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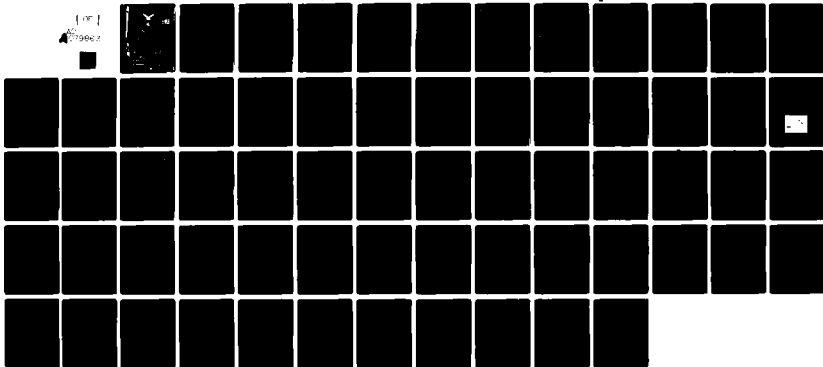
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A SINGLE PULSE SHOCK TUBE STUDY OF PYROLYSIS OF MONOMETHYLAMINE--ETC(U)
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A SINGLE PULSE SHOCK TUBE
STUDY OF PYROLYSIS OF MONOMETHYLAMINE

THESIS

Presented to the Faculty of the School of Engineering ✓
of the Air Force Institute of Technology
Air University

in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

by

William R. Nusz, Jr.
2d Lieutenant USAF

Graduate Astronautical Engineering

December 1979

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Preface

This thesis is the third in a series of theses which have studied the mechanism by which organo-nitrogen compounds present in fuels of origin other than petroleum are converted to NO_x pollutants. Due to current uncertainty in supply of petroleum the Air Force is interested in fuels derived from coal or oil shale. A concern is that use of these fuels carries the probability of high levels of NO_x pollutants will be formed in combustion.

The pyrolysis of monomethylamine was studied in a single pulse shock tube facility with product analysis by gas chromatography, as opposed to the two previous theses which used in situ infrared emission techniques. Results from this study support part of the model for decomposition of monomethylamine developed in the previous two theses, however, further work needs to be done. An activation energy and pre-exponential factor for the initial step in the decomposition reaction was determined.

I would like to thank those people whose help made completion of this thesis possible. Especially, I would like to thank Dr. E. A. Dorko, my thesis advisor and instructor at the Air Force Institute of Technology (AFIT) who provided me with the knowledge and guidance to complete this thesis. I would like to also thank Harold L. Cannon of AFIT for his help in operation of the shock tube, and

William Baker for his help in obtaining needed supplies.
Finally, I want to thank my wife, Lt. Gail M. Nusz, for
her assistance with the computer work and plotting, and
for her typing of the completed thesis.

William R. Nusz

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List of Symbols

(A)	concentration of A, moles/liter
a	acoustic velocity
$k_{\text{(subscript)}}$	reaction rate constant
→	reaction leading to
μ	prefix, 10^{-6} multiplier
T	temperature, °K
A	Arrhenius pre-exponential factor
E_a	activation energy, Kcal/mole
R	Universal gas constant
C_p	gas specific heat, constant pressure, cal/mole °K
C_v	gas specific heat, constant volume, cal/mole °K
γ	C_p/C_v
U	shock velocity, m/sec
M	mach #, U/a
t	time, seconds
y_i	dependent variable y, at time i
P	pressure, atm

decomposition

↓

Abstract

The decomposition of monomethylamine (MMA) was studied to model the decomposition mechanism. The decomposition of a 2.5% mixture of MMA in argon was studied behind a reflected shock by use of a single pulse shock tube with gas chromatography of the products $\overset{M}{\text{CH}}_4$, $\overset{M}{\text{NH}}_3$, and unreacted MMA. The temperatures behind the reflected shock ranged from 727 °K to 1438 °K. The reaction test time was 900 μsec . Total pressure ranged from 2.2 atm to 8.03 atm. The rate constants for the initiating C-N bond scissure were determined by a parametric study using a numerical model. The concentrations of $\overset{M}{\text{CH}}_4$, $\overset{M}{\text{NH}}_3$, and MMA were examined to determine the reasonableness of the model. The Arrhenius equation for the initial C-N bond scissure is $10^{6.64} \exp(-23.800/RT) \text{ sec}^{-1}$ as determined in this study.

A SINGLE PULSE SHOCK TUBE
STUDY OF PYROLYSIS OF MONOMETHYLAMINE

I. Introduction

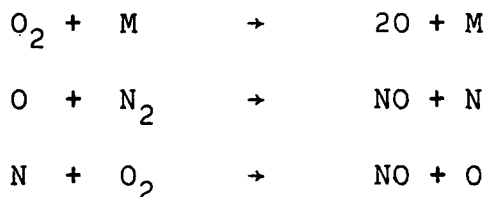
Background

The Air Force is presently interested in the production of fuels from sources of origin other than crude petroleum, such as "synthetic" crudes produced from coal or from oil shale. One problem with these alternate sources is that fuels, specifically JP-4 and Jet A, produced from oil shale or coal have a relatively large percentage, .3 to 2% by weight, of organo-nitrogen compounds (Ref 15:5), as compared to less than .01% for petroleum based fuels. During combustion these alternate fuels produce large quantities of NO_x pollutants, on the order of 140% more than petroleum based fuels (Ref 10:7). The symbol NO_x refers to the three oxides of nitrogen NO, NO₂, and N₂O₃ which are usually created in high temperature combustion (Ref 4). NO_x compounds in the atmosphere participate in the formation of photochemical smog and may have detrimental effects on the stratospheric ozone layer (Ref 4).

The Department of Transportation has recommended basic combustion research to reduce the amount of NO_x emission by aircraft. Since JP-4 and Jet A produced from coal and oil shale derived crude are projected to be produced in the future (Ref 4), the Air Force is interested in reducing the amount of NO_x formed when these fuels are burned.

It is currently perceived that in combustion modeling the combustion process can be represented by finite rate chemical reactions if the rate data are known accurately (Ref 7). Also while a partial mechanism can simulate the heat process due to combustion, knowledge of the complete mechanism is necessary in order to predict the pollutants accurately (Ref 7). To learn how to reduce the amounts of NO_x produced, it is first necessary to learn the mechanisms that lead to formation of NO_x by organo-nitrogen compounds. Once the mechanism is understood, the critical steps that lead to NO_x formation may be inhibited by adjustment of reaction conditions.

For the case of combustion of petroleum-based fuels, the main source of NO_x compound is known to be fixation of atmospheric nitrogen. The reaction is thought to proceed by the Zeldovich mechanism.



It is known that this mechanism can be suppressed by operating at lower temperatures. However, formation of NO_x from organo-nitrogen fuel components occurs readily even at low combustion temperatures with a conversion rate for fuel-bound nitrogen

of 50-100% (Ref 4). This knowledge has prompted studies to find the mechanisms by which organo-nitrogen compounds form NO_x . A compound which has been chosen in the past as a suitable model for such studies is monomethylamine (MMA) (Ref 12).

Research Objectives

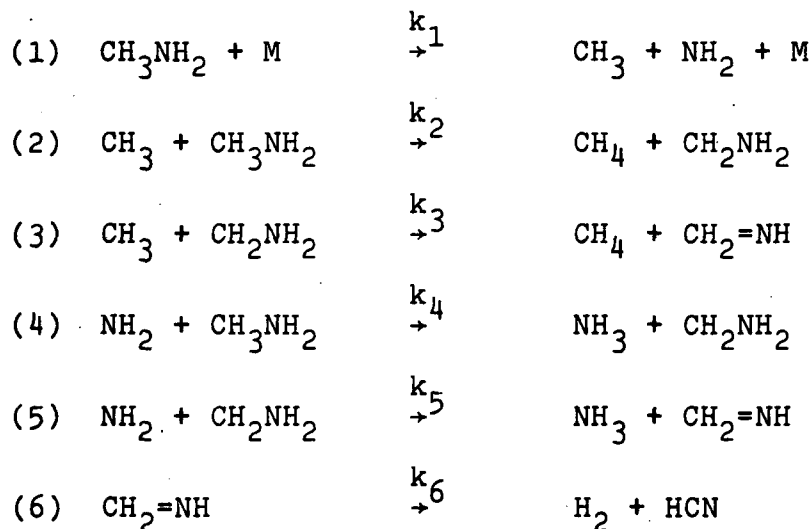
The objective of this thesis was to make a kinetic study of the decomposition of MMA in argon as a step toward modeling the mechanism by which organo-nitrogen compounds form NO_x . The pyrolysis of MMA was studied in a single pulse shock tube. The products of decomposition were analyzed by vapor phase chromatography (Ref 5). The arrhenius parameters for decomposition of monomethylamine were to be calculated by matching concentrations of CH_4 , NH_3 , and MMA obtained by integration of a numerical model to the concentrations of the same species found experimentally.

II. Theory

Mechanism

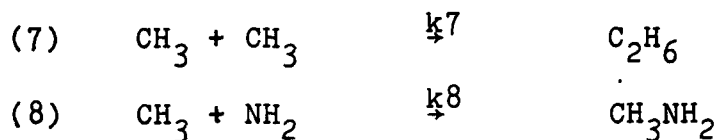
Monomethylamine, CH_3NH_2 , was chosen for this study because it has previously been used for kinetic studies in shock tubes using infrared emissions techniques (Ref 12, 16). MMA is the simplest organo-nitrogen compound, is stable, readily available, and is analogous to ethane, which has a well-known decomposition.

The initial steps in the pyrolysis of MMA has been previously studied. The most recent work in this area gives strong evidence to support the following mechanism (Ref 6)



This mechanism applies well for times from 0 to ~ 350 μsec and temperatures from $1275 - 1400^\circ\text{K}$. It is not yet known, however, if this mechanism is general enough to be applic-

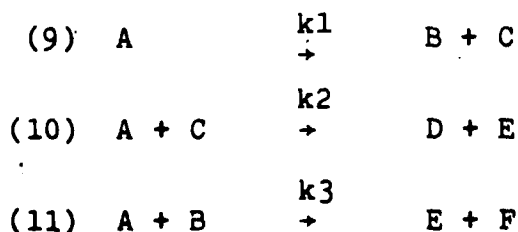
able in modified form in a lower temperature region and for longer times. At lower temperatures, recombination reactions are likely to become important. To account for recombination, the following reactions should be added to the above:



A study by Smith & Sawyer (Ref 14) using a flow reactor for the pyrolysis of MMA followed by analysis of the products by vapor phase chromatography covered a temperature range of 1087 - 1132 °K with a residence time range from 0 to 1.2×10^{-2} sec. They reported the formation of N_2 , solid hexamethylene-tetramine and 3-ethyl-4-methyl pyrrole in addition to the products of the mechanism just presented. They postulated that the hexamethylene-tetramine and pyrrole were formed from the $\text{CH}_2=\text{NH}$ imine intermediate at the relatively low temperatures, while at higher temperatures, $\text{CH}_2=\text{NH}$ forms H_2 and HCN.

