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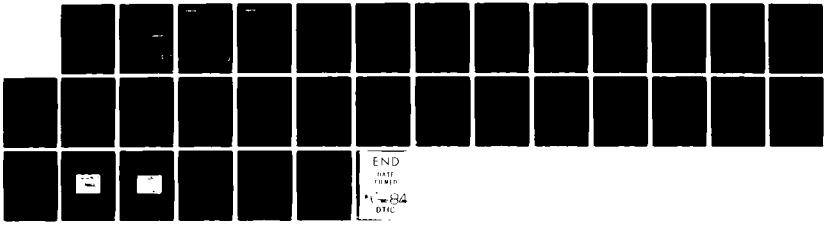

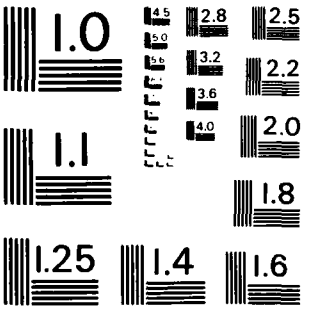

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INVESTIGATION OF THE THERMAL INITIATION OF DETONATION IN NITROMETHANE

J206-83-011/6223

Final Report

by

Raafat H. Guirguis

October 21, 1983

Prepared for:

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375

Under:

Contract Number N00014-82-C-2253

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October 21, 1983

Dr. J. P. Boris
Code 4040
Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375

SUBJECT: Final Report, Contract Number N00014-82-C-2253

Dear Dr. Boris:

JAYCOR is pleased to submit this Final Report entitled, *Investigation of the Thermal Initiation of Detonation in Nitromethane*, in accordance with the subject contract, CDRL Item Number A002.

If the Final Report is acceptable, please sign and forward the enclosed DD Form 250.

Questions of a technical nature should be addressed to Dr. Ernest C. Alcaraz while questions of a contractual nature should be addressed to Mr. Floyd C. Stilley, our Contracts Administrator.

Sincerely,

Martin C. Nielsen
Manager of Administration
and Counsel

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Shock tube experiments and extensive numerical simulations were used to provide information required to construct a detailed chemical mechnaism for the decomposition of gaseous nitromethane diluted in argon. Measurements were made of the time evolution of the pressure and the NO absorption at a fixed location in the shock tube, and mass and infrared spectroscopy were used to identify the products. Experiments were performed in the pressure range 0.3 to 2.5 atms and temperature range 700° to 2000° K using mixtures of 10 to 100 percent nitromethane in argon. A mechanism composed of elementary reactions describing nitro-

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20. ABSTRACT (Continued)
methane decomposition in the range of the experiments was compiled, tested and reduced to a set of 62 most significant reactions.

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I. INTRODUCTION

The Naval Research Laboratory (NRL) has been conducting a Combustion Research Program for several years. The program is coordinated by the Laboratory of Computational Physics (LCP) within NRL. This report discusses an effort conducted for LCP as an element of the Combustion Research Program, an Investigation of the Thermal Initiation of Detonation in Nitromethane. The effort was directed toward an in-depth understanding of the chemistry of decomposisiton for energetic materials (such as CH_3NO_2, RDX and HMX) and the effects of shock waves in condensed explosives, in order to produce safe, reliable explosives. The principal task was to develop appropriate mathematical models for the physical and chemical processes involved in the inititation of chemical reaction in explosives and subsequent decomposition, as well as design and implementation of efficient computational techniques to solve these models. This work was in collaboration with the Combustion and Fuels Branch of the Chemistry Division at NRL.

II. TECHNICAL DISCUSSION

In the area of chemical decomposition of explosives, nitromethane (CH_3NO_2) was chosen for an in-depth study because of its relatively simple chemical structure and because the subset of its gas phase kinetics derived from CH_3 radicals is related to the well-studied methane (CH_4) kinetics. Since earlier studies of the pyrolysis of nitromethane were concerned mainly with the initiation step of low-pressure gas phase reaction, very little was known about the mechanism through which nitromethane reaches its final products. The study began by collecting and synthesizing the elementary reactions pertinent to the reaction of nitromethane. Thermochemical data of some of the species expected to be involved in the reaction were missing. In particular, data for nitromethane itself was unavailable. Therefore, one of the early problems to solve was the production of thermochemical data for CH_3NO_2, CH_3ONO, CH_3NO, CH_3O, CH_2NO_2 and HCO_2.

The thermodata for the missing species was furnished by using group additivity theories[1], or by relating the species to similar ones in chemical structure and getting reasonable values for the vibrational frequencies of the missing or extra bonds to form the species in question. In this context, a program was designed and written[2] to extend the data of any hydrocarbon species from as few as four temperatures - specific heat data points[1] - to a much wider range of temperature. The expansion is based on the fact that the vibrational frequencies of most hydrocarbon's chemical bonds fall into four ranges:

(1)	very low	300 - 500 cm^{-1},
(2)	low	500 - 900 cm^{-1},
(3)	intermediate	900 - 1700 cm^{-1},
(4)	high	1700 - 3200 cm^{-1}.

By assuming that the vibrational frequencies of any species can be degenerately grouped into four average frequencies, they can be found if we know the value of the specific heat at four temperatures and assume four reasonable degeneracies. The problem is then reduced to solving a set of four non-linear algebraic equations, i.e., the quantum mechanical expression of the vibrational contribution to the specific heat.

The solution of the set of ordinary differential equations describing the collected elementary reactions to get the evolution of the species, temperature and pressure used the package "CHEMEQ"[3]. It allows the information about the chemical reactions to be input in the standard form of writing chemical reactions. It is equipped with an Automatic Rate Processor that formulates the describing ordinary differential equations from the read reactions. However, it does not derive the reverse reactions from the forward ones. A new program was written[4] that accepts the forward chemical reactions in their standard format (same format accepted by CHEMEQ) and then evaluates the reverse reaction rates in either an Arrhenuis or a modified-Arrhenius form assuming chemical equilibrium between foward and reverse reactions. The thermodata used are those of the NASA chemical equilibrium program. The program then produces the reverse reactions and their rates, again in the format acceptable by "CHEMEQ".

