrazine sulfate); B affords the weight of the salt directly, and hence the weight of ester; C affords the weight of residual sulfuric acid. The weight of A was corrected for solubility in ethanol. In another experiment it was found that about 95% of A could be recovered as the ester and the sulfate compound. An additional sample of the crude ester was analyzed for aldehyde with 2,4-dinitrophenylhydrazine. The results of the analysis for the crude ester obtained by heating sulfuric acid and ethanolhydrazine at 115°C and 5 mm for 15 min are as follows:

Component	Wt% Found
H_2SO_4	6.7
$(\text{HOCH}_2\text{CH}_2\text{NH}_2\text{NH}_2)^+(\text{HSO}_4)^-$	6.4
$\text{O}_3\text{SOCH}_2\text{CH}_2\text{NH}_2\text{NH}_2$	70
Aldehydes (as CH_3CHO)	<1.0
Residue	~16

The residue is assumed to consist of the ether formed from the dehydration of two molecules of ethanolhydrazine, and of various oxidation products.

D. SYNTHESIS OF THE SULFURIC ACID ESTER OF ETHANOLHYDRAZINE

1. While the yield of the desired ester is 70% when ethanolhydrazine and sulfuric acid react at 115°C, the isolation of the ester is tedious, and it was therefore desirable to synthesize the ester in another manner if possible.

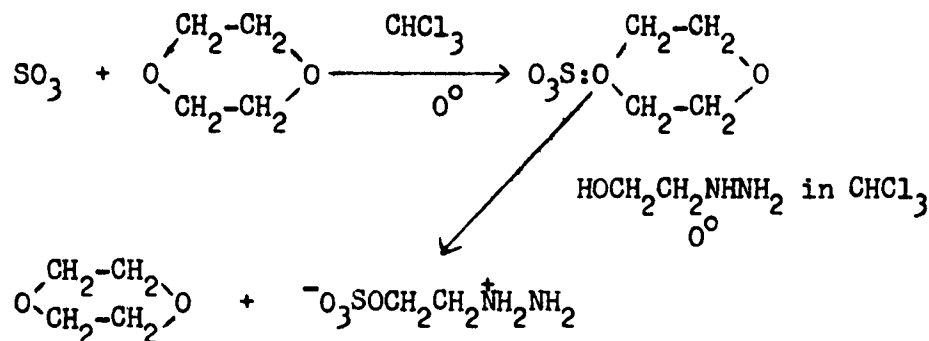
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III Research on the Preparation of New Rocket Propellants,
D (cont.)

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2. Rollins and Calderwood (Reference 19) report that the ester $^{-}O_3SOCH_2CH_2NH_3$ can be obtained in 95% yield by permitting ethanolamine and concentrated sulfuric acid to react for three days at room temperature. This method was applied to ethanolhydrazine, but afforded only ethanolhydrazine sulfate.

3. A more profitable reaction for the synthesis of the ester was found to be that in which sulfur trioxide in the form of its dioxane complex was used as the sulfating agent (References 20 and 21):



This reaction offers the decided advantage that ethanolhydrazine sulfate cannot form. Moreover, since the reaction is conducted at 0°C , the occurrence of side reactions, such as oxidation, is minimized or eliminated.

a. Sulfur trioxide was distilled from 30% oleum into a rapidly stirred solution of dioxane (0.1 mole) in chloroform (60 ml) at 0°C until a stoichiometric amount of sulfur trioxide had been absorbed. A stoichiometric amount of ethanolhydrazine in chloroform (30 ml) was added dropwise with constant stirring over a period of 1 hr. The solution was filtered, and the white solid was washed with chloroform and finally digested for a short time with ethanol to remove unreacted dioxane complex. The yield was found to be virtually quantitative. A portion of the material recrystallized twice from ethanol-water had a melting point of 122 to 124°C . A mixed melting point (at three compositions) with the material isolated from the reaction of ethanolhydrazine and sulfuric acid at 115°C showed no depression.

b. The decomposition of the pure ester, when prepared in this way, again afforded a product contaminated with aldehydes. It appears reasonable that the impurities are introduced through the saponification of the ester to ethanolhydrazine, which subsequently decomposes. It is therefore planned to investigate the use of solvents other than aqueous caustic in an attempt to find a suitable medium for carrying out the decomposition of the ester.