Kinetics

Consider the simple system:



If the above reactions and species comprise the entire system it is possible to write the chemical mechanism as a system of linear ordinary differential equations in terms of the species concentration and the rate constants as follows:

$$(12) \quad \frac{d}{dt}(A) = -k_1(A) - k_2(A)(C) - k_3(A)(B)$$

$$(13) \quad \frac{d}{dt}(B) = k_1(A) - k_3(A)(B)$$

$$(14) \quad \frac{d}{dt}(C) = k_1(A) - k_2(A)(C)$$

$$(15) \quad \frac{d}{dt}(D) = k_2(A)(C)$$

$$(16) \quad \frac{d}{dt}(E) = k_2(A)(C) + k_3(A)(B)$$

$$(17) \quad \frac{d}{dt}(F) = k_3(A)(B)$$

These equations may then be evaluated as an initial value problem, and the chemical behavior over a period of time may be found.

The eight equations of the mechanism for MMA pyrolysis may be similarly expressed in differential equation form as follows:

$$(18) \quad \frac{d}{dt}(\text{CH}_3\text{NH}_2) = -k_1(\text{CH}_3\text{NH}_2) - k_2(\text{CH}_3\text{NH}_2)(\text{CH}_3) - k_8(\text{CH}_3\text{NH}_2)(\text{NH}_2) + k_8(\text{CH}_3)(\text{NH}_2)$$

$$(19) \quad \frac{d}{dt}(\text{CH}_2\text{NH}_2) = k_2(\text{CH}_3\text{NH}_2)(\text{CH}_3) + k_4(\text{CH}_3\text{NH}_2)(\text{NH}_2) - k_3(\text{CH}_2\text{NH}_2)(\text{CH}_3) - k_4(\text{CH}_2\text{NH}_2)(\text{NH}_2)$$

$$(20) \quad \frac{d}{dt}(\text{CH}_3) = k_1(\text{CH}_3\text{NH}_2) - k_2(\text{CH}_3\text{NH}_2)(\text{CH}_3) \\ - k_3(\text{CH}_2\text{NH}_2)(\text{CH}_3) - k_7(\text{CH}_3)^2 \\ - k_8(\text{CH}_3)(\text{NH}_2)$$

$$(21) \quad \frac{d}{dt}(\text{NH}_2) = k_1(\text{CH}_3\text{NH}_2) - k_4(\text{CH}_3\text{NH}_2)(\text{NH}_2) \\ - k_5(\text{CH}_2\text{NH}_2)(\text{NH}_2) - k_8(\text{CH}_3)(\text{NH}_2)$$

$$(22) \quad \frac{d}{dt}(\text{NH}_3) = k_4(\text{CH}_3\text{NH}_2)(\text{NH}_2) \\ + k_5(\text{CH}_2\text{NH}_2)(\text{NH}_2)$$

$$(23) \quad \frac{d}{dt}(\text{CH}_4) = k_2(\text{CH}_3\text{NH}_2)(\text{CH}_3) \\ + k_3(\text{CH}_2\text{NH}_2)(\text{CH}_3)$$

$$(24) \quad \frac{d}{dt}(\text{CH}_2=\text{NH}) = k_3(\text{CH}_2\text{NH}_2)(\text{CH}_3) \\ + k_5(\text{CH}_2\text{NH}_2)(\text{NH}_2)$$

$$(25) \quad \frac{d}{dt}(\text{H}_2) = \frac{d}{dt}(\text{HCN}) = -k_6(\text{CH}_2=\text{NH})$$

Again, this system may be treated as an initial-value problem.

The rate constants for these reactions are temperature dependent according to the Arrhenius equation

$$(26) \quad k = Ae^{-E_a/RT}$$

In logarithmic form the equation is

$$(27) \quad \log k = \log A - E_a/2.303RT$$

If $\log k$ is plotted vs. $1/T$, a straight line results with a slope of $-E_a/2.303R$ and a y-intercept of $\log A$.

Shock Tube Studies

Gas phase kinetics have been studied by use of shock tubes (Ref 8). A shock tube is a device to produce a strong planar shock wave which is generated by bursting a diaphragm of appropriate material which separates a section of high pressure gas from a section of low pressure gas. The driven section, at low pressure, contains the gas to be reacted. The driver section, at high pressure, contains an inert gas. When the diaphragm is burst, a shock front traverses the length of the driven section, both heating and pressurizing the gas. Upon contacting the end wall of the driven section, the incident shock is reflected back into the already heated gas. This re-shocking multiplies again the pressure and temperature increase previously achieved. Then, in a single pulse tube as used in this study, a rarefaction wave caused by gas traveling to the dump tank reaches the reaction zone and cools the reacting gas at about 5×10^5 °K/sec, effectively "freezing" the chemistry at that time.

The concentration of species in the test gas can be studied in several ways. The method of interest in the current study involves taking a sample of the test gas after the shock and analyzing it via gas chromatography (Ref 8).

Analysis by gas chromatography is useful because it provides information on the absolute quantities of end

products of the reaction under study. Gas chromatography does have the disadvantages that it may only be used to determine chemically stable species, and that the technique can only look at the composition after one particular experimental time period.

The quantities required to determine the shock conditions are the initial pressure of the driven gas, P_1 , the initial temperature of the driven gas, T_1 , the composition of the driven gas, and the incident shock velocity, U_1 (Ref 8). The reflected shock zone parameters of interest are pressure, P_5 , temperature, T_5 , and the residence of reaction test time, t which is the time from reflection of the incident shock to the arrival of the rarefaction. T_5 and P_5 can be determined from the incident shock mach number, M , where $M = U_1/a_1$, a_1 = speed of sound in the gas, and γ is the heat capacity ratio = C_p/C_v . The ratios of T_5/T_1 and P_5/P_1 are

$$(28) \quad \frac{T_5}{T_1} = \frac{(2(\gamma-1)M^2 + (3-\gamma))((3\gamma-1)M^2 - 2(\gamma-1))}{(\gamma+1)^2 M^2}$$

$$(29) \quad \frac{P_5}{P_1} = \frac{(2\gamma M^2 - (\gamma-1))((3\gamma-1)M^2 - 2(\gamma+1))}{(\gamma+1)((\gamma-1)M^2 + 2)}$$

The shock parameters were calculated using the NASA 273 program assuming frozen chemistry. Program inputs were incident shock speed, initial temperature, and thermodynamic properties of the test gas (Ref 13). The reaction test time, t , was determined experimentally.

Numerical Integration

The differential equations of a chemical system are of the form:

$$(30) \quad \frac{dy_1}{dt} = f_1(y_1, y_2, y_3, \dots, y_n)$$

$$\frac{dy_2}{dt} = f_2(y_1, y_2, y_3, \dots, y_n).$$

.

.

.

$$\frac{dy_n}{dt} = f_n(y_1, y_2, y_3, \dots, y_n)$$

subject to initial conditions

$$(31) \quad y_1(0) = y_{10}$$

$$y_2(0) = y_{20}$$

.

.

.

$$y_n(0) = y_{n0}$$

Now consider the system as being represented by the vector equation:

$$(32) \quad \frac{d\bar{y}}{dt} = \bar{f}(\bar{y})$$

The numerical integration formula chosen was the fourth order Runge-Kutta type which is

$$(33) \quad \bar{y}_{i+1} = \bar{y}_i + \Delta t \left(\frac{1}{6} \bar{f}(\bar{y}_i) + \frac{1}{3} \bar{f}(\bar{y}_{i+\frac{1}{2}}^*) + \frac{1}{3} \bar{f}(\bar{y}_{i+\frac{1}{2}}^{**}) + \frac{1}{6} \bar{f}(\bar{y}_{i+1}^*) \right)$$

where

$$(34) \quad \bar{y}_{i+\frac{1}{2}}^* = \bar{y}_i + \frac{\Delta t}{2} \bar{f}(\bar{y}_i)$$

$$(35) \quad \bar{y}_{i+\frac{1}{2}}^{**} = \bar{y}_i + \frac{\Delta t}{2} \bar{f}(\bar{y}_{i+\frac{1}{2}}^*)$$

$$(36) \quad y_{i+1}^* = y_i + \Delta t \bar{f}(\bar{y}_{i+\frac{1}{2}}^{**})$$

is evaluated in that sequence (Ref 11). By input of the rate constants and initial species concentration for equations 18 to 23, the behavior of the chemical system can be simulated. The numerical model should behave as the experimental model given the same conditions. By comparing the results of the numerical integration against the experimental results, the correct rate constants may be found.

III. Experimental

Shock Tube

General Description. The shock tube used in this study was constructed of stainless steel tubing. The tube was of 1" diameter circular cross section with a driver section 54" long and a driven section 72" long. A dump tank of approximately 15 liter capacity was attached to the driver section 6.5 inches downstream of the diaphragm. Figure 1 shows an overall layout of the shock tube. The vacuum system consisted of an Alcatel Z2030C roughing pump and a Veeco 2-5W oil diffusion pump for the driven section and dump tank. With this system the driven section of the shock tube could be evacuated to less than 10^{-3} Torr.

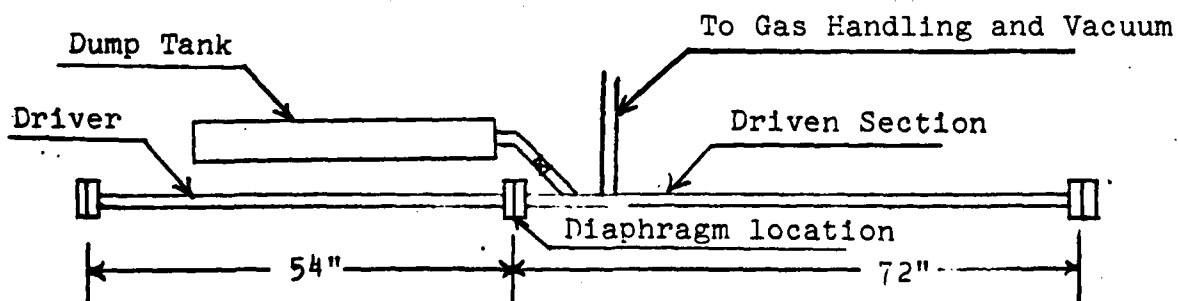


Figure 1, Shock Tube Overall Layout

Test Gas. The test gas mixture of 2.5% MMA was prepared from MMA (98.0% pure) and argon (99.995% pure), both purchased from Matheson Gas Products and used with no further processing. The sample was prepared in a stainless steel bottle by the following procedure: First, the bottle was evacuated to a pressure of less than 10^{-3} Torr, then filled with MMA to a pressure that would give the desired concentration of MMA at the final total pressure. The bottle was then closed and the gas manifold pumped down to less than 10^{-3} Torr. The manifold was then pressurized with argon to at least double the pressure of MMA in the bottle to prevent escape of the MMA, then the valve to the bottle was opened and the bottle filled with argon to the desired total pressure. The gas sample was allowed to stand overnight before use to insure homogeneity.

