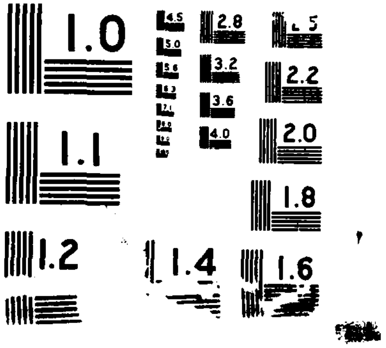
AD-A194 744 EXAMINATION OF MECHANISMS AND FUEL-MOLECULAR EFFECTS ON 1/2
SOOT FORMATION..(U) UNITED TECHNOLOGIES RESEARCH CENTER
EAST HARTFORD CT M COLKET ET AL. 13 FEB 88
UNCLASSIFIED UTRC/R88-957047 AFOSR-TR-88-0474 F/G 7/4 NL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DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release;
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4. PERFORMING ORGANIZATION REPORT NUMBER(S)
UTRC/R88-957047

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR-TR- 88-0474

6a. NAME OF PERFORMING ORGANIZATION
United Technologies
Research Center

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
AFOSR/NA

6c. ADDRESS (City, State, and ZIP Code)
East Hartford, Connecticut 06108

7b. ADDRESS (City, State, and ZIP Code)
Building 410, Bolling AFB DC
20332-6448

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
AFOSR/NA

8b. OFFICE SYMBOL (If applicable)
NA

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F49620-85-C-0012

8c. ADDRESS (City, State, and ZIP Code)
Building 410, Bolling AFB DC
20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
61102F	2308	A2	

11. TITLE (Include Security Classification)
(U) Examination of Mechanisms and Fuel-Molecular Effects on Soot Formation

12. PERSONAL AUTHOR(S)
Colket, Meredith III; Seery, D. J.; and Sangiovanni, Joseph J.

13a. TYPE OF REPORT
Final

13b. TIME COVERED 84
FROM 11/15/~~86~~ TO 11/14/87

14. DATE OF REPORT (Year, Month, Day)
Feb. 13, 1988

15. PAGE COUNT
110

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Hydrocarbon pyrolysis, ~~and~~ oxidation, acetylene, ethylene, vinylacetylene, benzene, formation of aromatics, soot formation

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A variety of hydrocarbons has been pyrolyzed in a single-pulse shock tube over the temperature range of 1000 to 2400 K and for dwell times of 500 to 700 microseconds. Gas samples of reactant, intermediate, and final products were collected and analyzed using gas chromatography. Chemical kinetic models in good agreement with data were developed for several of the hydrocarbons that were pyrolyzed. Specific mechanisms and rate coefficients have been proposed in order to describe formation of aromatic hydrocarbons. These latter processes are believed to lead to the formation of polycyclic aromatic hydrocarbons, soot precursors, and eventually soot. The work has focused on the pyrolysis of acetylene, since this species appears to be the dominant species in soot-forming regions of flames and has been shown to play a major role in the soot-forming process.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☑ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Julian M Tishkoff

22b. TELEPHONE (Include Area Code)
(202) 767-

22c. OFFICE SYMBOL
AFOSR/NA

DD Form 1473, JUN 86 Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

AFOSR-TR- 88-0474

R88-957047

Examination of Mechanisms and Fuel-Molecular Effects on Soot Formation

by M. B. Colket III,

J. J. Sangiovanni, and D. J. Seery

Final Report

Contract No. F49620-85-C-0012

Prepared for

Air Force Office of Scientific Research
Bolling Air Force Base, D. C. 20332

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January 12, 1988

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R88-957047

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Examination of Mechanisms and Fuel-Molecular Effects on Soot Formation

Final Report

I. SUMMARY

A variety of hydrocarbons has been pyrolyzed in a single-pulse shock tube over the temperature range of 1000 to 2400 K and for dwell times of 500 to 700 microseconds. Gas samples of reactant, intermediate, and final products were collected and analyzed using gas chromatography. Experimental data were used in conjunction with a computer model to develop (or confirm existing) detailed chemical kinetic models for several of the hydrocarbons that were pyrolyzed. Model results agreed well with experimental data not only for the decomposition of the parent compound and formation of products. A major focus of the modeling effort was to describe accurately the formation of aromatic species. Specific mechanisms and rate coefficients have been proposed in order to describe the experimental data. These latter processes are believed to lead to the formation of polycyclic aromatic hydrocarbons, soot precursors, and eventually soot. The work also has focused on the pyrolysis of acetylene, since this species appears to be the dominant species in soot-forming regions of flames and has been shown to play a major role in the soot-forming process.