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III Research on the Preparation of New
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E. PROPERTIES OF N-AMINOETHYLENIMINE

Several properties of N-aminoethylenimine (contaminated to some extent with acetaldehyde and hydrazine) have been described (Reference 1). In addition, molecular-weight determinations by freezing-point lowering in benzene show that no polymerization of the material occurs during a period of 9 days at 155°F. It is intended to redetermine the physical properties of a pure sample of N-aminoethylenimine as soon as this is available.

IV. STUDY OF IGNITION DELAY OF TRIETHYL TRITHIOPHOSPHITE WITH NITRIC ACID

Results of the determination of the ignition delays of solutions of triethyl trithiophosphite containing 0, 10, 20, and 30 vol% n-heptane with specially adjusted nitric acid are given in Reference 22. Difficulty was encountered in obtaining reproducible values when 30% of the non-hypergolic diluent was present, and since the small rocket starter motor and associated instrumentation was being repeatedly damaged by excessive pressure rises, no tests were made with the solution containing 40% n-heptane. The pure fuel and solutions containing up to 20 vol% diluent give sufficiently short ignition delays at the test temperatures of 75, 32, and -40°F for the material to be used as a hypergolic fuel or as a starter fluid for non-hypergolic combinations.

V. IMPROVEMENT OF DINITROGEN TETROXIDE AS A ROCKET PROPELLANT

The results of the addition of various ethers and nitro derivatives to dinitrogen tetroxide have been previously reported (References 1 and 23). It was the purpose of this investigation to determine the degree of deviation from ideal freezing-point depression caused by various functional groups; in this manner an additive might be selected that would produce the required freezing point by the addition of a minimum weight percent. As an extension of this work, samples of dimethylnitrosamine, $(\text{CH}_3)_2\text{NNO}$, and dimethylnitramine, $(\text{CH}_3)_2\text{NNO}_2$, were prepared in the laboratory for the study of their freezing point vs composition curves with dinitrogen tetroxide. Results of the freezing-point studies and the thermal stabilities of the systems are not yet available.

The stability and ether-like properties of the nitrites make them good possibilities as additives to dinitrogen tetroxide. A small quantity of ethyl nitrite has been prepared to note how it differs on a molar basis from nitromethane, a previously investigated additive. If the results are encouraging, ethylene dinitrite, $\text{C}_2\text{H}_4(\text{ONO})_2$, will be synthesized in order to determine the effect of the additional nitrite group.

VI. STUDY OF HYDRAZINE FREEZING-POINT DEPRESSANTS

A. Since the determination of the freezing point curve for the system consisting of hydrazine with unsym.-dimethylhydrazine (Reference 24), it has been learned that the removal of the last 10% of the water from the

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VI Study of Hydrazine Freezing-Point Depressants, A (cont.)

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methylhydrazines is far more difficult than it is with unsubstituted hydrazine, and that the material used in the previous investigation must have contained a relatively large amount of water. A redetermination of this curve was therefore made with anhydrous hydrazine and 97.6% dimethylhydrazine, the results of which are shown in Figure 5. The basic shape of the curve remains the same, but it appears that if no water were present in either component, the freezing point of unsym.-dimethylhydrazine could not be depressed by the addition of hydrazine. The eutectic temperature shown is an experimental halt-point in the cooling curve of the 93% point, although the eutectic composition is estimated.

B. Although the work was not performed on this contract, a sample of unsym.-dimethylhydrazine remaining from the above study of this fuel was furnished to another group for the determination of its ignition delay with nitric acid. Because such information is of interest to this contract it is reported here.

1. The apparatus used for studying the ignition properties of unsym.-dimethylhydrazine was identical with that used for determining the ignition delays of various solutions of triethyl trithiophosphite with nitric acid (Reference 22). The sample of dimethylhydrazine analyzed 95.0% pure by acid titration.

2. Delays recorded at 50°F were 4.5, 5.5, and 6.0 millisecc with AN Specification WFNA containing added water to make the total water content 8%, and 3.5, 4, and 3 millisecc at -65°F with this same acid. Tests made with AN Specification WFNA exhibited ignition delays of 3 and 5 millisecc at -40°F, and 4.5, 4.5, and 5 millisecc at +50°F.