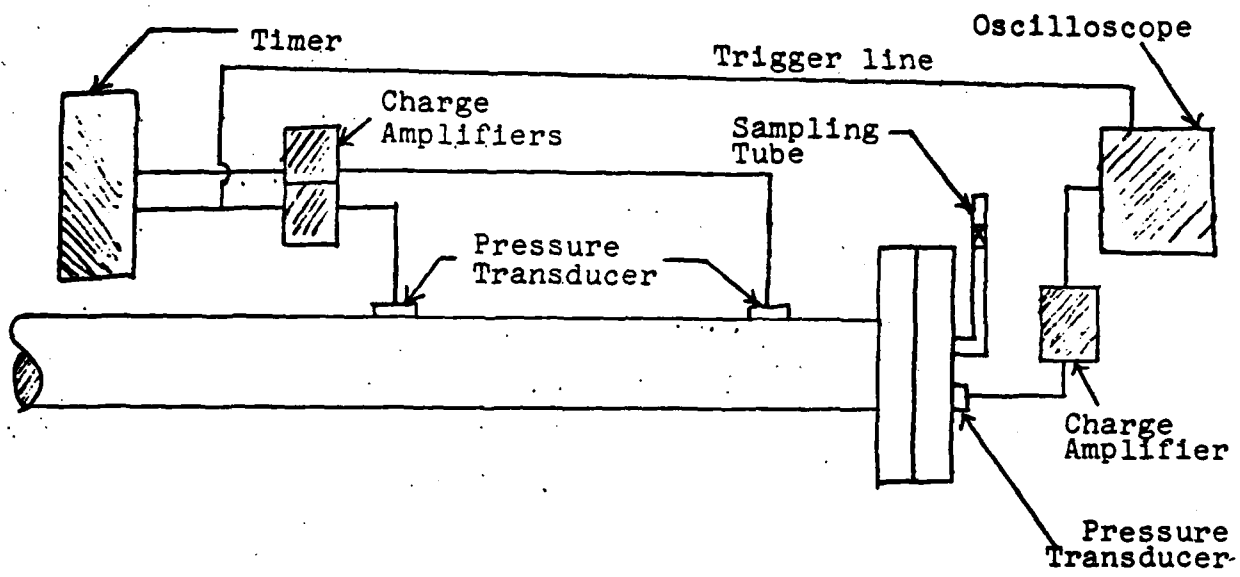
Instrumentation. The purpose of the instrumentation on the shock tube was to provide accurate information on initial driven section pressure, incident shock velocity, and dwell time of the reflected shock at the back wall of the tube. Pressures from 1 to 200 Torr were measured by a Wallace & Tiernan FA-160 aneroid type pressure gauge. Pressures in the range of 1 to 10^{-3} Torr were measured by a Consolidated Vacuum Corporation DV-180 cold cathode gauge. Incident shock velocity was measured by two Kistler piezo-electric pressure transducers, placed 10

inches apart as shown in Figure 2. These transducers were connected through charge amplifiers to an electronic counter. The time interval was measured by a Hewlett-Packard 5325B counter with accuracy of $\pm 0.1 \mu\text{sec}$. The reaction rest time of the reflected shock was measured by a Kistler piezo-electric transducer, located in the back wall of the tube, and connected to a Hewlett-Packard 551 oscilloscope through a charge amplifier. The oscilloscope was triggered by the same transducer which started the timer to measure incident shock velocity. Figure 3 shows a sample oscilloscope trace reflected shock dwell time.

Shock Tube Operation. The shock tube was operated by first evacuating all sections of the tube. The dump tank was then filled with argon to the desired initial pressure and isolated from the driven section which was then again evacuated. The driven section was then filled with the test gas mixture and shocked by bursting the diaphragm by admitting high pressure helium to the driven section. Diaphragm material was 1.6 mil mylar sheet weakened by scoring with a divider point to allow bursting in the proper pressure range. A more detailed description of the operation appears in Appendix A.

Vapor Phase Chromatography

• Description. Analysis of the product gas mixture was performed on a Hewlett-Packard model 720 gas chromatograph



Scale: 1/5

Figure 2, Shock Tube End Detail

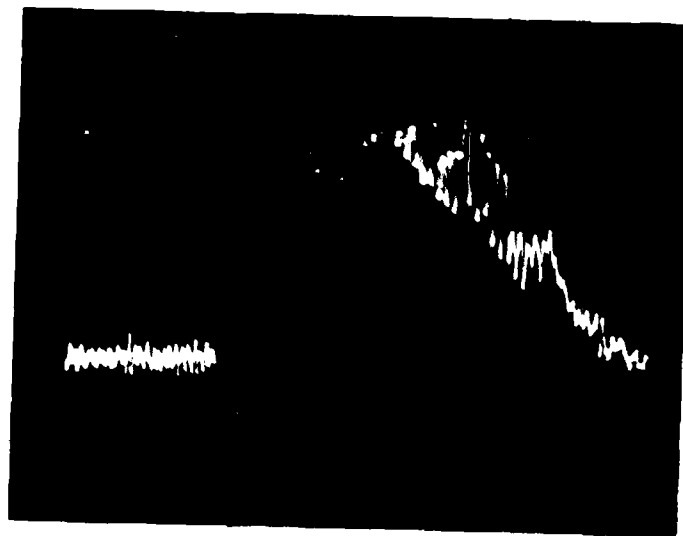


Figure 3, Shock Pressure Trace

equipped with thermal conductivity detector. Column materials initially considered were Chromosorb 102, Chromosorb 103, Chromosorb 104, Porapak P, Porapak N, Linde Molecular Sieve 13-X, and Linde Molecular Sieve 5A. Chromosorb 103 was found to be suitable for use in determining MMA and NH_3 concentrations, and Linde Molecular Sieve 5A was found to be suitable for the determination of CH_4 . The operating conditions of the columns are listed in Table I. Typical chromatograph traces for each column are reproduced in Figure 4. The Sargent Model SR x-y recorder used for recording the traces from the chromatograph was equipped with a disc integrator which was used to determine the areas under the peaks. The chromatograph was calibrated using a mixture of 5% MMA, 5% NH_3 , and 5% CH_4 in argon. The calibration curves appear in Figures 5 - 7.

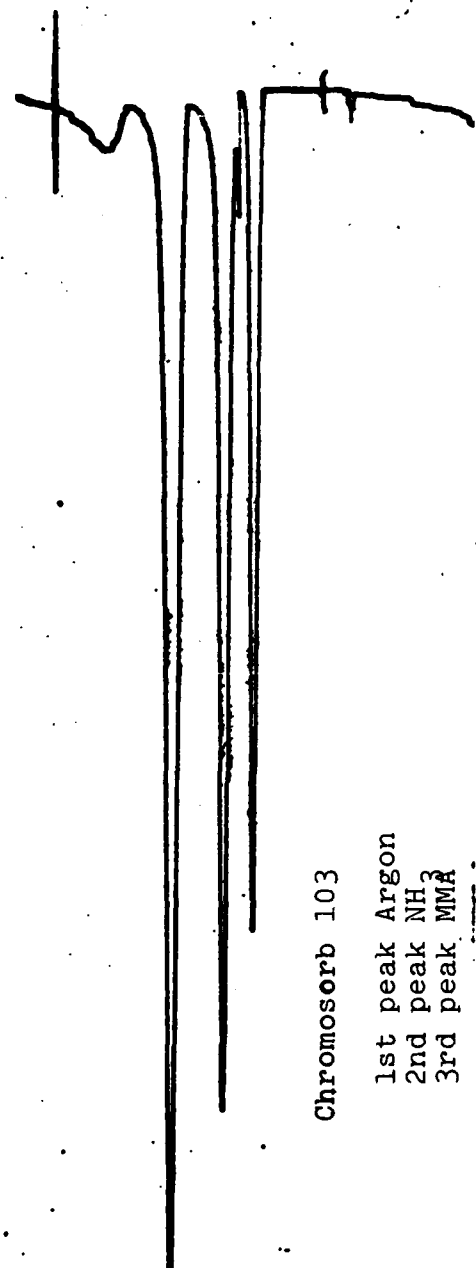
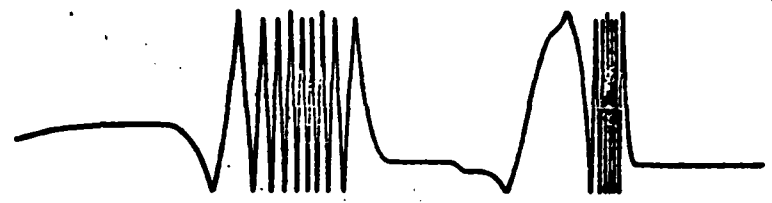
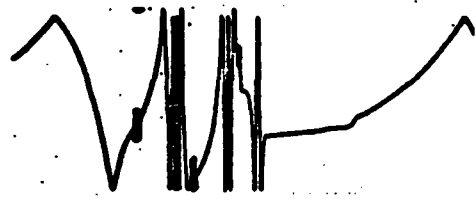
Operation. At the start of each day both columns were seasoned by the injection of a 2.0 ml sample of the 5% MMA, 5% NH_3 , and 5% CH_4 mixture at ~ 350 Torr. Samples were introduced by a Precision Sampling 2.0 ml gas-tight syringe and the pressure of the sample in the gas bottle was determined by use of a mercury manometer. The attenuation of the chromatograph amplifier was increased to allow the argon peak to remain within the range of the x-y recorder and reset to maximum sensitivity after passage of the argon peak. The sample size and pressure were recorded on the chromatograph trace.