After collecting all these items, a chemical kinetic scheme able to reasonably describe the thermal decompostion of nitromethane in the pressure range 1-3 atmospheres and temperature range 1000°-1500° K, was constructed. The results of integrating the set of ordinary differential equations describing the scheme compared favorably with the shock tube measurements[5]. The details of the scheme were presented and will be published in the proceedings of the Ninth International Colloquium on the Dynamics of Explosions and Reactive Systems, Poitiers, France (1983). A copy of the paper appears in Appendix A.

In the area of shock wave effects in condensed explosives, a 1-D reactive shock code[6] was designed and written in which the hydrody-

namic processes, equation of state, external energy deposition, chemical processes, etc., are completely separated from each other. This separation allows any number of processes in any number of materials to be combined. The program is fully vectorized making large runs efficient on the TIASC (NRL computer) vector computer. This code has been transmitted under separate cover.

The 1-D reactive shock code was used to solve the problem of formation and propagation of a detonation wave from a hot spot in liquid nitromethane. The problem was addressed to assess the possibility of achieving uniform ignition by uniform heating. It was found that ignition will start at the hot spots which are produced from either the inhomogeneties in the material or in the heating beam and consume the whole material before any appreciable reaction occurs at the background temperature. Figure 1 shows the result of a 1200° K hot spot surrounded by a 1000° K background temperature. Obviously, a detonation front is formed and consumes ~ 0.5 cm of liquid nitromethane in ~ 1.28 μsec. At 1000° K, ignition would have occurred uniformly in ~ 30 μsec.

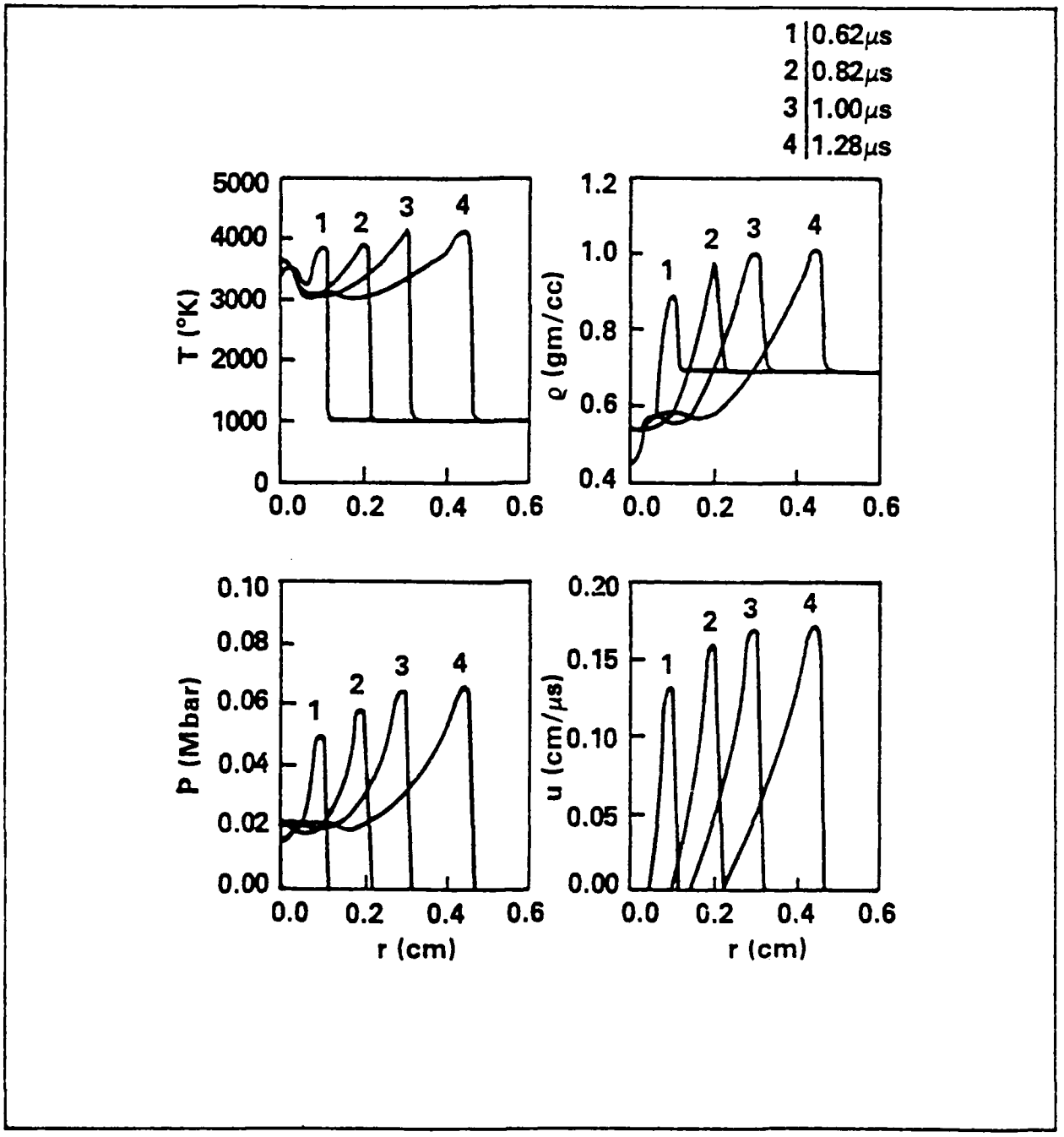
1 0.62μs
2 0.82μs
3 1.00μs
4 1.28μs
T (°K)
5000
4000
3000
2000
1000
0
ϱ (gm/cc)
1.2
1.0
0.8
0.6
0.4
P (Mbar)
0.10
0.08
0.06
0.04
0.02
0.00
u (cm/μs)
0.20
0.15
0.10
0.05
0.00
0.0
0.2
0.4
0.6
r (cm)

Figure 1

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1. Sidney Benson, "Thermochemical Kinetics," 2nd Edit., John Wiley and Sons, Inc., 1976.

2. R. Guirguis, NRL - LCP Library.

3. T. Young and J. Boris, NRL - LCP Library.

4. R. Guirguis, NRL - LCP Library.

5. Performed by D. Hsu and D. Bogan, NRL, Chemistry Division.

6. R. Guirguis, NRL - LCP Library.

APPENDIX A

DECOMPOSITION OF GASEOUS NITROMETHANE

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ABSTRACT

Shock tube experiments and extensive numerical simulations were used to provide information required to construct a detailed chemical mechanism for the decomposition of gaseous nitromethane diluted in argon. Measurements were made of the time evolution of the pressure and the NO absorption at a fixed location in the shock tube, and mass and infrared spectroscopy were used to identify the products. Experiments were performed in the pressure range 0.3 to 2.5 atms and temperature range 700 to 2000°K using mixtures of 10 to 100% nitromethane in argon. A mechanism composed of elementary reactions describing nitromethane decomposition in the range of the experiments was compiled, tested, and reduced to a set of 62 most significant reactions.