VII. SENSITIVITY OF METHYLACETYLENE

Authorization was received during this report period to proceed with the sensitivity testing of methylacetylene. Equipment for the program was available, but the methylacetylene was not received from the supplier during the period covered by this report.

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TABLE I

THERMAL DECOMPOSITION OF NITROMETHANE

Effect of Surface-to-Volume Ratio

Temperature: 355°C, Duration: 31 min

<u>Run No.</u>	<u>Initial Pressure of Nitromethane psia</u>	<u>% Decomposed</u>	<u>Relative Surface-to- Volume Ratio</u>
73	274	32.1	4-fold increase
74	245	29.0	3.5-fold increase
*	250	26.0	No increase

* Values taken from Figure 1.

Table I

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TABLE II

THERMAL DECOMPOSITION OF NITROMETHANE

Rate Constants for 1.3-Order Reaction

Temperature: 355°C

Duration: 31 min

<u>Run No.</u>	<u>Initial Pressure of Nitromethane psia</u>	<u>$k_{1.3\text{-order}}$ $\text{cc}^{0.3} \text{mole}^{-0.3} \text{min}^{-1}$</u>
83	76	0.122
78	82	0.126
72	92	0.107
71	145	0.104
62	162	0.119
67	177	0.108
55	188	0.130
65	234	0.100
58	246	0.119
80	258	0.130
93	260	0.130
64	263	0.0854
66	288	0.108
61	298	0.119
60	321	0.111
59	366	0.126

Table II

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TABLE III

THERMAL DECOMPOSITION OF NITROMETHANE

Effect of Added Nitric Oxide

Temperature: 355°C Duration: 31 min

<u>Run No.</u>	<u>Initial Pressure of Nitromethane psia</u>	<u>Initial Pressure of Nitric Oxide psia</u>	<u>% Decomposed</u>
75	289	2.7	27.2
94	275	2.7	26.2
*	280	0	27.0

* Values taken from Figure 1.

Table III

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TABLE IV

NITROMETHANE DECOMPOSITION PRODUCTS

Complete Analyses

31-min Runs

Initial Pressure (psia)	<u>Run 76*</u>	<u>Run 92</u>
	289	310
<u>Constituent</u>	<u>Composition, Mole %</u>	
N ₂ O	1.8	1.1
NO	11.1	10.5
N ₂	5.9	4.2
CO ₂	10.5	12.4
CO	7.5	4.8
CH ₄	3.4	1.9
CH ₃ CN	2.0	1.6
HCN	17.2	17.2
H ₂ O	40.6	46.4
<u>Relative Material Balance</u>		
C	1	1
N	1.1	1
O	1.9	2.2
H	2.8	3.1

* 1% NO added to nitromethane.

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TABLE V

NITROMETHANE DECOMPOSITION PRODUCTS

20-min Runs

	<u>Run 82</u>	<u>Run 87</u>	<u>Run 85*</u>
Initial Pressure (psia)	142	151	237
<u>Constituent</u>	<u>Composition, Mole %</u>		
N ₂ O	1.8	1.3	4.0
NO	41.9	41.2	17.5
N ₂	11.9	9.8	21.9
CO ₂	23.1	24.1	25.0
CO	14.0	15.7	26.6
CH ₄	7.3	7.9	5.1

Note: A large air correction was applied to this sample.

*Represents only material volatile at -78°C.

Table V

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TABLE VI

NITROETHANE DECOMPOSITION PRODUCTS

31-min Runs

	<u>Run 78*</u>	<u>Run 32</u>	<u>Run 68</u>	<u>Run 92</u>
Initial Pressure (psia)	82	194	292	310
<u>Constituent</u>	<u>Composition, Mole %</u>			
N ₂ O	0.7 (0)	--	--	3.0 (0)
NO	47.6 (50.9)	18.3	33.3	30.1 (32.9)
N ₂	9.2 (9.8)	22.7	12.8	12.1 (13.2)
CO ₂	25.2 (27.0)	45.4	38.5	35.7 (39.0)
CO	11.6 (12.4)	13.6	15.4	13.7 (15.0)
CH ₄	5.7 (0)	--	--	5.5 (0)

NOTE: Runs 78 and 92 have been recalculated excluding N₂O and CH₄ for comparison with Runs 32 and 68; the values are given in parentheses after the true ones.