Table I

Column Operating Conditions

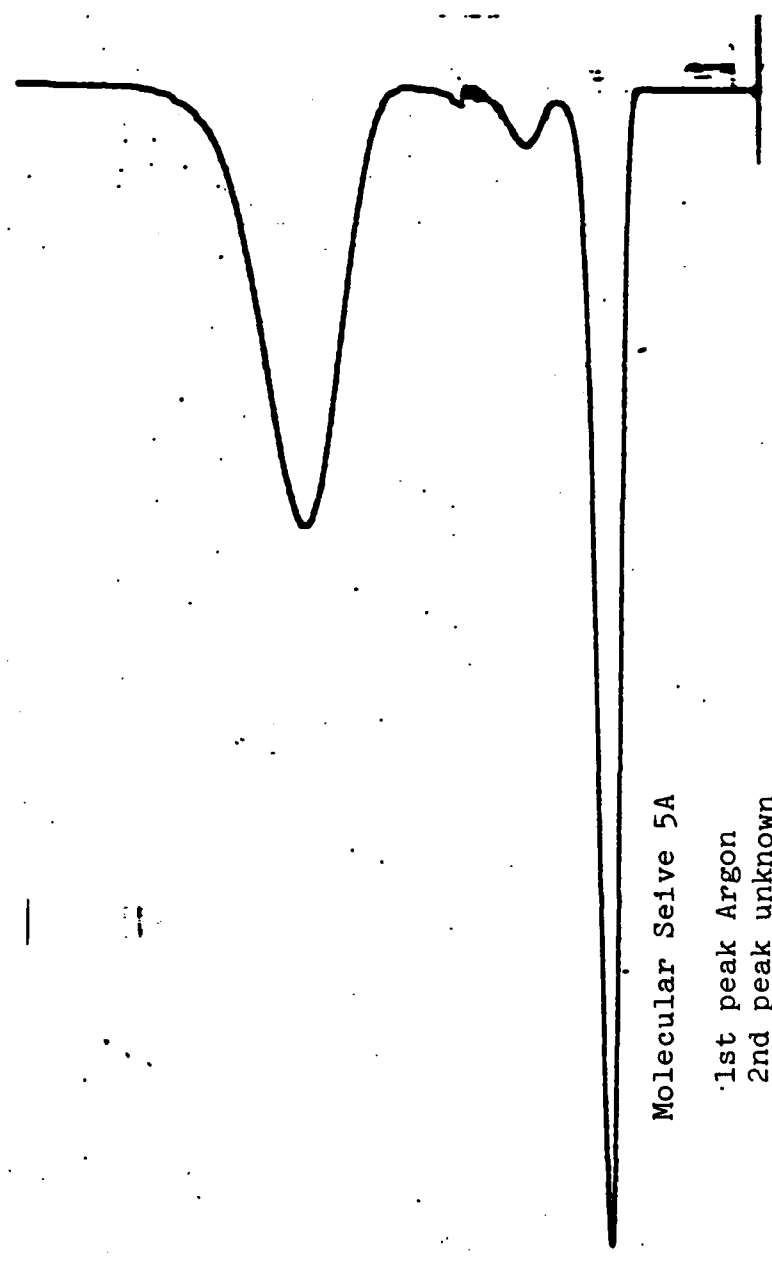
Column: $\frac{1}{4}$ " O.D. Stainless Steel, 6'
Packing: Chromosorb 103 80/100 mesh
Temperature Cycle: 150°C, Isothermal
Carrier Gas Flow: 40 std ml/min He
Carrier Gas Pressure: 35 PSIG
To Detect: CH_3NH_2 , NH_3

Column: $\frac{1}{4}$ " O.D. Stainless Steel, 6'
Packing: Linde Molecular Sieve 5A
Temperature Cycle: 50°C, Isothermal
Carrier Gas Flow: 40 std ml/min He
Carrier Gas Pressure: 35 PSIG
To Detect: CH_4