In the reaction mechanism proposed, initiation starts with the C-N bond breaking giving CH_3 and NO_2. Methoxy and CH_2NO_2 radicals then propagate the reaction through two major parallel pathways both producing CH_2O. Formaldehyde is then reduced to HCO which reacts with NO_2 to yield the products. The predictions of this mechanism, were compared to experiments and it was found that the mechanism predicts correct induction times and NO behavior for the pressure and temperature range of the experiments. Ignition does not occur until all the nitromethane is consumed. Ways to produce HCN and C_2H_2, traces of which have been detected by infrared spectroscopy, are required to complete the proposed mechanism.

INTRODUCTION

Recent advances in diagnostic techniques and computational methods have given new impetus to research aimed at unravelling the controlling chemical processes in explosive materials. The work reported here is a study of the decomposition of gaseous nitromethane in the low pressure - high temperature regime. We have chosen to study nitromethane because it has a relatively simple chemical structure and because the subset of its gas phase kinetics derived from CH_3 radical is related to the well-studied methane kinetics.

The first studies of nitromethane pyrolysis were reported by Taylor and Vesselovsky (1935). Considerably later, plausible initiation steps were deduced by Cottrell, Graham and Reid (1951). The first accurate measurement of the rate of unimolecular decomposition of nitromethane and the effects of pressure was done by Glanzer and Troe (1972) using a shock tube. Most recently, Perche, Tricot and Lucquin (1979) made the first attempt towards constructing a detailed chemical kinetic mechanism for the decomposition of nitromethane. Their scheme adequately describes their extremely low pressure, low temperature static experiment.

The present study, which combines both shock tube experiments and extensive numerical simulations, is the first in a series of studies aimed at constructing a detailed chemical reaction mechanism for gaseous nitromethane which will be valid over a wide range of pressures and temperatures. The experiments were performed using concentrations of 10 to 100% nitromethane diluted in argon, in the pressure range 0.3 to 2.5 atms and temperature range 700 - 2000°K. A chemical kinetic scheme that yields induction times and NO concentrations in general agreement with the experiment has been compiled, extensively tested, and reduced to the most important set of rates. It

appears that within the range of experimental pressures and temperatures considered, nitromethane is not explosive but undergoes a slow conversion to products. The reaction mechanism predicts an explosive behavior at higher temperatures and pressures.

EXPERIMENT

A 6.35 cm internal diameter shock tube was used which had a 2.5m driver section. In the current setup the shock section is extended from 3.8 to 4.4m when the effects of the incident shock alone are to be measured. Helium was pumped in the driver section until the diaphragm burst, so that varying Mach number shocks were achieved by varying the diaphragm thickness. Four piezoelectric gauges detected the instant of shock arrival and allowed us to evaluate the incident shock velocity. A CO laser probe and a quartz pressure gauge measured the NO (or CO) absorption and the pressure evolution at a fixed location 4.5 cm from the end wall. A second pressure gauge measured the pressure evolution at the end wall.

After all of the wave effects in the shock tube died out and mixing was complete, samples of the products were extracted for later analysis by mass spectroscopy. The contents of the shock tube were then pumped through a liquid nitrogen trap. After warming up the contents to room temperature, an infrared spectrometer was used to identify the condensible products.

The unshocked gas consisted of mixtures of 10 to 100% nitromethane in argon at pressures up to a few torr. To avoid damaging the quartz and piezoelectric gauges, the mixture pressure was reduced when higher concentrations of nitromethane were used. In general, driver pressures of 1.3 to 5.7 atm generated incident shock Mach numbers in the range 3 to 5.7, causing temperatures of 700 to 1250°K and pressures of 0.2 to 0.7 atm. Upon reflection at the end wall, temperatures of 1200 to 2050°K and pressures of 1.7 to 2.5 atm were achieved. The above shock wave parameters have been evaluated from the observed incident shock velocity assuming frozen compositions across the shock waves.

PROPOSED REACTION MECHANISM

Our initial compilation of reactions for nitromethane decomposition included over 150 elementary steps. Analysis of the relative importance of their contribution allowed us to deduce a simplified scheme of 62 reaction steps, given in Table I. The initiation step is that suggested by Glanzer and Troe for low pressures,

$$CH_3NO_2 + M \rightarrow CH_3 + NO_2 + M.$$

After the C-N bond splits, the reaction mainly proceeds by two parallel pathways, as shown in Fig. (1). The first starts with CH_3NO_2 attacked by radicals to form CH_2NO_2, which unimolecularly decomposes to form formaldehyde. The second pathway starts with the methyl and nitrogen dioxide reacting to form methoxy radicals, which decompose almost instantaneously to give formaldehyde. The CH_2O from both pathways is then attacked to produce formyl radicals. These react later with NO_2 to yield the products NO, CO, and CO_2.

A third minor pathway (not shown in Fig. (1)) is included at the end of Table I. It begins with the methyl radicals recombining to form ethane, ethyl radicals, and ethylene. Ethane and ethyl radicals are then reduced to ethylene which when attacked by OH radicals gives CH_2O and CH_3.

RESULTS

Figure (2a) illustrates typical pressure (bottom) and NO-absorption (top) oscilloscope traces at the fixed location 4.5 cm from the end wall, for a 26% nitromethane in argon mixture. The first two numbers at the top of the figure refer to the oscillosocope gain and the third one refers to the time increment per division. The calculated pressure and temperature after the reflected shock is 1.69 atms and 1145°K. The sudden jump in the NO absorption trace marks the instant when the reflected shock arrive. At ~ 100 μs, after the pressure jump caused by the reflected shock, there is another pressure jump that signals the end of the induction period. This coincides with the NO trace suddenly leveling off. Figure (2b) illustrates the pressure trace recorded at the end wall of a 24% nitromethane in argon mixture. The calculated pressure and temperatue is 1.7 atms and 1465°K. The measured induction time is 88 μs.