* Run 78 represents only material volatile at -78°C.

Table VI

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TABLE VII

NITROMETHANE DECOMPOSITION PRODUCTS

31-min Runs, Nitric Oxide Added

	<u>Run 94*</u>	<u>Run 76</u>
Initial Pressure (CH ₃ NO ₂) (psia)	275	76
Initial Pressure (NO) (psia)	2.7	3.2
<u>Constituent</u>	<u>Composition, mole %</u>	
N ₂ O	2.0	4.5
NO	30.9	27.8
N ₂	14.7	14.7
CO ₂	30.0	26.2
CO	16.0	18.7
CH ₄	6.5	8.2

* Represents only materials volatile at -78°C.

Table VII

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TABLE VIII

NITROETHANE DECOMPOSITION PRODUCTS

45-min Runs

	<u>Run 89*</u>	<u>Run 91*</u>
Initial Pressure (psia)	281	301
<u>Constituent</u>	<u>Composition, Mole %</u>	
N ₂ O	3.9	3.0
NO	20.1	22.8
N ₂	15.5	13.1
CO ₂	35.8	39.6
CO	19.5	16.2
CH ₄	5.4	5.4

* Represents only materials volatile at -78°C.

Table VII

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TABLE IX

NITROMETHANE DECOMPOSITION PRODUCTS

Change with Time

Initial Pressure, 273 to 310 psia

	<u>Run 85</u> *	<u>Run 94</u> ^{††}	<u>Run 76</u> [†]	<u>Run 68</u>	<u>Run 92</u>	<u>Run 89</u> *	<u>Run 91</u> [†]
Time Interval (min)	20	31	31	31	31	45	45
<u>Constituent</u>	<u>Composition, Mole %</u>						
N ₂ O	4.0	2.0	4.5	—	3.0	3.9	3.0
NO	17.5	30.9	27.8	33.3	30.1	20.1	22.8
N ₂	21.9	14.7	14.7	12.8	12.1	15.5	13.1
CO ₂	25.0	30.0	26.2	38.5	35.7	35.8	39.6
CO	26.6	16.0	18.7	15.4	13.7	19.5	16.2
CH ₄	5.1	6.5	8.2	—	5.5	5.4	5.4

* A large air correction was applied to this sample.

† 1% NO was added to the nitromethane.

†† Represents only materials volatile at -78°C.