II. INTRODUCTION

The production of soot in diffusion flames, such as that existing in gas turbine engines, is directly related to the chemical nature of the fuel. In addition, research has shown recently that chemical kinetic processes control the growth of polynuclear aromatics and probably the formation of soot precursors. The production rate of soot precursors, in turn, limits the production rate of the number of soot particles and hence effects the total mass of soot produced. This work focuses on obtaining experimental data on the pyrolysis and oxidative pyrolysis of hydrocarbons under soot-forming conditions. A single-pulse shock tube has been selected for the experimental tool since it is one of the few devices capable of obtaining detailed information on product distribution over the range of 1200 to 2400 K in an environment free from complications due to diffusional effects. Using the experimental data and single-pulse information obtained from other work, detailed chemical kinetic mechanisms describing the pyrolysis of a variety of hydrocarbons are being developed. Chemical mechanisms describing the formation of aromatic hydrocarbons (from aliphatic hydrocarbons) are included in the model.

III. RESULTS

(A) Experimental Effort

Seventeen separate series of single-pulse shock tube experiments were completed during the first year of this contract using both contract (AFOSR) and Corporate (UTRC) funds (see Table I). During the second year, ten series of experiments were completed under contract sponsorship and eight under Corporate sponsorship. (See Table II). During the final year of the program, seven new series of experiments were performed under the AFOSR contract and six under corporate sponsorship. Initial reactant concentrations for these thirteen experiments are listed in Table III. Each series represents a collection of individual shock tube experiments along with chemical analysis of reactant and products (via gas chromatography) for a given initial reactant condition (species, initial concentration). Shock strengths were varied to produce a range in initial post-shock temperature from approximately 1100 to 2400 K.

Examples of the type of experimental data obtained from the shock tube are shown in Figs. 1a-3a for the pyrolysis of ethene and in Figs. 4-8 for a fuel-rich oxidation (-2% oxygen) with about 3 1/2 percent ethene in argon. Preliminary modeling results for the pyrolysis are included in Figs. 1b-3b, using a chemical kinetics sequence slightly modified from that presented in Appendix D. The formation of aromatic species varies substantially with oxygen concentration. In Figs. 9-11, the formation of benzene, phenylacetylene and styrene are shown for three different oxygen concentrations (2, 0.5 and 0%). It is clear that as oxygen concentration increases from zero, the production of aromatics occurs at lower and lower temperatures. Other interesting features during oxidation include high formation rates of methane and a high CO/C_2H_2 ratio. The presence of methane indicates the importance of methyl radicals during oxidation whereas the high CO/C_2H_2 ratio substantiates suggestions that ethene and/or vinyl radicals decompose via addition of oxidative radicals (O or OH) rather than extraction of H-atom by such radicals.

Other experiments include pyrolysis of styrene (an alkylated aromatic) and 1,3,5-hexatriene. Styrene was selected due to its poential role in the growth from single to double ring aromatics. The linear six-membered aliphatic, 1,3,5-hexatriene, was selected since it is the parent of two radical intermediates, i.e., 1,3,5-hexatrien-1-yl and 1,3,5-hexatrien-3-yl which have been postulated as intermediates in the production of benzene from alipatics. As much as 55% of the initial hexatriene is converted to benzene at low temperatures (1300-1400K), thus confirming that a rapid conversion from the linear to aromatic compound will occur. There is some difficulty in interpretation of the experiments on styrene due to a 15 percent uncertainty in the ability to accurately measure styrene. Below 1400 K, there is relatively little decomposition of the aromatic ring although styrene does decompose principally to benzene, phenylacetylene, hydrogen, ethene and acetylene. At these temperatures, there is a slight preference to form phenylacetylene but the trend is opposite at higher temperatures. At 1450 K and above, there is rapid loss of the initial styrene although there is not a compensorate production of low molecular weight products. Presumably the styrene is converted to unobservable high molecular weight species. Mechanisms describing this phenomena are under investigation and they may be related to the formation of soot precursors.