Chromosorb 103

- 1st peak Argon
- 2nd peak NH₃
- 3rd peak MMA



Molecular Sieve 5A

- 1st peak Argon
- 2nd peak unknown
- 3rd peak CH₄

Figure 4, Gas Chromatograph Trace

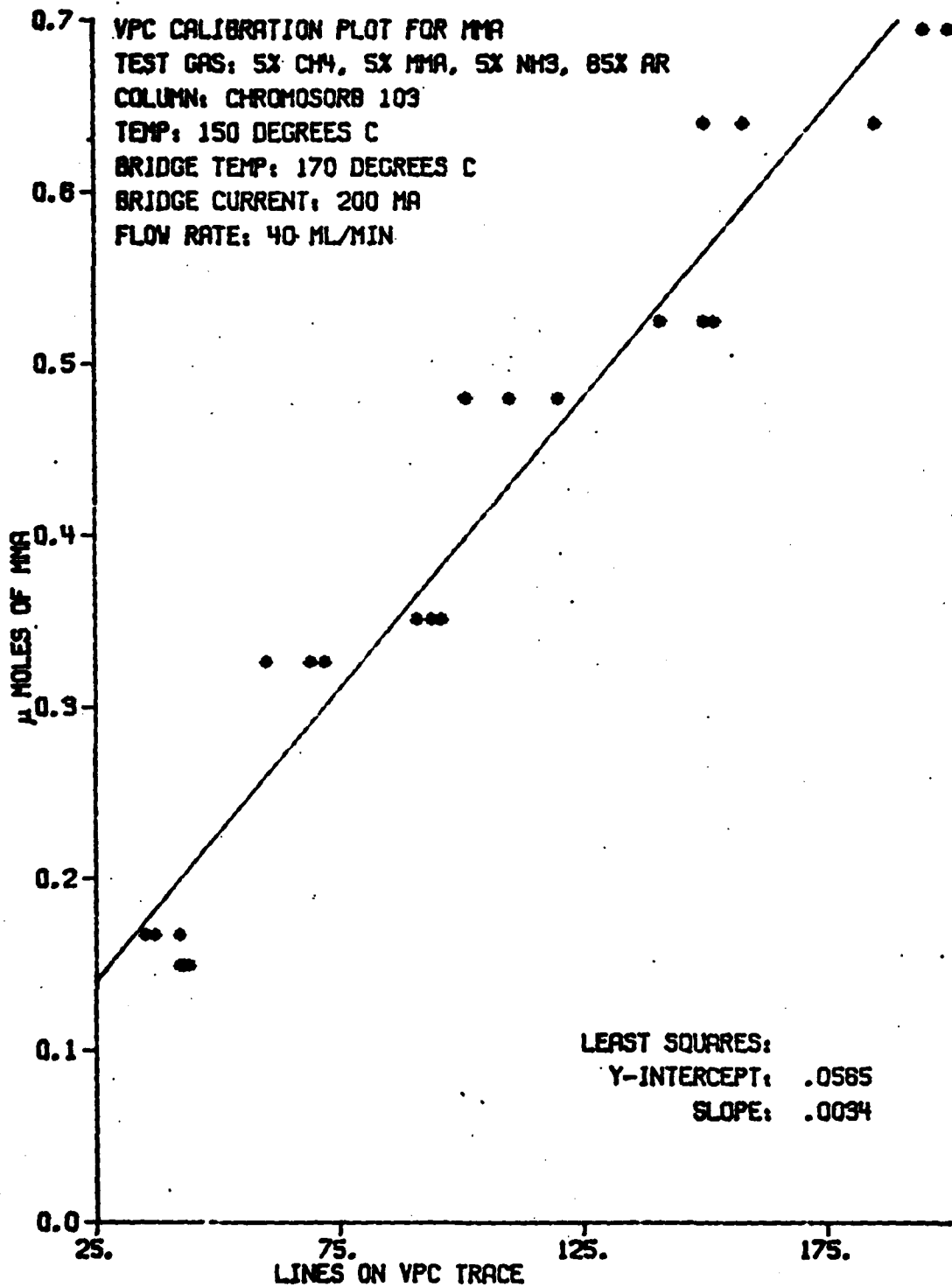


FIGURE 5, MMA CALIBRATION CURVE

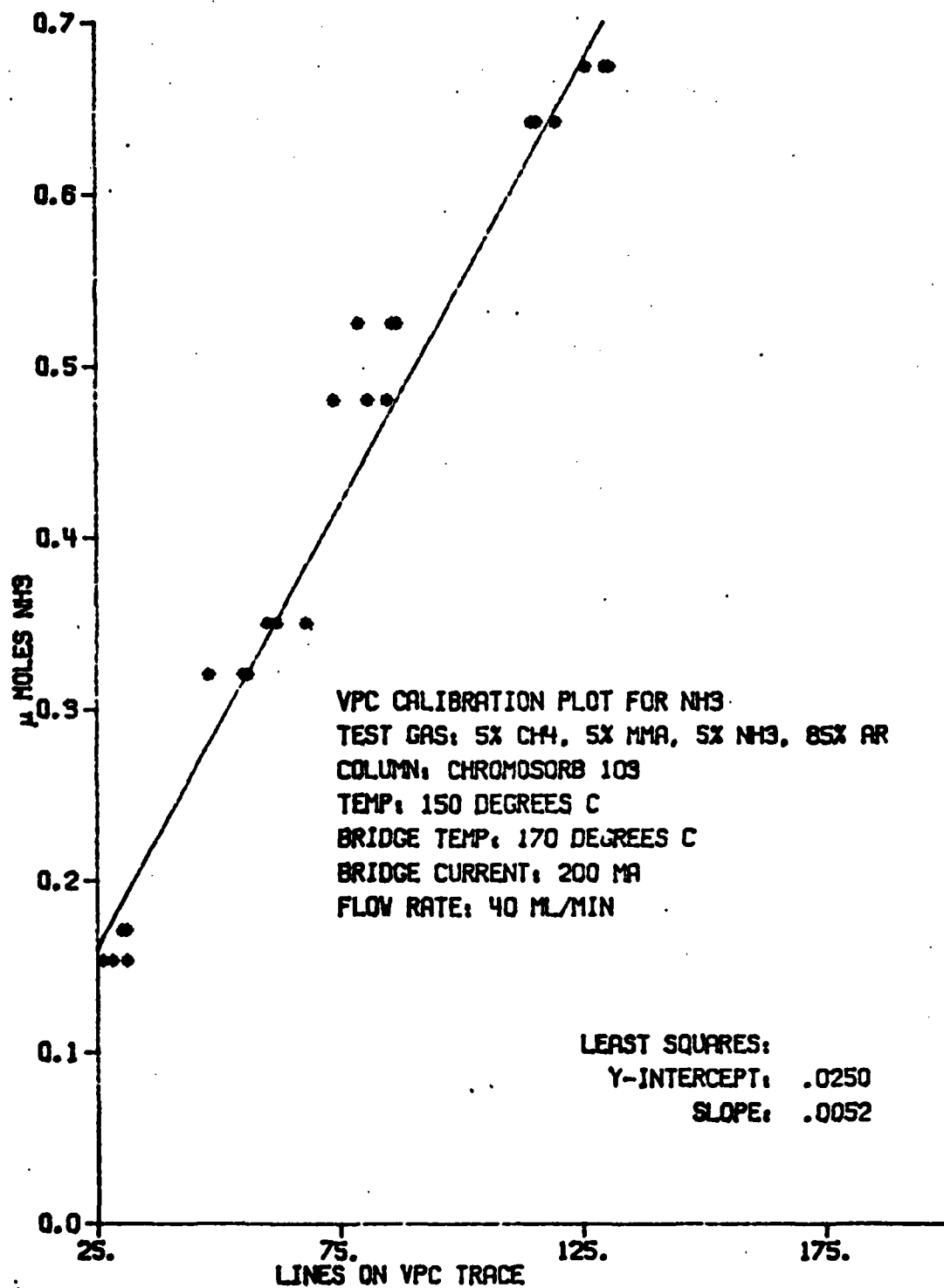


FIGURE 6, NH₃ CALIBRATION CURVE

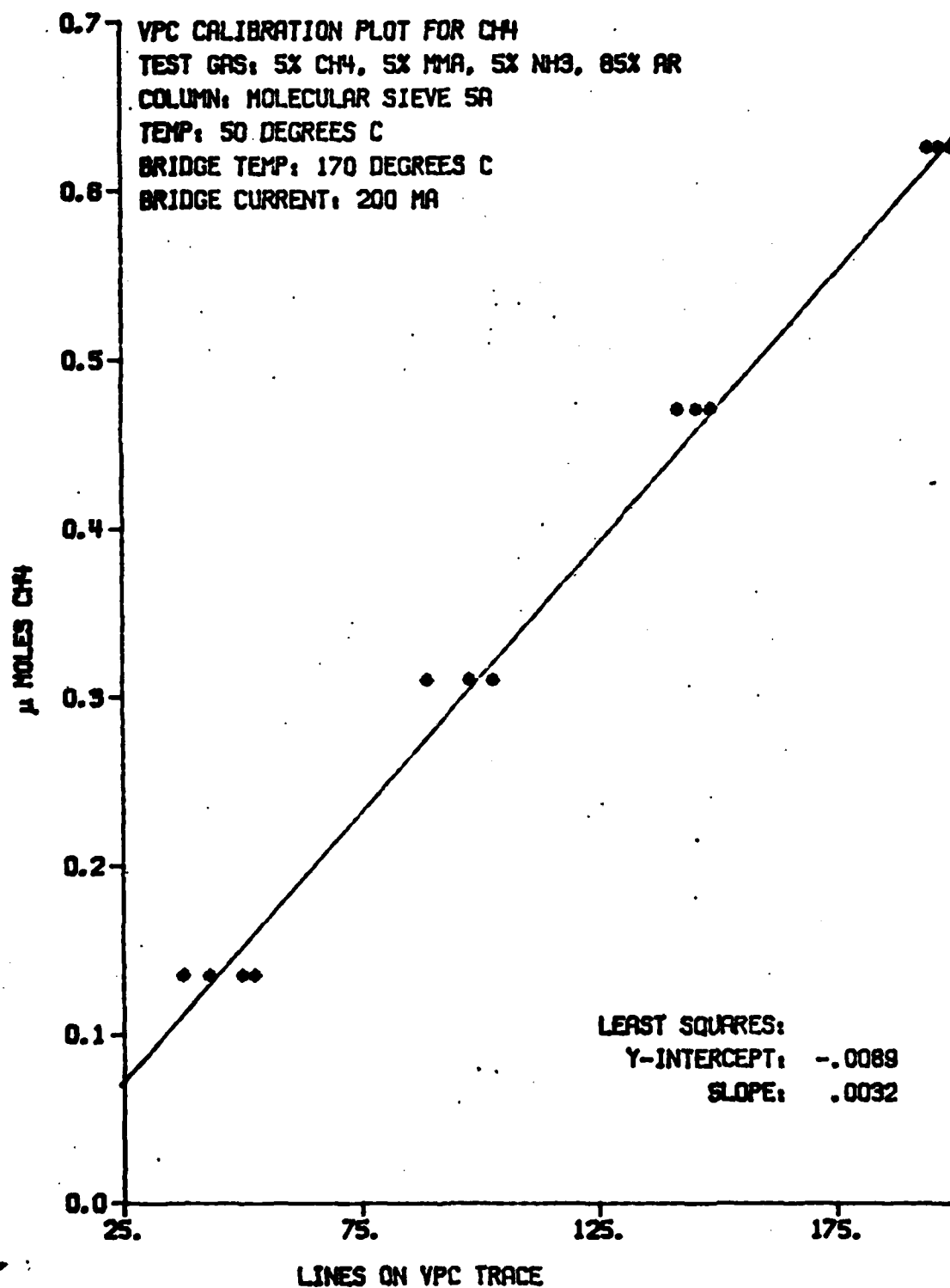


FIGURE 7. CH₄ CALIBRATION CURVE

Data Reduction

Chromatograph. For each sample introduced into the chromatograph, the initial number of moles of MMA present before the shock was calculated from measurement of the pressure and volume of the sample and application of the ideal gas equation of state. The area under each of the species peaks on the chromatograph traces was determined by the disc integrator and the number of moles of each species (MMA, CH_4 , and NH_3) was then determined from the calibration curves. The concentration of each species present was then expressed in the form of (moles of species)/(100 initial moles of MMA).

Shock Tube. The initial composition, pressure, temperature, and the incident shock velocity were used as inputs for the NASA 273 program. The shock parameters were computed using the assumption of frozen chemistry.

Over the temperature range in this study, the reaction test time is dependent primarily upon tube geometry and is 900 μsec .

Numerical Smoothing. The final species concentrations were plotted as a function of temperatures and subjected to a fourth order least squares polynomial curve fit using the CC6600 library subprogram PLSCF (Ref 1). The program is listed in Appendix B. The least squares polynomial curves for decomposition of MMA and formation of CH_4 and

NH_3 thus obtained were evaluated at 50°K intervals from 1000°K to 1450°K . These evaluations were then taken to be the final species concentration for the given temperature for further processing.

Numerical Integration. Equations 18 to 24 were incorporated into the numerical integration program which is listed in Appendix C. The program used the CC6600 library integration subprogram RKDF (Ref 1). Inputs to the program were initial concentrations of each species and all rate constants except the particular rate constant that was being determined. Initial assumed rate constants appear in Table II. The program worked by assuming an upper and lower limit for the rate constant under search, calculating the species concentrations in each case, comparing the numerical results with the experimental, then halving the interval and repeating the process until the rate constant is known to the desired tolerance.

k_1 was determined from 1000°K to 1400°K . The k 's were then plotted as $\log k$ vs. $1/T$ and the appropriate Arrhenius parameters were determined. The time interval over which the system was integrated was chosen as that time between the arrival of the reflected shock and the time that pressure behind the reflected shock had fallen to $3/4$ of the maximum pressure attained.

Table II

Initially Assumed Arrhenius Parameters

<u>k</u>	<u>log A</u>	<u>Ea(kcal/mole)</u>	<u>Source</u>
k ₁	17.	79.	(Ref 3:70)
k ₂ ,k ₄	11.	8.7	(Ref 9)
k ₃ ,k ₅	10.	10.0	(Ref 9)
k ₇	10.5	0.	(Ref 3:104)
k ₈	10.5	0.	(Ref 3:104)

IV. Results

For each of the end product species, MMA, CH_4 , and NH_3 that were analyzed, plots of amount of species present after shock vs. shock temperature were plotted and a least squares polynomial curve fit as described earlier was made.

For MMA, there was essentially no decomposition at shock temperatures below 1000°K , and an evenly increasing rate of decomposition with increasing temperature until at shock temperatures greater than 1400°K there was no detectable amount of MMA in the gas sampled after shock. The plot for MMA appears in Figure 8.

Essentially no NH_3 was formed at shock temperatures below 1000°K , with an increasing yield to about 1275°K followed by a rapid fall-off with essentially no remaining NH_3 for shock temperatures above 1400°K . The rise of NH_3 concentration corresponds directly to the decomposition of MMA, the fall-off at higher temperatures is not readily explainable by the chosen mechanism. The plot for NH_3 appears in Figure 9.

The formation of CH_4 was also at variance with the postulated mechanism. Essentially no CH_4 was detected for temperatures of less than 1200°K , then a strongly increasing yield of CH_4 was noted for temperatures up to the high limit of 1400°K . The plot for CH_4 appears in Figure 10.

The rate constants for k_1 that were found by program KFOUND are plotted as $\log k$ vs. $1/T$ in Figure 11. The activation energy and pre-exponential factor found by this plot differ greatly from expected values.

The concentration of MMA, NH_3 , and CH_4 as determined by least squares curve fit are compared with the concentrations of those species as predicted in the numerical model in Figures 12, 13, and 14. Note that the calculated concentration from the numerical model for MMA closely follows the observed, the calculated concentration vs. the observed concentration for NH_3 is in good agreement to 1250°K , and the calculated concentration of CH_4 is far greater than that observed, and indeed, methane formation is not noted at temperatures below 1200°K .