Table IX

CONFIDENTIAL

C-3365

KHM:em

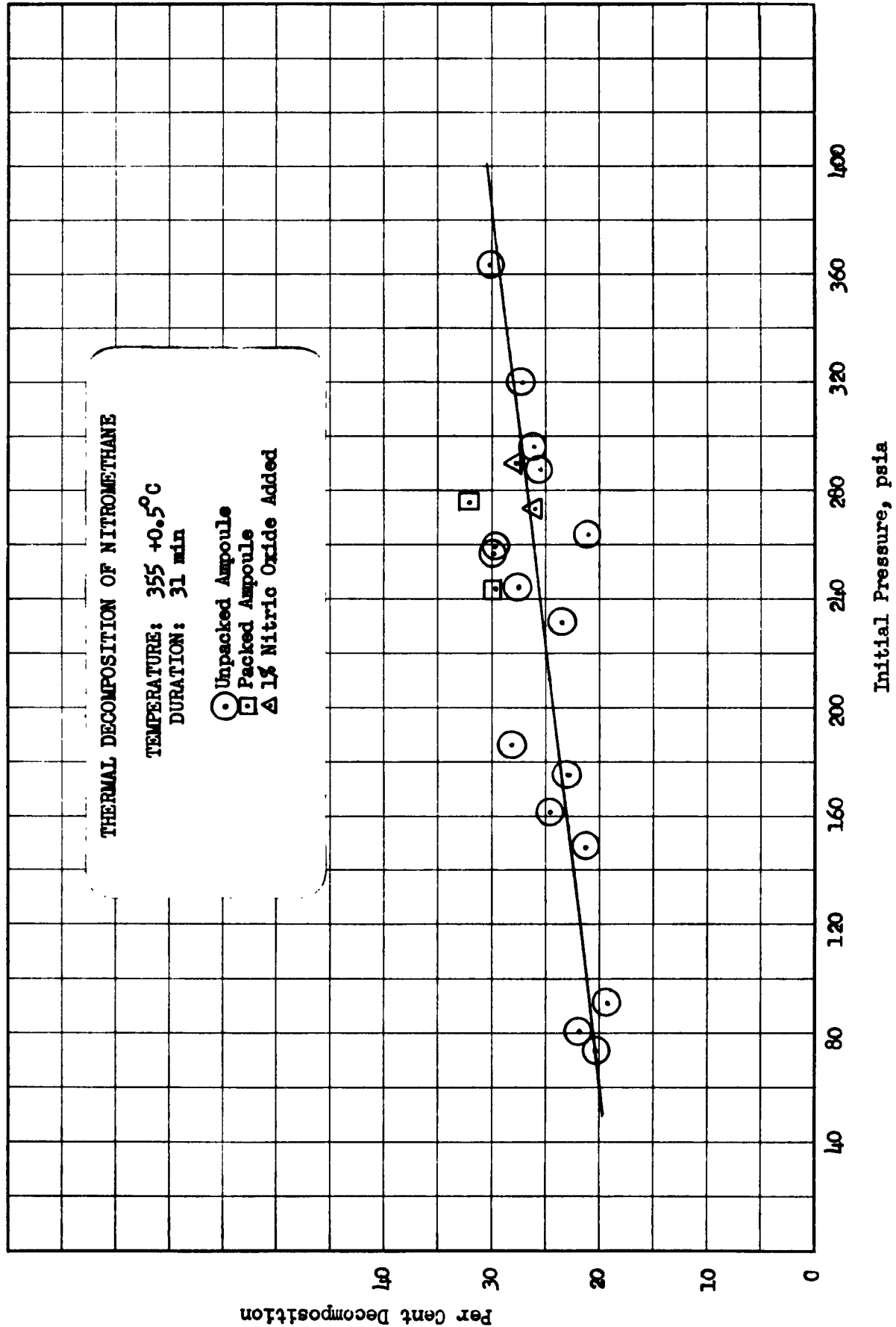