Related to the experimental work is a computer code which has been written to help organize, document, and plot experimental data. During the course of this research, the analytical capabilities were upgraded (under corporate sponsorship) in order to obtain analysis of not only the C_1 to C_{10}-hydrocarbons, hydrogen and oxygen, but also the analysis of the carbon oxides (CO and CO_2) at parts-per-million concentration levels using catalytic hydrogenation. In addition, the ability to quantitatively analyze methane and the C_2-hydrocarbons has been enhanced by a duplication in measurements; that is, these species are separated and measured on capillary and packed columns.

(B) Model Effort

(1) Code Development

Enhancement to the computer codes for development of models used in this contract have been made under a Corporate-sponsored program. Yet the advancements enhanced the progress in the present contract work and therefore will be described briefly.

Chemical kinetic modeling is performed using CHEMKIN, LSODE, CHEMSEN and a shock tube code for CHEMKIN originally written by personnel at Sandia National Laboratories. As described in the proposal for this contract, the original shock tube code had already been modified in-house in order to model the quenching process in a single-pulse shock tube. Plotting packages have been developed under corporate-sponsorship to facilitate interpreting data from CHEMKIN and CHEMSEN. Plots of

1. Species concentrations
2. Reaction contribution to the formation/destruction of each species
3. Principal initiation and termination reactions and their respective rates
4. Reactions which are (nearly) equilibrated.
5. Sensitivity coefficients

can now readily be obtained.

These new capabilities may not appear as highlights in a publication or a presentation, but have been of great value in meeting the overall research objectives of this contract.

(2) Chemical Kinetic Modeling

During the course of this program, detailed chemical kinetic modeling has been performed for the pyrolysis of acetylene, ethylene, vinylacetylene, and benzene. In addition, the pyrolysis of biacetyl, acetaldehyde, and pyridine has been performed under corporate sponsorship. To perform this work, it was necessary to include in the modeling a great number of other species, including radicals (see Tables VI and II of Appendices A and C, respectively). Throughout this effort, there was a strong attempt to ensure that models (mechanisms and kinetics) describing the growth to higher molecular weight species were consistent via thermochemistry with models describing the decomposition of these larger molecules. The constraints of describing the decomposition of the different reactants while simultaneously predicting the formation of many products was very severe. Consequently, we have a lot of confidence regarding the general validity and rate constant expressions determined in this study. A depiction of the model showing formation and destruction of a single ring aromatic is shown in Table IV and specific reactions and rate constants are in Table V.

A focus of this three-year program was the kinetics and mechanisms of acetylene pyrolysis. The importance of this work was two-fold. First, acetylene has been identified as the dominant hydrocarbon species present in soot-forming regions of flames as well as suggested to be the main growth species of soot precursors and soot itself. The chemistry of acetylene pyrolysis clearly plays a major role in the growth of soot precursors. Secondly, recent published articles (see Refs. 6 and 7 of Appendix A) have proposed that acetylene pyrolyzes not by a chain radical involving H-atoms as a chain carrier but rather via vinylidene, a diradical, as an intermediate. These proposal could lead to a relatively simple model describing the formation of soot precursors (and eventually, soot). Unfortunately if the proposal of vinylidene is inaccurate, the use of such mechanisms in a soot model could lead to serious errors in predictions with slight changes in the environment.

These arguments led to a major study on acetylene pyrolysis incorporating data obtained from low temperature studies in flow reactors. The modeling of acetylene pyrolysis has been completed (described in Appendix A) and the major conclusion from ths analysis has been that acetylene pyrolyzes indeed via a radical, chain mechanism which is initiated by the presence of impurities of acetone. The acetone is a stabilizer added to acetylene and is difficult to remove below levels of 1 part in 1000. An early version of the manuscript did not include the contribution of acetone and was weakened by a requirement for an unusually high A-factor for the initiation rate.