Figures (3a) and (3b) show the most significant production rates calculated for an adiabatic constant volume process at the same initial conditions of Fig. (2a). From left to right, Fig. (3a) shows the methyl and nitrogen dioxide radicals recombining very early to form methoxy and nitric oxide. The dashed curve, almost coinciding with $CH_3 + NO_2 \rightarrow CH_3O + NO$ curve, shows that CH_3O almost instantaneously decomposes after its formation to give CH_2O and H. The H radicals later react with NO_2 to form OH radicals and more NO. Next, the hydrogen and hydroxyl radicals attack the formaldehyde to form the formyl radicals which then react with NO_2 to form the products.

Figure (3b) shows the production rates for the pathway CH_3NO_2 + radicals $\rightarrow CH_2NO_2 \rightarrow CH_2O + NO$. The dashed curve $NO_2 + H \rightarrow OH + NO$ is

the major OH production reaction. It production rate curve coincides with the $CH_3NO_2 + OH \rightarrow CH_2NO_2 + H_2O$ curve, showing that OH radicals are consumed as soon as they are formed.

Finally, all the rates drop sharply at 100 μs, which is the induction time observed in Fig. (2). The same induction time is observed again in Fig. (4a) showing the time evolution of the intermediate species. The methoxy and hydroxyl radicals, which are consumed almost as fast as they are formed, have a very low nearly steady state concentration. Formaldehyde, on the other hand, has the highest concentration of any intermediate, and its depletion begins late in the induction period. At the end of the induction period, all the radical concentrations drop sharply. In our calculations, this time coincides consistently with that of consumption of all the nitromethane. Figure (4b) shows the product concentration of products steadily increasing until the end of the induction time when they level off. This, too, compares favorably with the experiment.

CONCLUSION

The reaction mechanism proceeds by two major parallel pathways, through methoxy radicals and through CH_2NO_2 radicals. Both pathways produce CH_2O which, when attacked by the existing radicals, gives HCO radicals that carry the reaction towards completion. It is believed that the radical reactions do not release enough energy to compensate fo that energy consumed by the decomposition of nitromethane. As a result, although the concentration of the radicals reaches its maximum steady state level early in the reaction process, ignition does not occur until all the nitromethane is consumed. The energy released then by the radical reactions increases the temperature, and rapid ignition occurs.

We have compared the results of integrating the chemical kinetic scheme to the shock tube experiment. In general, it appears that the mechanism proposed gives the correct induction times in the pressure and temperature ranges considered and the correct behavior for the time evolution of the species NO, which was directly measured. Future improvements should incorporate require us to way to explain the production of HCN and C_2H_2. These are not major products, but they were detected in greater than trace amounts by infrared spectroscopy than is predicted by the present mechanism. Finally, we need to investigate other initiation steps that could compete with splitting of the C-N bond.

ACKNOWLEDGEMENTS

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Table I

Reaction rate constants, $K = AT^n e^{-E/RT}$

Reactants	Products	A	n	E	Ref.
Initiation					
$CH_3NO_2 + M$	$CH_3 + NO_2 + M$	1.30(17)	0.00	42.00	(1)
$CH_3 + NO_2$	CH_3NO_2	5.00(11)	0.00	0.00	(2)
Formaldehyde Formation I. CH_3O Propagates Reaction					
$CH_3 + NO_2$	$CH_3O + NO$	1.30(13)	0.00	0.00	(1)
$CH_3O + M$	$CH_2O + H + M$	4.00(40)	-7.50	22.60	(3)
$CH_2O + H + M$	$CH_3O + M$	4.75(37)	-6.92	0.08	R*
$NO_2 + H$	$NO + OH$	2.90(14)	0.00	0.81	(4)
$CH_3O + NO$	$CH_2O + HNO$	3.20(12)	0.00	0.00	(4)
$CH_2O + HNO$	$CH_3O + NO$	2.85(12)	0.00	28.80	R
$H + NO + M$	$HNO + M$	5.40(15)	0.00	-0.60	(5)
$HNO + M$	$H + NO + M$	2.88(16)	0.00	48.80	R
$CH_3O + NO_2$	$CH_2O + HNO_2$	4.00(11)	0.00	0.00	(4)
$HNO_2 + M$	$NO + OH + M$	3.00(18)	0.00	46.70	(4)
$NO + OH + M$	$HNO_2 + M$	7.91(15)	0.00	-2.20	R
$CH_3 + NO$	CH_3NO	4.00(12)	0.00	0.00	(2)
CH_3NO	$CH_3 + NO$	7.00(13)	0.00	38.00	(2)
$CH_3O + NO$	CH_3ONO	6.30(13)	0.00	0.00	(4)
CH_3ONO	$CH_3O + NO$	4.00(15)	0.00	41.10	(6)
$CH_3O + H$	$CH_2O + H_2$	1.00(14)	0.00	0.00	(3)
$CH_3O + H$	$CH_3 + OH$	9.09(17)	0.00	15.20	R
$CH_3 + OH$	$CH_2O + H_2$	8.00(12)	0.00	0.00	(7)
$CH_3O + OH$	$CH_2O + H_2O$	3.20(13)	0.00	0.00	(3)
$H_2 + OH$	$H_2O + H$	5.20(13)	0.00	6.50	(7)
$H_2O + H$	$H_2 + OH$	2.22(14)	0.00	21.80	R
$CH_3O + CH_3O$	$CH_3OH + CH_2O$	1.10(13)	0.00	0.00	(4)