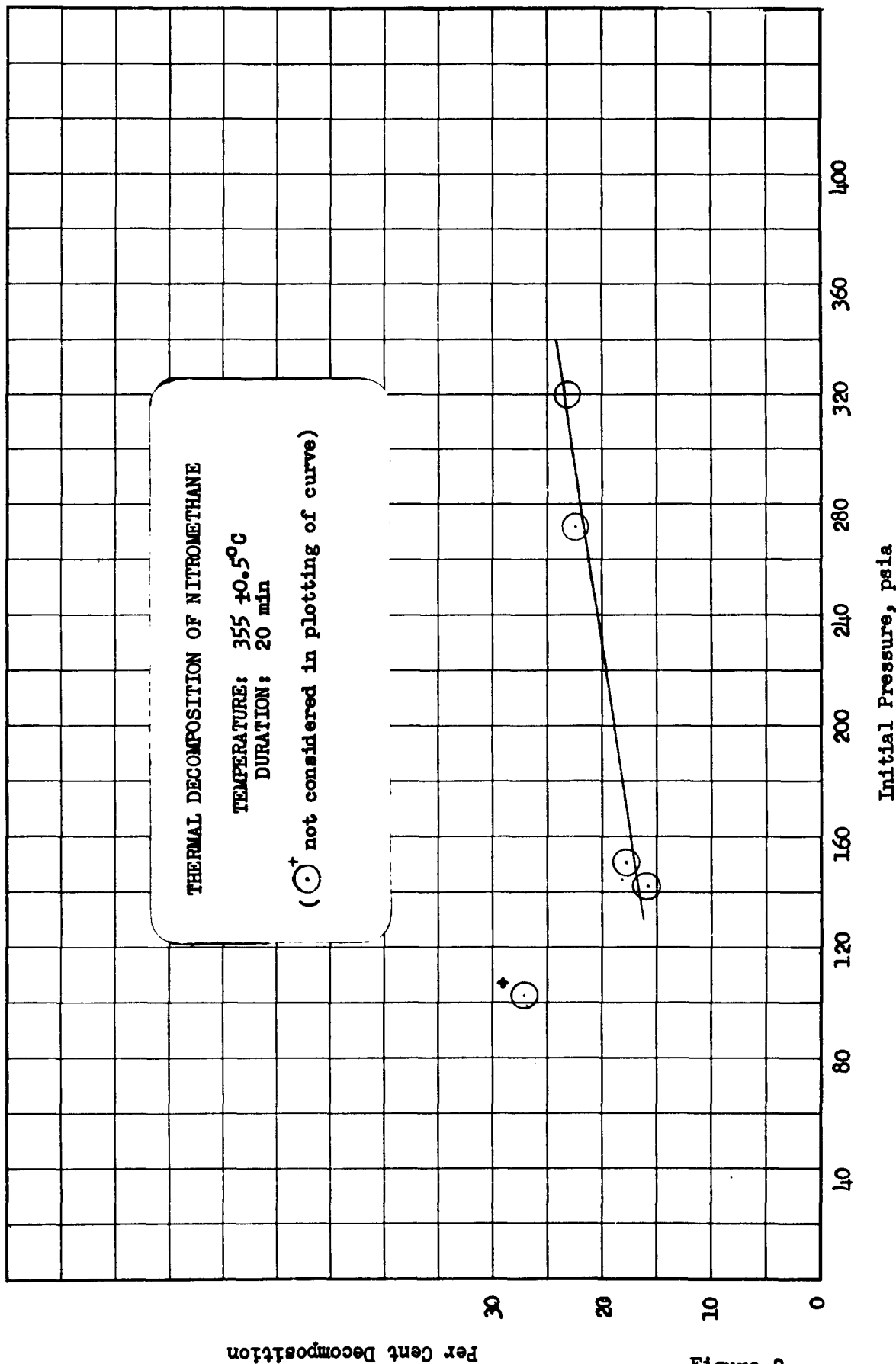