In a second paper (See Appendix C) on acetylene pyrolysis, mechanisms for growth to 3-ringed aromatics were analyzed. By using rate constants and a model which predicts concentrations of low molecular weight species accurately, basic concepts describing ring growth were found to be similar to that described previously, although some specific mechanisms were found to be substantially different from those proposed previously. As described in Appendix C, a dominant reaction sequence for the growth from one to two rings is shown in Table VI. At the present time, there is little experimental data which supplies evidence to confirm the existence of such a mechanism and the conclusion is drawn solely from thermodynamic and chemical kinetic considerations. Despite the lack of data with which model calculations can be compared, there is an optimism for the ability to predict the formation of soot precursors and the formation rate of incipient particles. Reasons for this optimism are described in Appendix B. A plausible kinetic mechanism for describing these processes is presented in Apendix C.

(C) Model of Soot Particle Formation

Most practical applications of combustion processes utilize the diffusion flame concept because of the simplicity and broad range of stability provided by this combustion mechanism. Since the diffusion flame does not promote rapid mixing of fuel and oxidizer, however, the fuel vapor undergoes high temperature pyrolysis before it is oxidized completely, resulting in a tendency for the intermediate formation of soot particulates. Despite numerous research efforts to better understand soot particle formation in combustion processes for the purpose of developing soot emission control strategies, soot formation in practical combustors is still a problem. Moreover, theoretical modeling of soot particle formation within combustion processes has not been very successful because of the complexity of the many chemical and physical processes involved.

Since we believe that the results of this program provide a basis for understanding of the pre-particle chemistry of large aromatic species which form during the pyrolysis of fuel, the development of a theoretical model which describes soot particle formation in combustion processes has been initiated at UTRC. Model development will be completed under separate funding. This theoretical model will simulate the evolution of a spatially homogeneous soot particle (aerosol) as a function of the time-dependent particle size disribution. The physical phenomena to be included are: (1) particle nucleation or inception from a time varying source of gas phase chemical species, (2) particle growth due to heterogeneous condensation of gas phase chemical species (often called gas-to-particle conversion), and (3) coagulation of particles via particle collisions. By judicious use of the theory developed under this program on the chemical formation of pyrolysis products from hydrocarbon fuels, models will be developed for use in predicting the gas phase composition and the rates of particle inception and gas-to-paarticle conversion as functions of time. Numerical solution of the equations which govern soot particle formation will be accomplished by utilizing an existing computer code named MAEROS, a general multicomponent aerosol computer model which was developed by F. Gelbard at Sandia National Laboratories, Albuquerque, New Mexico. A copy of this code has been obtained by UTRC personnel and modifications to the code for describing soot-formation have been initiated.

IV. LIST OF PUBLICATIONS

A paper entitled "The Pyrolysis of Acetylene Initiated by Acetone" by M. B. Colket, H. B. Palmer, and D. J. Seery has been submitted for publication in Combustion and Flame. (See Appendix A)

A paper entitled "The Pyrolysis of Acelylene and Vinylacetylene in a Single-Pulse Shock Tube" by M. B. Colket has been accepted for publication in the Twenty-First Symposium (International) on Combustion (see Appendix D).

An article entitled "Single-Pulse Shock Tube Examination of Hydrocarbon Pyrolysis and Soot Formation" by M. B. Colket has been published in Shock Waves and Shock Tubes, Proceedings of the Fifteenth International Symposium on Shock Wave and Shock Tubes, Edited by D. Bershader and R. Hanson, p. 311, Stanford University Press, Stanford, California 1986 (see Appendix F).

Under corporate-sponsorship, a manuscript entitled "Shock Tube Pyrolysis of Pyridine and the Thermochemistry of the Pyridyls" by J. C. Mackie and M. B. Colket is nearly complete and will be submitted to the Twenty-Second Symposium (International) on Combustion.

V. MEETING INTERACTIONS

The Principal Investigator of this program attended the following meetings during this program.