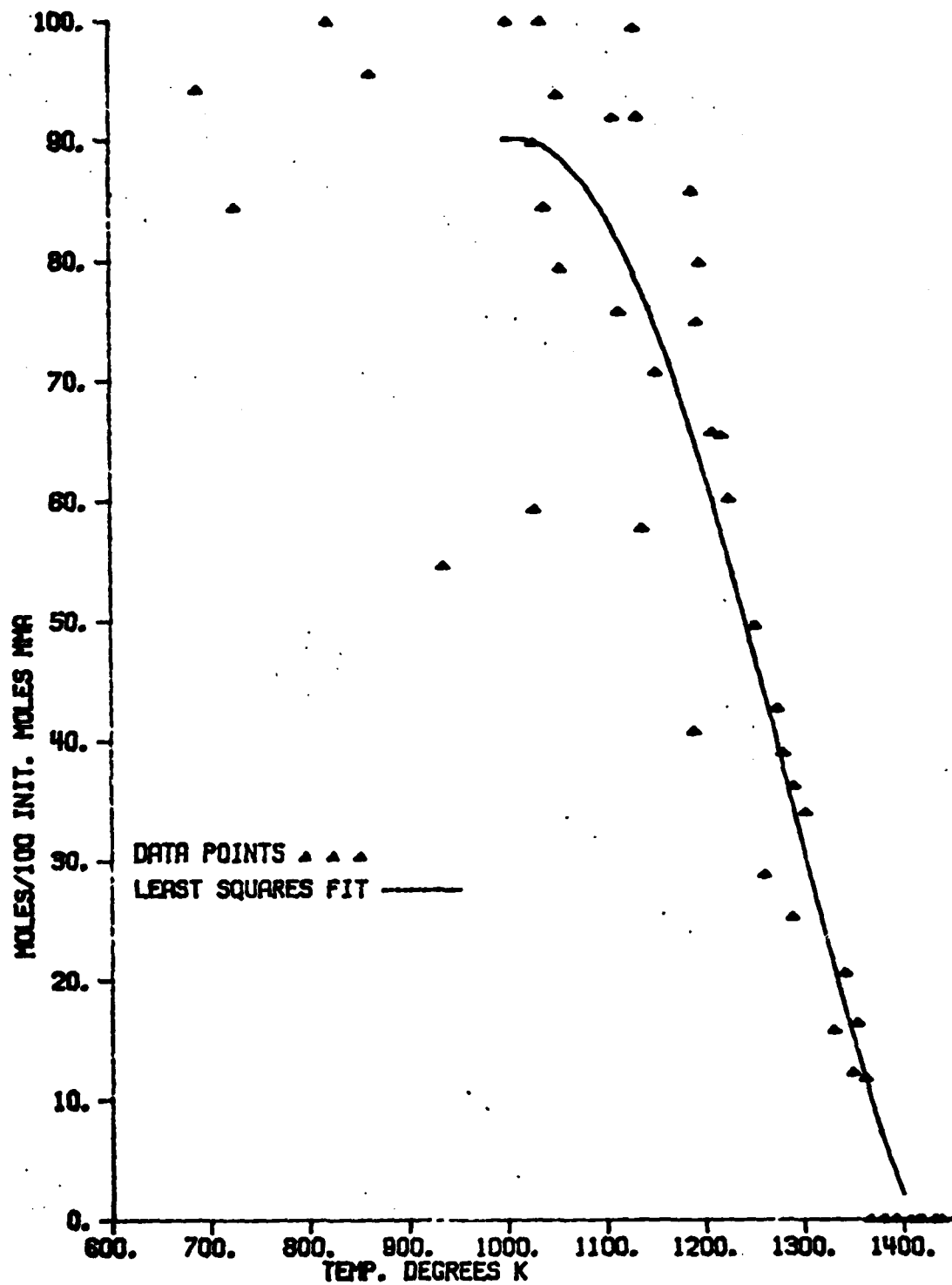


FIGURE 8, CONCENTRATION DATA AND LEAST SQUARES FIT FOR MMA

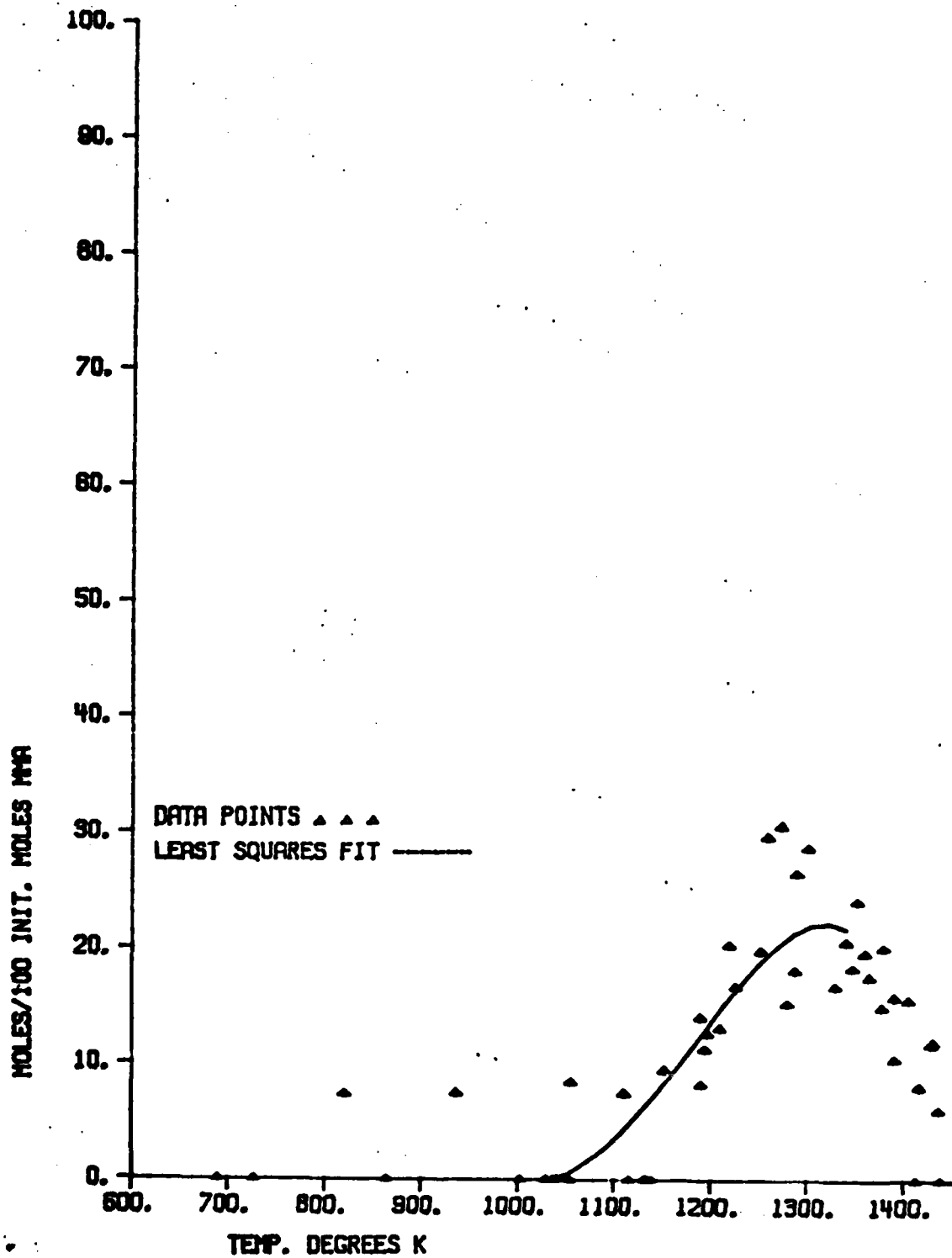


FIGURE 9, CONCENTRATION DATA AND LEAST SQUARES FIT FOR NH₃

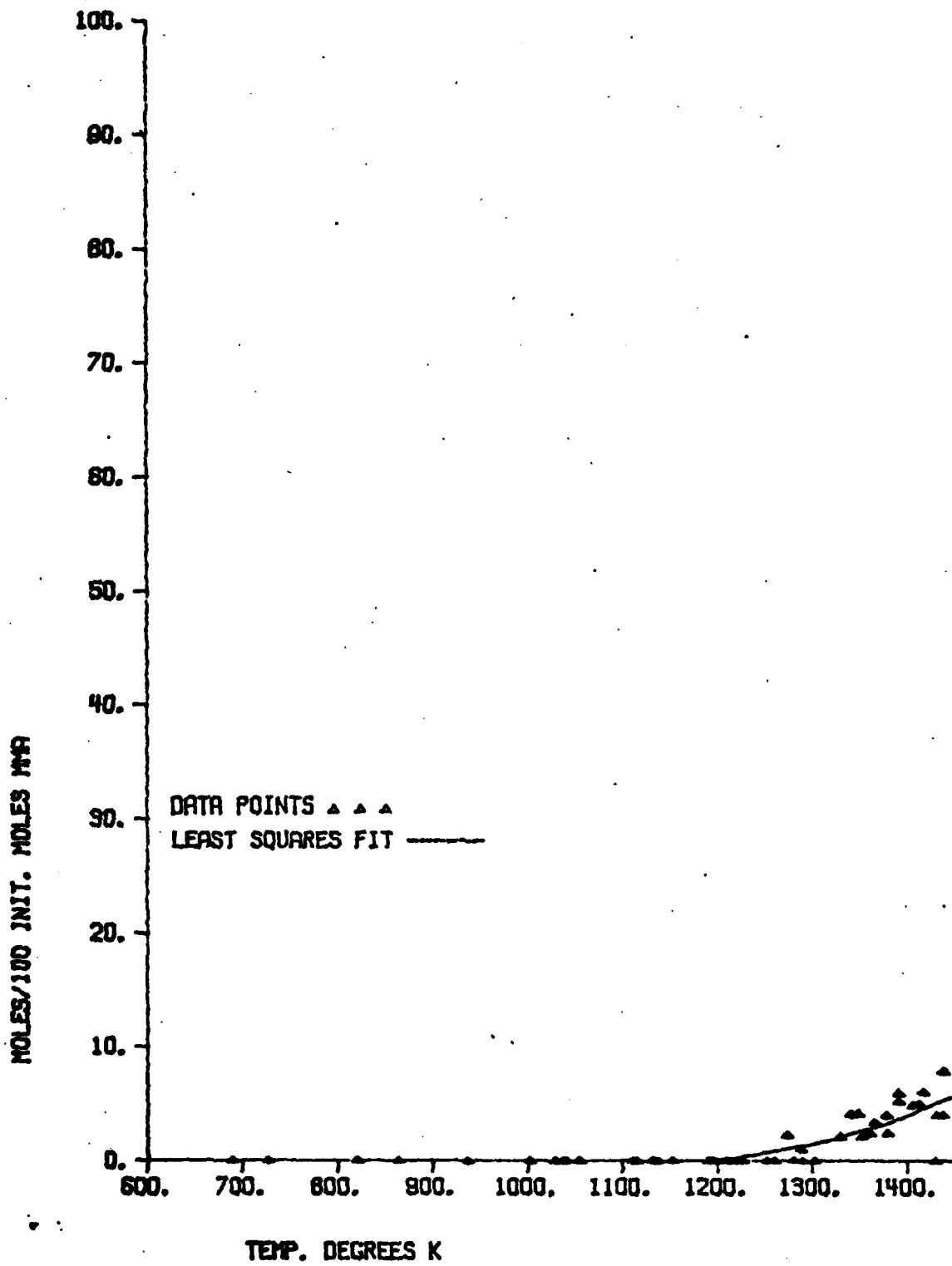


FIGURE 10, CONCENTRATION DATA AND LEAST SQUARES FIT FOR CH₄

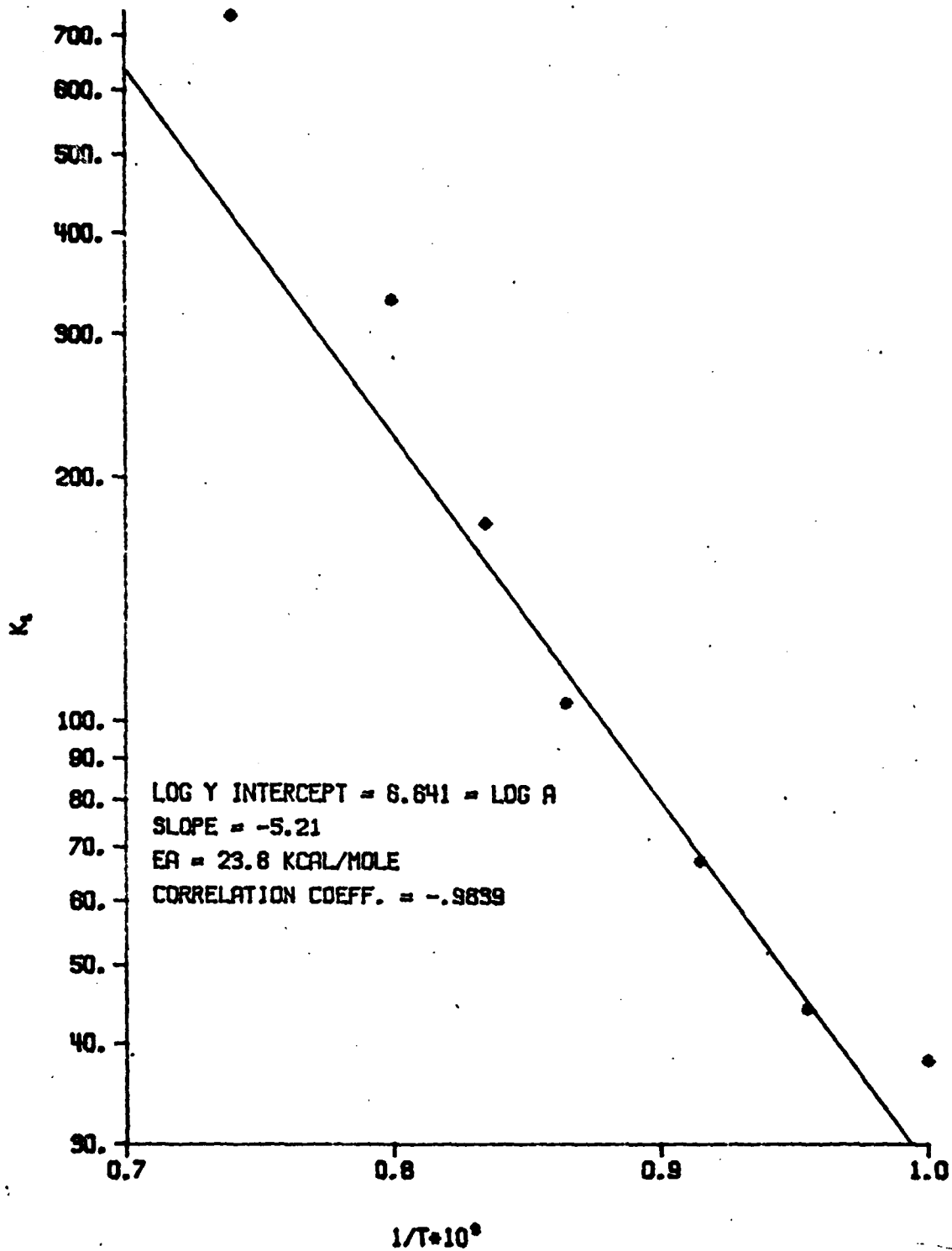


FIGURE 11, PLOT OF LOG K1 VS. 1/T TO DETERMINE LOG A

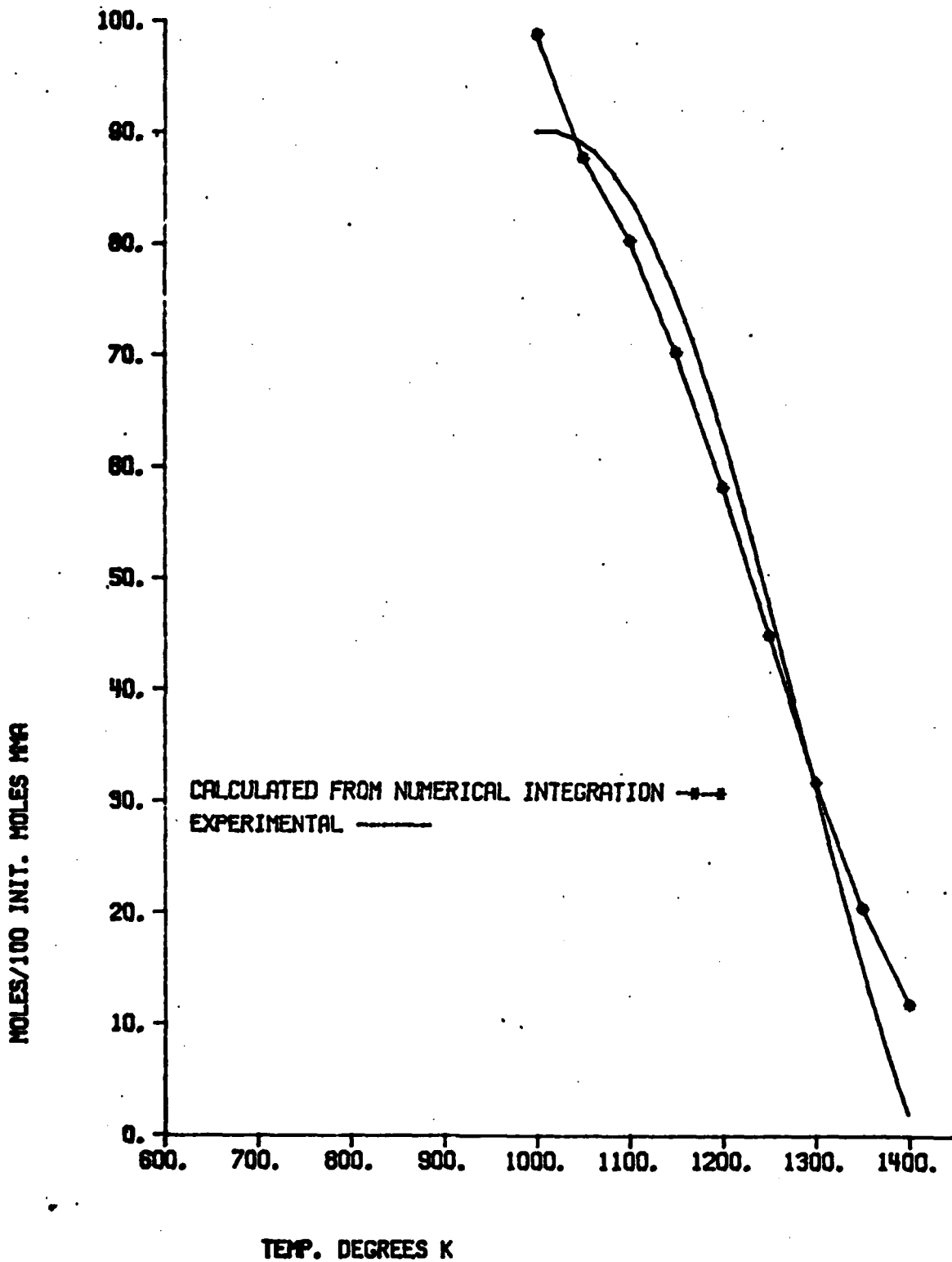


FIGURE 12, COMPARISON OF EXPERIMENTAL AND CALCULATED MMR CONCENTRATION

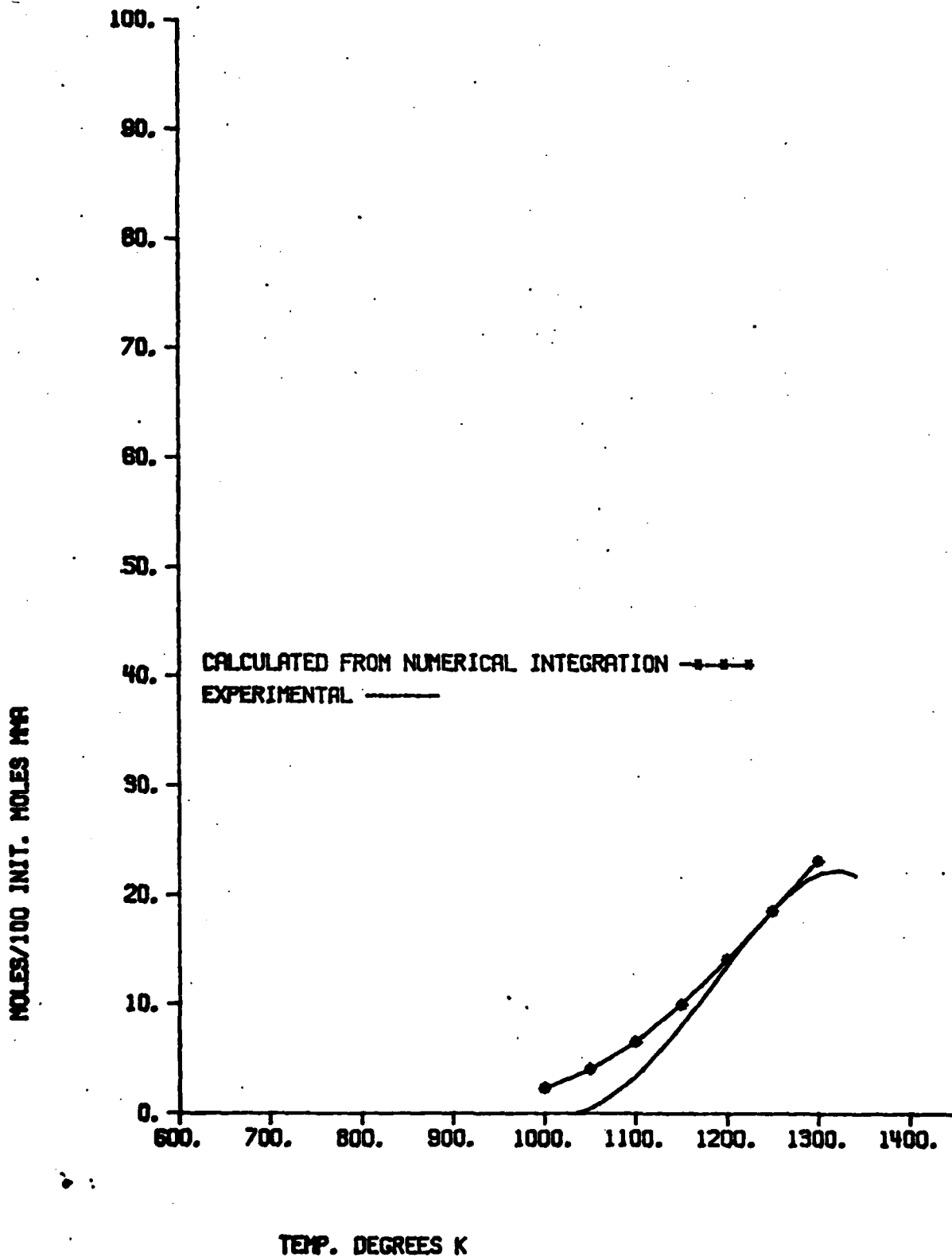


FIGURE 13, COMPARISON OF EXPERIMENTAL AND CALCULATED NH₃ CONCENTRATION

V. Discussion

The most unusual result obtained in this study is the low values for the Arrhenius parameters obtained for the C-N bond scissure of MMA. The Arrhenius parameters are compared in Table III. Values of k_1 lower than those that would be expected theoretically have been reported elsewhere (Ref 6,14) and have been attributed to a free radical mechanism, such as the postulated mechanism used here.

Table III
Arrhenius parameters for MMA Decomposition

<u>log A</u>	<u>Ea(kcal/mole)</u>	<u>Source</u>
14.62	43.3	(Ref 12)
10.84	48.15	(Ref 5)
17.0	79.0	(Ref 3)
9.0	58.6	(Ref 14)
6.64	23.8	this work

The results of the numerical simulation support the mechanism of a C-N bond scissure followed by hydrogen abstraction via the NH_2 fragment. However, the rate of