Figure 1

C-3367 KHM:em 2-26-53

C-3367

KHM:em



C-3366 KHM:em 2-26-53

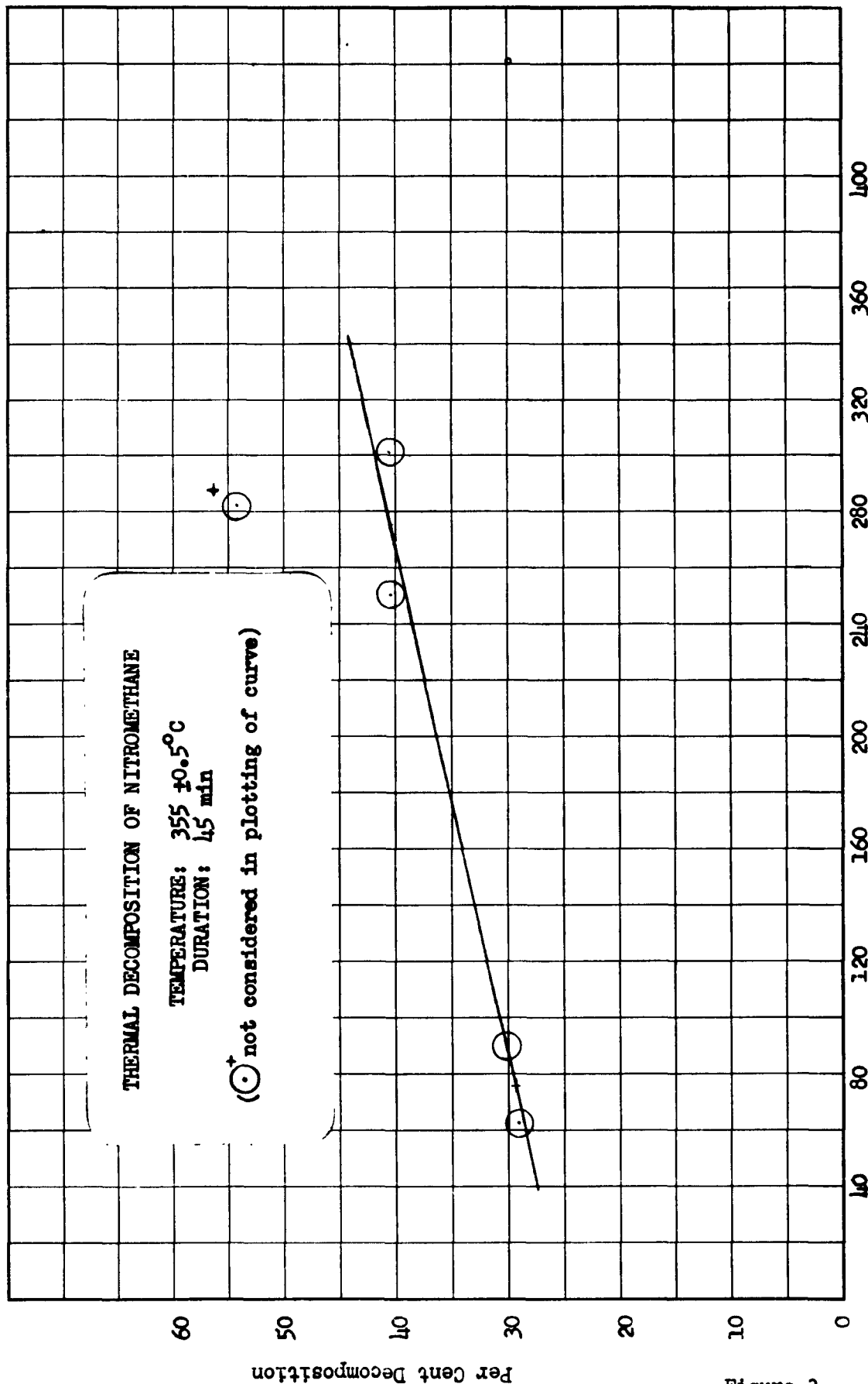
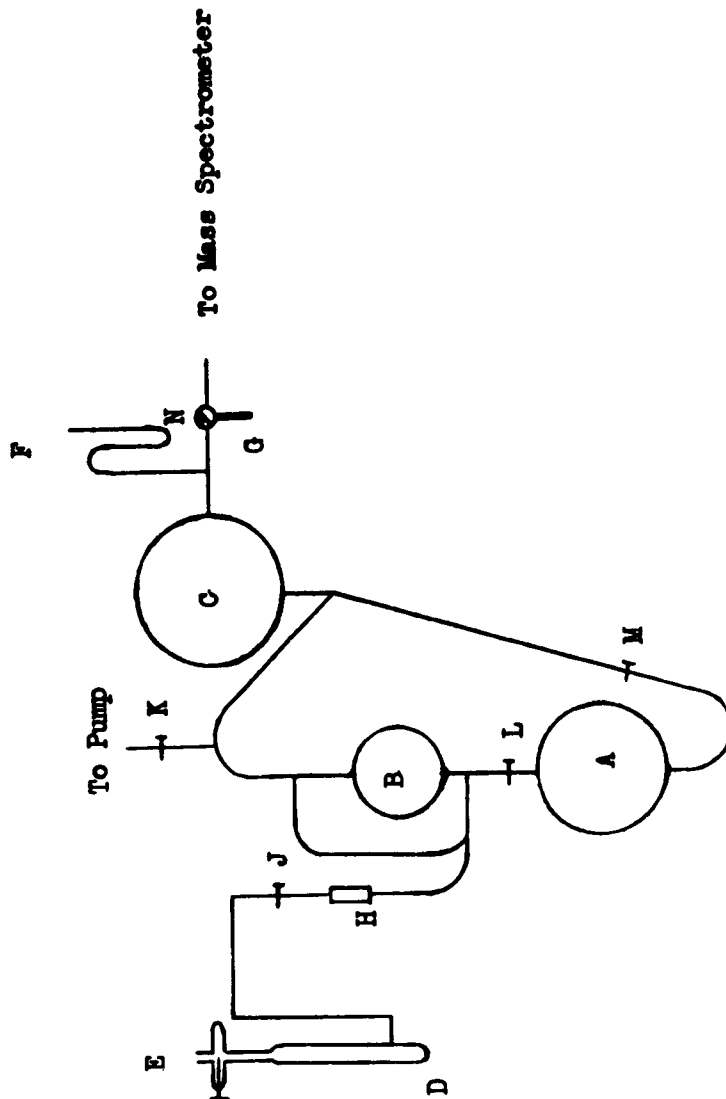