1. Eastern Section of the Combustion Institute, Gaithersburg, MD, November 2-6, 1987. M. B. Colket presented a paper entitled "Some Thoughts on Pre-Particle Chemistry". (See Appendix B)

2. Division of Fuel Chemistry, New Orleans National Meeting, American Chemical Society, August 31-September 4, 1987. M. B. Colket presented a paper entitled "Kinetic Mechanism for Pyrolysis of Acetylene Near 1000K" at the Symposium on Advances in Soot Formation Chemistry. (Appendix C) Also see ACS, Division of Fuel Chemistry preprints, 32 (3), 417 (1987).

*3. Department of Energy, Combustion Research Contractors' Meeting, Mills College, Oakland, California. June 2-5, 1987. M. Colket was invited by Dr. A. Laufer to be an observer and participant in discussions at the D.O.E. meeting. (See Appendix D)

4. Twenty-first Symposium (International) on Combustion in Munich, W. Germany, August 1986. A paper (See Appendix D) entitled "The Pyrolysis of Acetylene and Vinylacetylene in a Single-Pulse Shock Tube" was presented by M. B. Colket. In addition M. Colket served as Poster Chairman and member of the Program Advisory Committee, the Program Sub-committee and the Publications Committee.

*5. The 1986 Spring Technical Meeting of the Central States Section of the Combustion Institute in Cleveland, Ohio, May 1986. A paper entitled "Formation of C_2-hydrocarbons and Benzene from Pyrolysis of Biacetyl" was presented by M. B. Colket.

*6. Department of Energy, Basic Sciences Contractors Meeting, Arlie House, Va, May 1986. M. Colket was invited by Dr. A. Laufer to be an observer and participant in discussions at the D.O.E. meeting.

7. Division of Fuel Chemistry, New York City National Meeting, American Chemical Society, April 13-16, 1986. A paper entitled "Pyrolysis of C_6H_6," by M. B. Colket, III, was presented. (Appendix H). Also see ACS, Division of Fuel Chemistry preprints, 31 (2), p. 98, 1986.

8. Eastern Section of the Combustion Institute, Philadelphia, PA, Nov. 4-6, 1985. A paper entitled "Pyrolysis of Vinylacetylene," by M. B. Colket, III was presented. (Appendix G).

*9. International Conference on Chemical Kinetics, National Bureau of Standards, Gaithersburg, MD, June 1985. A poster paper entitled "Pyrolysis of Acetylene in a Single-Pulse Shock Tube," by M. B. Colket, III. was presented.

*10. Eastern Section of the Combustion Institute, Clearwater Beach, Florida, December 1984. A paper entitled "Addition of Alkyl Radicals to Aromatic Rings," by M. B. Colket, III was presented. (Appendix F).

* Corporate-sponsored research

TABLE I

SERIES OF EXPERIMENTS COMPLETED DURING FIRST YEAR OF PROGRAM

Reactant	Initial Concentration (%)
Benzene, C_6H_6	0.12
Benzene, C_6H_6	0.012
Vinylacetylene, C_4H_4	1.0
Vinylacetylene, C_4H_4	0.11
Vinylacetylene C_4H_4	0.01
C_2H_2/C_6H_6	0.82/0.06
C_2H_2/C_6H_6	0.115/0.0085
C_2H_2/C_6H_6	0.016/0.0012
Acetylene	4.9
Acetylene	0.6
Acetylene	0.069
Toluene, C_7H_8	* 0.05
Toluene, C_7H_8	* 0.035
Toluene, C_7H_8	* 0.016
Toluene, C_7H_8	* 0.0175
C_2H_2/C_7H_8	* 3.3/0.51
Acetaldehyde, CH_3CHO	* 0.105

All fuels were diluted in argon and (except for the experiments on pure toluene) were conducted at total pressures of approximately six to nine atmospheres.

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* Research conducted under Corporate-sponsored program.