Reactants	Products	A	n	E	Ref.
Formaldehyde Formation II. CH_2NO_2 Propagates Reaction					
$CH_3NO_2 + CH_3$	$CH_2NO_2 + CH_4$	2.40(11)	0.00	9.00	(2)
$CH_3NO_2 + NO_2$	$CH_2NO_2 + HNO_2$	3.07(12)	0.00	18.34	R
$CH_2NO_2 + HNO_2$	$CH_3NO_2 + NO_2$	1.00(12)	0.00	0.00	(2)
$CH_3NO_2 + H$	$CH_2NO_2 + H_2$	2.50(09)	1.27	2.64	(7)
$CH_2NO_2 + H_2$	$CH_3NO_2 + H$	6.20(05)	2.17	9.46	R
$CH_3NO_2 + OH$	$CH_2NO_2 + H_2O$	6.90(04)	2.65	-1.90	(7)
CH_2NO_2	$CH_2O + NO$	1.00(13)	0.00	36.00	(2)
Formyl Formation					
$CH_2O + H$	$HCO + H_2$	2.50(09)	1.27	2.64	(7)
$CH_2O + OH$	$HCO + H_2O$	6.90(04)	2.65	-1.90	(7)
$CH_2O + NO$	$HCO + HNO$	2.86(14)	0.00	42.00	R
$HCO + HNO$	$CH_2O + NO$	3.20(13)	0.00	1.36	(3)
$CH_2O + CH_2NO_2$	$HCO + CH_3NO_2$	2.50(13)	0.00	10.00	(2)
Products Formation					
$HCO + NO_2$	$HNO_2 + CO$	1.00(14)	0.00	0.00	(4)
$HCO + NO_2$	$H + CO_2 + NO$	1.00(14)	0.00	0.00	(4)
$HCO + NO_2$	$OH + CO + NO$	1.00(14)	0.00	0.00	(4)
$HCO + M$	$H + CO + M$	1.00(15)	0.00	14.70	(7)
$H + CO + M$	$HCO + M$	1.67(15)	0.00	0.34	R
$HCO + NO$	$HNO + CO$	2.00(11)	0.50	2.00	(3)
$HNO + CO$	$HCO + NO$	7.60(11)	0.60	36.80	R
$CO + OH$	$CO_2 + H$	1.50(07)	1.30	-0.77	(7)
$CO + O + M$	$CO_2 + M$	2.80(13)	0.00	-4.54	(7)

Reactants	Products	A	n	E	Ref.
Formaldehyde Formation III. C_2H_4, C_2H_5, C_2H_6 Propagate Reaction					
$CH_3 + CH_3$	C_2H_6	2.50(12)	0.00	0.00	(8)
$CH_3 + CH_3$	$C_2H_5 + H$	8.00(14)	0.00	26.60	(7)
$C_2H_5 + H$	$CH_3 + CH_3$	5.26(16)	0.00	15.12	R
$CH_3 + CH_3$	$C_2H_4 + H_2$	1.00(16)	0.00	32.00	(7)
$C_2H_6 + CH_3$	$C_2H_5 + CH_4$	5.50(14)	0.00	21.50	(7)
$C_2H_5 + CH_4$	$C_2H_6 + CH_3$	3.25(15)	0.00	28.40	R
$C_2H_6 + OH$	$C_2H_5 + H_2O$	6.30(13)	0.00	3.60	(7)
$C_2H_5 + H_2O$	$C_2H_6 + OH$	6.32(13)	0.00	25.40	R
$C_2H_6 + H$	$C_2H_5 + H_2$	1.30(14)	0.00	9.37	(7)
$C_2H_5 + H_2$	$C_2H_6 + H$	3.05(13)	0.00	16.00	R
$C_2H_5 + M$	$C_2H_4 + H + M$	4.70(14)	0.00	26.60	(7)
$C_2H_4 + H + M$	$C_2H_5 + M$	9.54(13)	0.00	-10.82	R
$C_2H_5 + OH$	$C_2H_4 + H_2O$	2.00(13)	0.00	0.00	(7)
$C_2H_4 + OH$	$CH_2O + CH_3$	5.00(12)	0.00	0.00	(7)
$CH_2O + CH_3$	$C_2H_4 + OH$	2.84(12)	0.00	16.06	R
$CH_4 + OH$	$CH_3 + H_2O$	3.20(13)	0.00	5.00	(3)
$CH_3 + H_2O$	$CH_4 + OH$	5.43(12)	0.00	19.86	R

*Reverse reactions dennoted by R are evaluated from preceeding forward rate and equilibrium thermochemistry.

(1) Glanzer and Troe (1972); (2) Perche et al. (1979);
(3) Westley (1980); (4) Fifer (1978); (5) Baulch et al. (1973);
(6) Benson and O'Neal (1970); (7) Hsu et al. (1982);
(8) Troe (1979)

FIGURE CAPTIONS

Fig. (1) Major pathways for the decomposition of gaseous nitromethane.

Fig. (2a) Pressure and NO-absorption traces at a fixed location 4.5 cm from the end wall. Mixture of 5.0 torr nitromethane and 14.5 torr argon. Incident shock velocity 0.086 cm/μs.

Fig. (2b) Pressure trace at the end wall for a mixture of 3.02 torr nitromethane and 9.32 torr argon. Incident shock velocity 0.102 cm/μs.

Fig. (3a) Most significant production rates: CH_3O radicals propagate raction. Mixture of 25% nitromethane, 75% argon. Adiabatic constant volume process starting at 1145°K, 1.7 atm.

Fig. (3b) Most significant production rates: CH_2NO_2 radicals propagate reaction. Mixture of 25% nitromethane, 75% argon. Adiaatic constant volume process starting at 1145°K, 1.7 atm.

Fig. (4) Time evolution of species concentrations: (a) Intermediate species, (b) Products. Mixture of 25% nitromethane, 75% argon. Adiabatic constant volume process starting at 1145°K, 1.7 atm.