Figure 3

C-3368 TBE:em 2/27/53



- A. Mercury reservoir
- B. Bulb, 300 cc
- C. Bulb, 1000 cc
- D. Trap
- E. Breaker
- F. Manometer
- G. Small Bulb
- H. Float Valve
- J, K, L, M, N. Stopcocks

AUXILIARY VACUUM SYSTEM FOR
MASS SPECTROMETER

O-3381 Revision 2/27/53

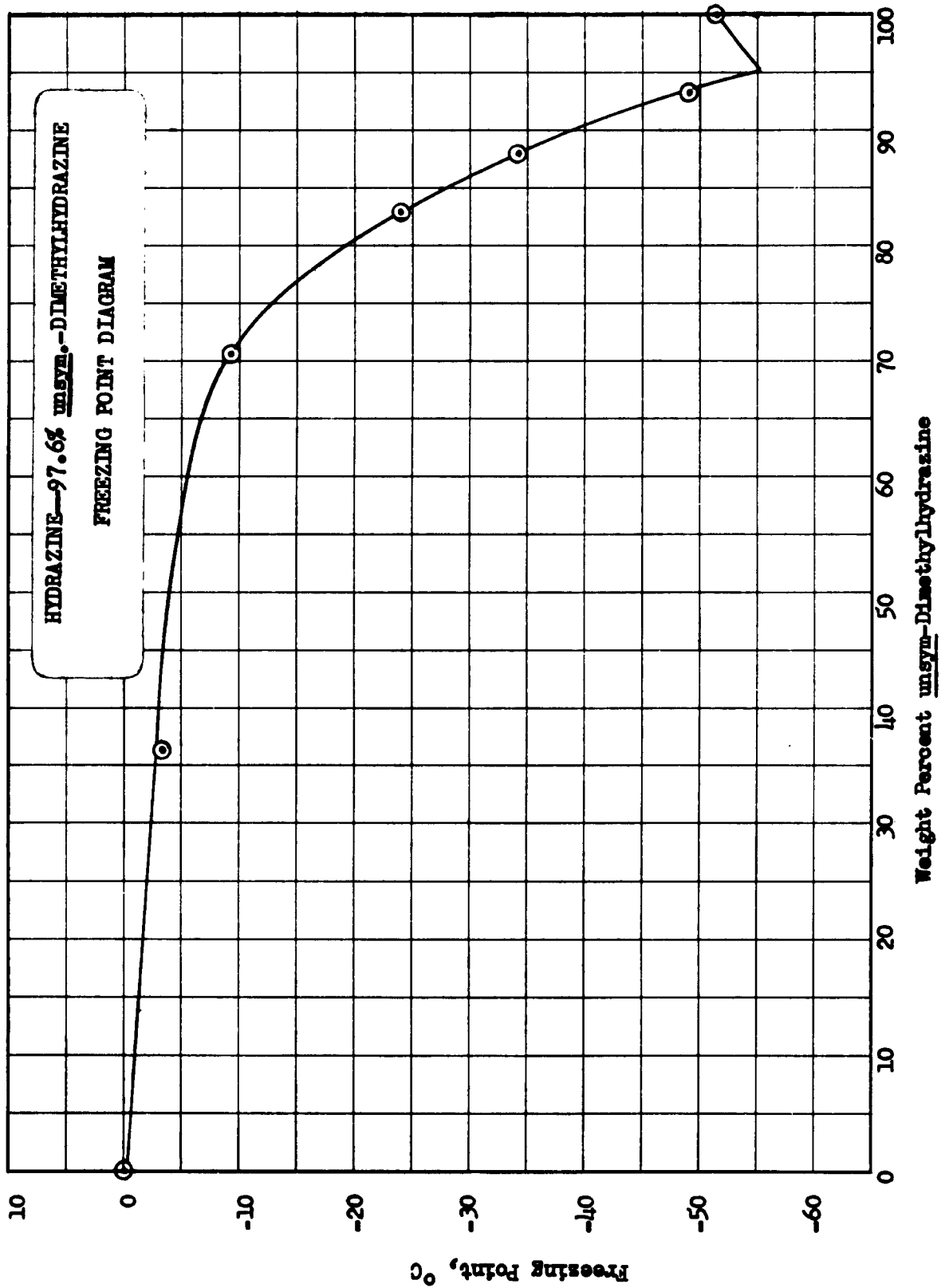


Figure 5