formation of CH_4 lagged far behind that expected. Smith & Sawyer (Ref 14) also observed a rate of formation of CH_4 only .42 times the rate of formation of NH_3 .

As an experiment in this study, the Arrhenius parameters for k_2 and k_3 were changed by decreasing the pre-exponential factor by two orders of magnitude and increasing E_a by 50% in an effort to suppress CH_4 formation in the numerical model. This change did not suppress CH_4 formation, which is the expected result, as the reactions involving the radical species are rapid enough to allow for a quasi-equilibrium situation with very low CH_3 and NH_2 concentrations. It is also of interest that due to the low radical concentration, the recombination reactions producing CH_3NH_2 and C_2H_6 are not significant as these reactions are second order in the concentrations of the radical species.

The flow reactor study of Smith & Sawyer (Ref 14) reported other results which are interesting to compare to the results obtained here. At the 1060 to 1140°K temperature range they operated at, large quantities of residue collected on the sampling probe used. The two main constituents of the residue were hexamethylenetetramine and 3-ethyl-4-methyl pyrrole. The pyrrole could be formed by an attack of the $\text{CH}_2=\text{NH}$ species by the CH_3 species through a series of reactions and could account for the relative absence of CH_4 at temperatures below 1200°K. Above 1200°K,

the $\text{CH}_2=\text{NH}$ tends to shed hydrogen and become H_2 and HCN as in equation 6.