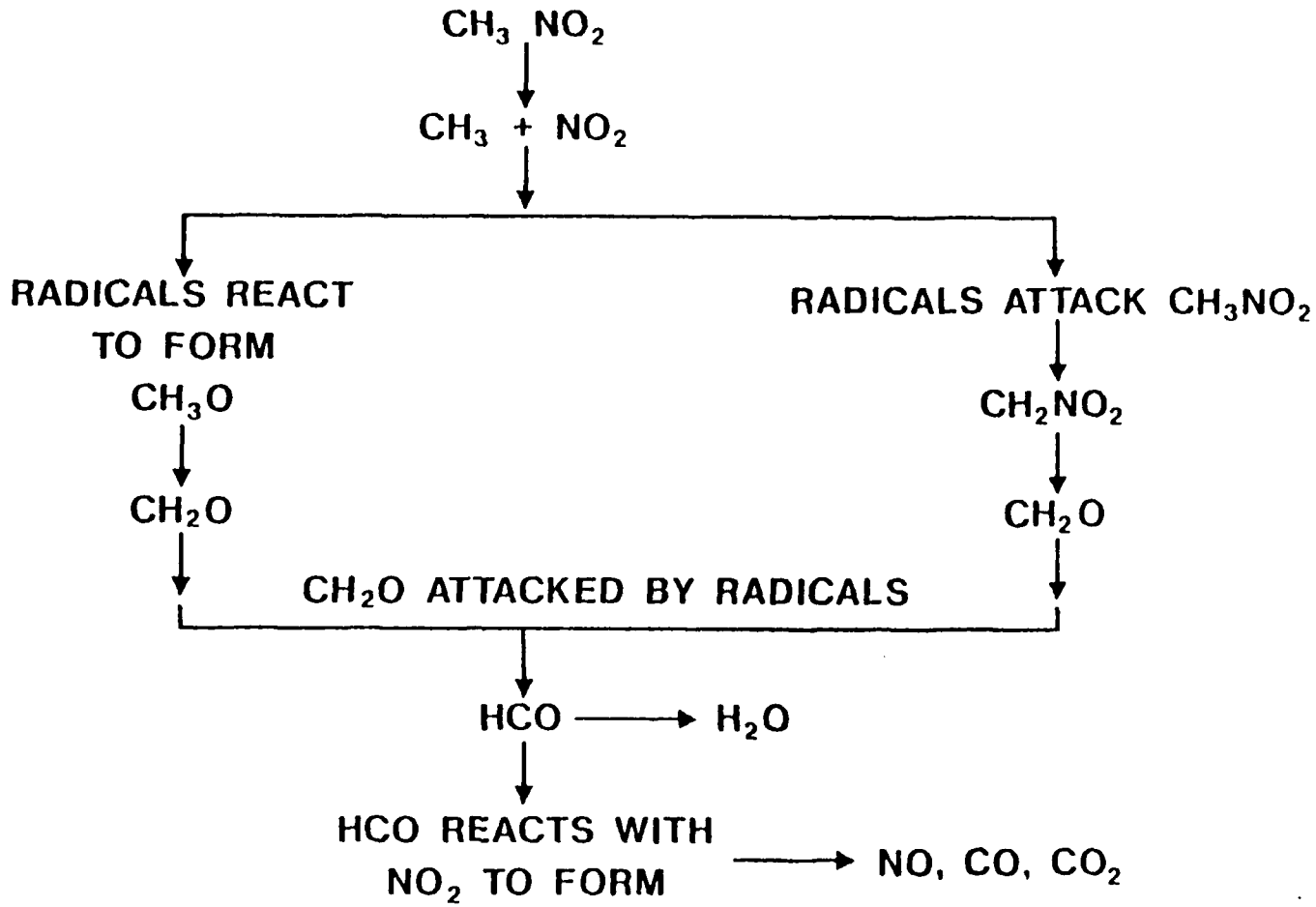
$CH_3\ NO_2$
$CH_3 + NO_2$
RADICALS REACT TO FORM CH_3O
CH_2O
RADICALS ATTACK CH_3NO_2
CH_2NO_2
CH_2O
CH_2O ATTACKED BY RADICALS
HCO → H_2O
HCO REACTS WITH NO_2 TO FORM → NO, CO, CO_2

Figure 1

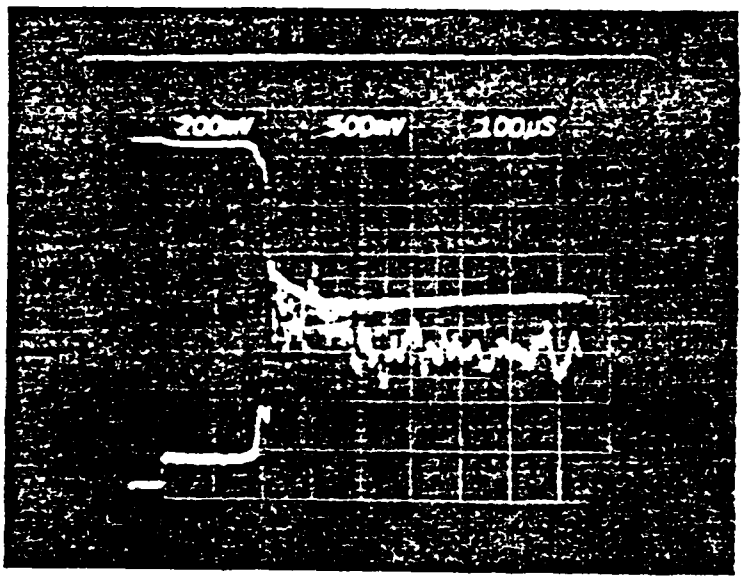

Figure 2(a)

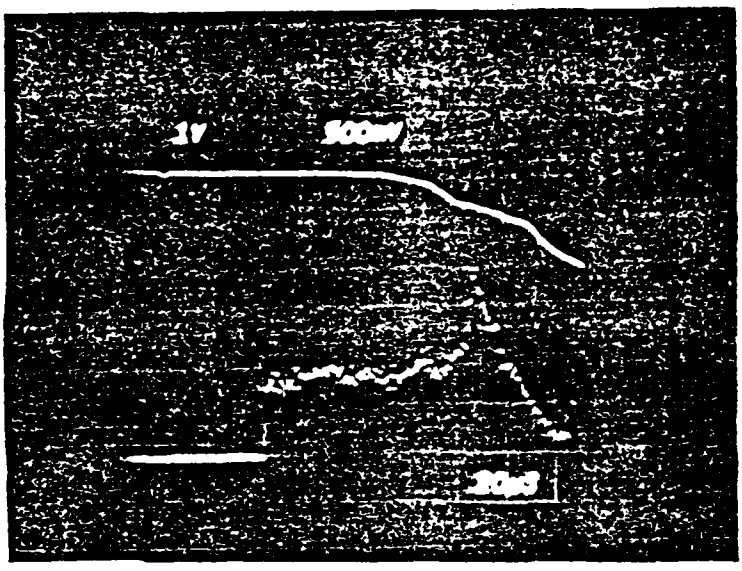

Figure 2(b)

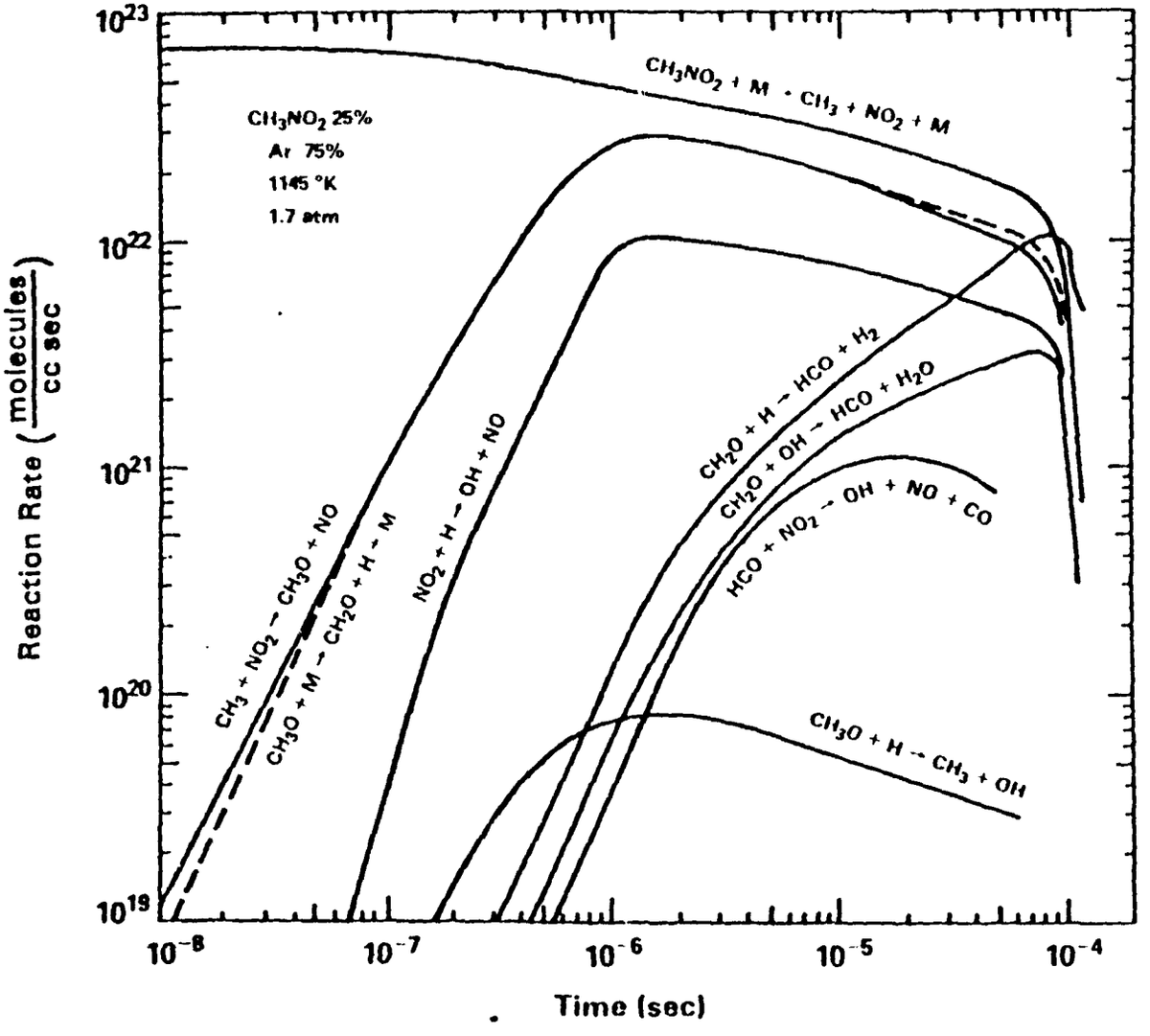
CH_3NO_2 25%
Ar 75%
1145 °K
1.7 atm
$CH_3NO_2 + M \rightarrow CH_3 + NO_2 + M$
$CH_3 + NO_2 \rightarrow CH_3O + NO$
$CH_3O + M \rightarrow CH_2O + H + M$
$NO_2 + H \rightarrow OH + NO$
$CH_2O + H \rightarrow HCO + H_2$
$CH_2O + OH \rightarrow HCO + H_2O$
$HCO + NO_2 \rightarrow OH + NO + CO$
$CH_3O + H \rightarrow CH_3 + OH$
Reaction Rate (molecules / cc sec)
10^{23}
10^{22}
10^{21}
10^{20}
10^{19}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
Time (sec)

Figure 3(a)

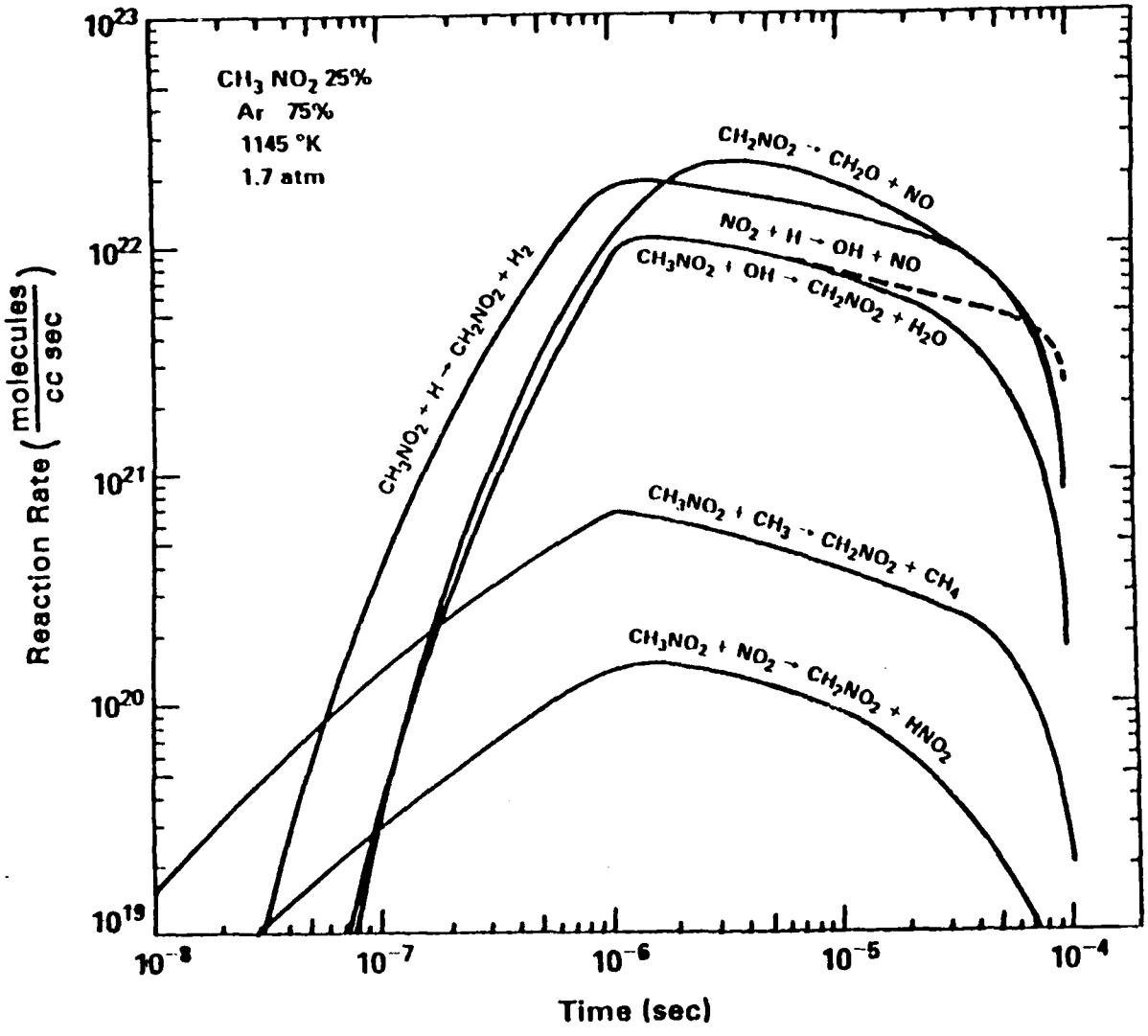
CH_3NO_2 25%
Ar 75%
1145 °K
1.7 atm
$CH_2NO_2 \rightarrow CH_2O + NO$
$NO_2 + H \rightarrow OH + NO$
$CH_3NO_2 + OH \rightarrow CH_2NO_2 + H_2O$
$CH_3NO_2 + H \rightarrow CH_2NO_2 + H_2$
$CH_3NO_2 + CH_3 \rightarrow CH_2NO_2 + CH_4$
$CH_3NO_2 + NO_2 \rightarrow CH_2NO_2 + HNO_2$
Reaction Rate $\left(\frac{\text{molecules}}{\text{cc sec}}\right)$
10^{23}
10^{22}
10^{21}
10^{20}
10^{19}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
Time (sec)