The disappearance of NH_3 at temperatures above 1300°K is somewhat of a puzzle. The NH_3 is probably not dissociating and recombining as N_2 and H_2 , as Bamford (Ref 2:12) reports that no significant homogeneous dissociation of NH_3 occurs below about 2000°K . The same source, however, reports that heterogeneous (i.e. at vessel wall) decomposition may occur at lower temperatures. It can be assumed that NH_3 is reacting with other species in the gas mixture at temperatures above 1275°K , rather than undergoing homogeneous decomposition.

VI. Conclusions and Recommendations

Conclusions

As a result of this study, the following conclusions are made:

1. The postulated mechanism of a C-N bond scissure followed by a series of free radical reactions is a good description for the process of decomposition of MMA and formation of NH_3 .

2. The postulated mechanism is not a good model for formation of CH_4 or for tracking of the carbon containing species.

3. As determined by the methods of this study, the Arrhenius equation for C-N bond scissure of mono-methylamine is

$$k = 10^{6.64} \exp(-23.800/RT) \text{ sec}^{-1}$$

4. The numerical model behaves in a consistent fashion over the range of temperatures and concentrations in this study.

Recommendations

To help better answer some of the problems suggested, the following recommendations are made:

1. Procedures for better determination of gas concentration by gas chromatography be developed, with special attention being given to resolution of N_2 , N_2H_4 , C_2H_6 , C_2H_4 , C_2H_2 , HCN, and H_2 . Use of a flame ionization detector for the species containing carbon would greatly increase sensitivity. Other analytical

techniques such as mass spectrometry might also be employed.

2. Theoretical study of $\text{CH}_2=\text{NH}$ and CH_3 reactions should be made to attempt to model the behavior of these species for incorporation into the numerical model.

3. Further numerical studies should be made incorporating the reactions developed in recommendation 2 to try to better approximate the experimental behavior of the monomethylamine pyrolysis thus developing a better understanding of the decomposition mechanism.

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APPENDIX A
SHOCK TUBE OPERATING
PROCEDURE

The shock tube was operated by use of the following procedure:

1. A diaphragm and sample bottle were installed and all sections of the tube were evacuated with the driven section and dump tank evacuated to less than 10^{-3} Torr.

2. The driven section and dump tank were filled with argon to the desired initial pressure, then the dump tank was isolated from the driven section:

3. The driven section and sample bottle were evacuated to 10^{-3} Torr or less and the sample bottle was then isolated from the system.

4. The driven section was filled with test gas to a pressure 2-3 Torr higher than the desired initial pressure. This was to ensure that the pure argon in the dump tank would not flow into the driven section and change the test gas mixture when the driven section and dump tank were connected.

5. The counter and oscilloscope were reset, and the shutter on the oscilloscope camera was opened.

6. The dump tank was reconnected to the driven section by opening the valve between them. The driven section was then isolated from the gas manifold to prevent damage to the pressure gauges.

7. High pressure helium was introduced to the driven section until the diaphragm was burst by the pressure.

8. A sample of the gas after the shock was taken by opening the previously evacuated sample bottle to the driven section of the tube for 10 seconds.

9. The counter reading was recorded and the photograph of the oscilloscope developed.

10. The tube was pressurized with argon to atmospheric pressure before opening to change diaphragms.

APPENDIX B

LEAST SQUARES CURVE FIT

PROGRAM

```

PROGRAM CFIT(INPUT,OUTPUT,PLOT)
100  FORMAT(F4.0,8X,F4.1)
200  FORMAT(" ",IER=",I2,"NDEG=",I2,"NMAX=",I2)
300  FORMAT(" ",C(",I1,") ",F12.6)
400  FORMAT(" ",F6.0,2X,F6.1)
      DIMENSION X(49),Y(49),W(49),C(7),WORK(200)
      DIMENSION XP(51),YP(51),U(22),V(22)
      DO 10 I=1,49
10    READ 100,X(I),Y(I)
      DO 15 I=1,49
15    PRINT 400,X(I),Y(I)
      NP=49
      NDEG=4
      NMAX=0
      IN=0
      W(1)=0.0
      CALL PLSCF(X,Y,W,NP,NDEG,NMAX,C,IN,XD,XO,WORK,IER)
      PRINT 200,EIR,NDEG,NMAX
      NDEG=NDEG+1
      DO 20 I=1,NDEG
20    PRINT 300,I,C(I)
      DO 30 I=1,20
      U(I)=950.+(I*25.)
      V(I)=(U(I)**4)*C(5)+(U(I)**3)*C(4)+(U(I)**2)*C(3)+
1    (U(I)*C(2))+C(1)
30    PRINT 400,U(I),V(I)
      DO 40 I=1,49
      XP(I)=X(I)
40    YP(I)=Y(I)
      CALL PLOT(1.,1.,-3)
      CALL SCALE(XP,6.,49,1)
      CALL SCALE(YP,6.,49,1)
      U(21)=XP(50)
      U(22)=XP(51)
      V(21)=YP(50)
      V(22)=YP(51)
      CALL AXIS(0.,0.,15HTEMP. DEGREES K,-15,6.,0.,XP(50),XP(51))
      CALL AXIS(0.,0.,24HMOLES/100 INIT.MOLES MMA,24,6.,90,
1 YP(50),YP(51))
      CALL LINE(XP,YP,49,1,-1,2)
      CALL LINE(U,V,20,1,0,0)
      CALL PLOTE(N)
      STOP
      END

```

APPENDIX C
RATE CONSTANT FINDING PROGRAM

```

PROGRAM KFINDD(INPUT,OUTPUT)
100  FORMAT(F4.0,1X,F7.5,2X,F4.1)
200  FORMAT(" ", "IER=", I2, 1X, "TEST=", F6.2, 2X, "COUNT=", F4.1)
300  FORMAT(" ", "TEMP=", F6.1, 2X, "K=", F13.1)
EXTERNAL F
COMMON RK(8)
DIMENSION Y(8),P(6),TG(9),CONI(9),CON(9)
DO 10 I=1,9
10  READ 100,TG(I),CONI(I),CON(I)
DO 20 NTRY=1,9
C  COMPUTE RATE CONSTANTS
RK(1)=10.**17.*EXP(-79000./((1.987*TG(NTRY)))
RK(2)=10.**11.*EXP(-8700./((1.987*TG(NTRY)))
RK(4)=RK(2)
RK(3)=10.**11.*EXP(-10000./((1.987*TG(NTRY)))
RK(5)=RK(3)
RK(7)=10.**10.5
RK(8)=RK(7)
CT=0.
RU=RK(1)*8.
RL=RK(1)*.2
1  RM=(RU+RL)/2.
CT=CT+1.
RK(1)=RM.
X=0.
DX=.0009
N=6
DO 2 I=1,6
2  Y(I)=0.
Y(1)=CONI(NTRY)
CALL RKDF(X,Y,N,DX,IER)
TEST (Y(1) CONI(NTRY))*100.
PRINT 200,IER,TEST,CT
IF(TEST.LT.CON(NTRY))RU=RM
IF(TEST.GT.CON(NTRY))RL=RM
IF(CT.GT.25.)GO TO 20
IF(ABS((TEST-CON(NTRY))/CON(NTRY)).GT..01)GO TO 1
20  PRINT 300,TG(NTRY),RK(1)
STOP
END

```

```

SUBROUTINE F(X,Y,P,N)
COMMON RK(8)
DIMENSION Y(N),P(N)
P(1)=-RK(1)*Y(1)-RK(2)*Y(1)*Y(3)-RK(4)*Y(1)*Y(4)
1   +RK(8)*Y(3)*Y(4)
P(2)=RK(2)*Y(1)*Y(3)+RK(4)*Y(1)*Y(4)-RK(3)*Y(2)
1   *Y(3)-RK(5)*Y(2)*Y(4)
P(3)=RK(1)*Y(1)-RK(2)*Y(1)*Y(3)-RK(3)*Y(2)*Y(3)
1   -RK(7)*Y(3)*Y(3)-RK(8)*Y(3)*Y(4)
P(4)=RK(1)*Y(1)-RK(4)*Y(1)*Y(4) - RK(5)*Y(2)*Y(4)
1   RK(8)*Y(3)*Y(4)
P(5)=RK(2)*Y(1)*Y(3)+RK(3)*Y(2)*Y(3)
P(6)=RK(4)*Y(1)*Y(4)+RK(5)*Y(2)*Y(4)
RETURN
END

```

APPENDIX D

EXPERIMENTAL DATA

Temperature, °K.	Moles/100 initial moles MMA		
	MMA	NH ₃	CH ₄
1356	16.3	24.1	2.1
1362	11.7	19.6	2.4
1381	0.0	20.1	2.4
864	95.5	0.0	0.0
1291	36.1	26.5	0.0
1407	0.0	15.5	4.8
1349	12.2	18.3	4.1
1331	15.7	16.7	2.1
1261	28.7	29.7	0.0
821	104.4	7.3	0.0
1289	25.2	18.1	1.0
1003	100.0	0.0	0.0
1275	42.6	30.6	2.2
1431	0.0	0.0	7.8
1303	33.9	28.7	0.0
1220	65.3	20.3	0.0
1253	49.5	19.8	0.0
1198	79.8	12.6	0.0
1342	20.5	20.6	4.1
1430	0.0	11.7	0.0
1132	99.3	0.0	0.0
1414	9.9	0.0	4.9
937	54.5	7.4	0.0
1281	38.9	15.2	0.0
1211	65.6	13.1	0.0
689	94.2	0.0	0.0
1035	89.7	0.0	0.0
1116	75.7	0.0	0.0
1438	0.0	6.0	4.0
1418	0.0	8.0	6.0
1145	74.8	11.3	0.0
1392	0.0	15.8	5.9
1379	0.0	14.9	4.0
1432	0.0	11.9	4.0
1227	60.1	16.7	0.0

T, °K	MMA	NH ₃	CH ₄
1153	70.6	9.4	0.0
1111	91.8	7.4	0.0
1054	93.7	0.0	0.0
1190	40.7	14.0	0.0
1139	57.6	0.0	0.0
1041	84.4	0.0	0.0
1030	59.2	0.0	0.0
1392	0.0	10.4	5.2
1366	0.0	17.5	3.3
1037	113.0	0.0	0.0
1191	85.7	8.2	0.0
1135	91.9	0.0	0.0
727	84.4	0.0	0.0
1056	79.3	8.4	0.0

VITA

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The decomposition of monomethylamine (MMA) was studied to model the decomposition mechanism. The decomposition of a 2.5% mixture of MMA in argon was studied behind a reflected shock by use of a single pulse shock tube with gas chromatography to determine the products CH ₄ , NH ₃ , and unreacted MMA. The temperatures behind the reflected shock ranged from 727 K to 1438 K. The reaction time was 9 x 10 ⁻⁸ sec. The rate constants for the initiating C-N bond scissure were determined by a parametric study using a		

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numerical model. the concentrations of CH_4 , NH_3 , and MMA were examined to determine the reasonableness of the model. The Arrhenius equation for the initial C-N bond scissure is $10^{8.84} \cdot \exp(-28,300/RT) \text{sec}^{-1}$ as determined in this study.

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