Figure 3(b)

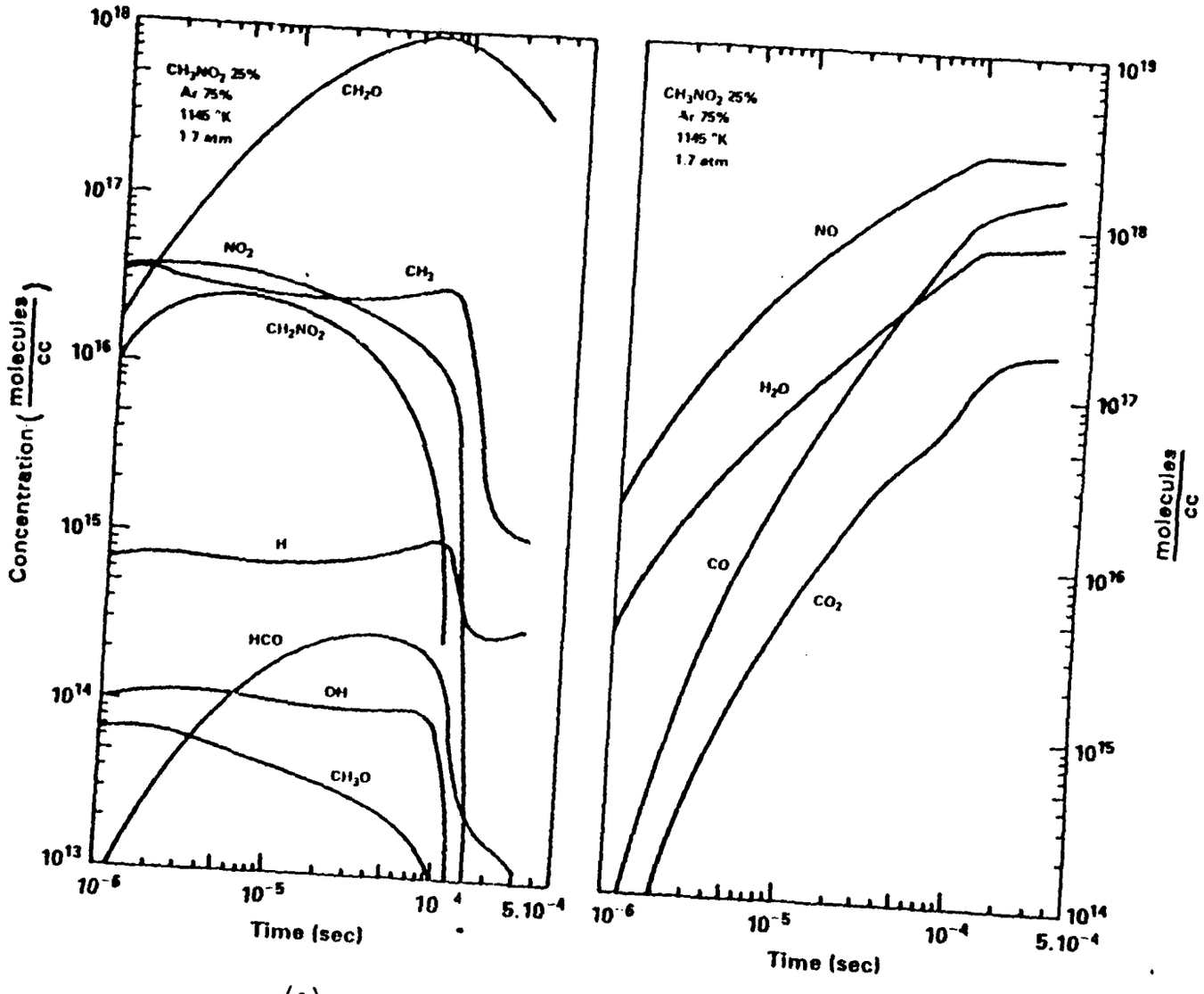
CH_3NO_2 25%
Ar 75%
1145 °K
1.7 atm
CH_2O
NO_2
CH_3
CH_3NO_2
H
HCO
OH
CH_3O
Concentration (molecules / cc)
Time (sec)
(a)
CH_3NO_2 25%
Ar 75%
1145 °K
1.7 atm
NO
H_2O
CO
CO_2
molecules / cc
Time (sec)
(b)

Figure 4