TABLE II

SERIES OF EXPERIMENTS COMPLETED DURING SECOND YEAR OF PROGRAM

Reactant	Initial Concentration %
Ethene, C_2H_4	3.5
Ethene, C_2H_4	0.3
Ethene, C_2H_4	0.05
Styrene, C_8H_8	0.4
Styrene, C_8H_8	0.2
C_2H_4/O_2	3.3/2.05
C_2H_4/O_2	0.22/0.13
1,3,5-Hexatriene, C_6H_8	1.0
1,3,5-Hexatriene, C_6H_8	0.09
Acetaldehyde, CH_3CHO	* 0.01
Biacetyl, $(CH_3CO)_2$	* 0.22
Biacetyl, $(CH_3CO)_2$	* 0.022
$C_2H_2/(CH_3CO)_2$	* 3.5/0.18
$C_2H_2/(CH_3CO)_2$	* 0.3/0.15
Toluene, C_7H_8	* 1.0
Toluene, C_7H_8	* 0.1
Toluene, C_7H_8	* 0.01

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* Research conducted under Corporate-sponsored program

TABLE III

Series of Experiments Completed During Third Year of Program

Reactant	Initial Concentration
trans-3-penten-1-yne, C_5H_6	1.0%
trans-3-penten-1-yne, C_5H_6	0.05%
cis-3-penten-1-yne, C_5H_6	1.0%
cis-3-penten-1-yne, C_5H_6	0.052%
ethylene/oxygen, C_2H_4/O_2	3.54/0.52%
ethylene/oxygen, C_2H_4/O_2	0.23/0.034%
acetylene/benzene, C_2H_2/C_6H_6	3%/0.3%
Toluene, C_7H_8	*+1.0%
Toluene, C_7H_8	*+0.084%
Pyridine, C_5H_5N	*0.7%
Pyridine, C_5H_5N	*0.148%
Pyrrole, C_4H_5N	*0.5%
Pyrrole, C_4H_5N	*0.075%

All fuels were diluted in argon and were conducted at total pressures of approximately six to nine atmospheres.

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* Research conducted under corporate-sponsored program

+ Sampling system and gas chromatograph modified to collect and analysis for polyaromatic species

TABLE IV

Model for Production of First Aromatic Ring from Acetylene

$$\begin{tikzcd}
C_2H_3 \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & n\text{-}C_4H_5 \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & \ell\text{-}C_6H_7 \arrow[r, leftrightarrow] & c\text{-}C_6H_7 \arrow[d, leftrightarrow] & \\
C_2H_2 & C_4H_4 \arrow[d, leftrightarrow] & & C_6H_6 \arrow[d, leftrightarrow] \arrow[lld, bend right] & \\
& n\text{-}C_4H_3 \arrow[r, leftrightarrow] & \ell\text{-}C_6H_5 \arrow[r, leftrightarrow] & c\text{-}C_6H_5 \arrow[r, leftrightarrow] & C_8H_7 \arrow[d, leftrightarrow] \\
& & & & C_8H_6
\end{tikzcd}$$

Vertical translation represents addition or loss of an H-atom and horizontal translation represents addition or loss of acetylene (except for

TABLE V

REACTIONS AND RATE COEFFICENTS FOR STEPS LEADING TO FORMATION OF AROMATIC RING

Low Temperature Sequence

	Log A	E/1000
$H + C_2H_2 \rightleftarrows C_2H_3$	12.74	2.5
$C_2H_3 + C_2H_2 \rightleftarrows n\text{-}C_4H_5$	12.05	4.0
$n\text{-}C_4H_5 + C_2H_2 \rightleftarrows \ell\text{-}C_6H_7$	12.81	9.0
$\ell\text{-}C_6H_7 \rightleftarrows c\text{-}C_6H_7$	11.36	0.4
$c\text{-}C_6H_7 \rightleftarrows C_6H_6 + H$	13.12	24.6

High Temperature Sequence

$H + C_2H_2 \rightleftarrows C_2H + H_2$	13.6	20.5
$C_2H + C_2H_2 \rightleftarrows n\text{-}C_4H_3$	13.56	3.0
$n\text{-}C_4H_3 + C_2H_2 \rightleftarrows \ell\text{-}C_6H_5$	11.71	-0.1
$\ell\text{-}C_6H_5 \rightleftarrows c\text{-}C_6H_5$	10.22	1.4
$c\text{-}C_6H_5 + H_2 \rightleftarrows C_6H_6 + H$	12.39	9.5
$c\text{-}C_6H_5 + C_2H_2 \rightleftarrows C_8H_6 + H$	12.00	4.0

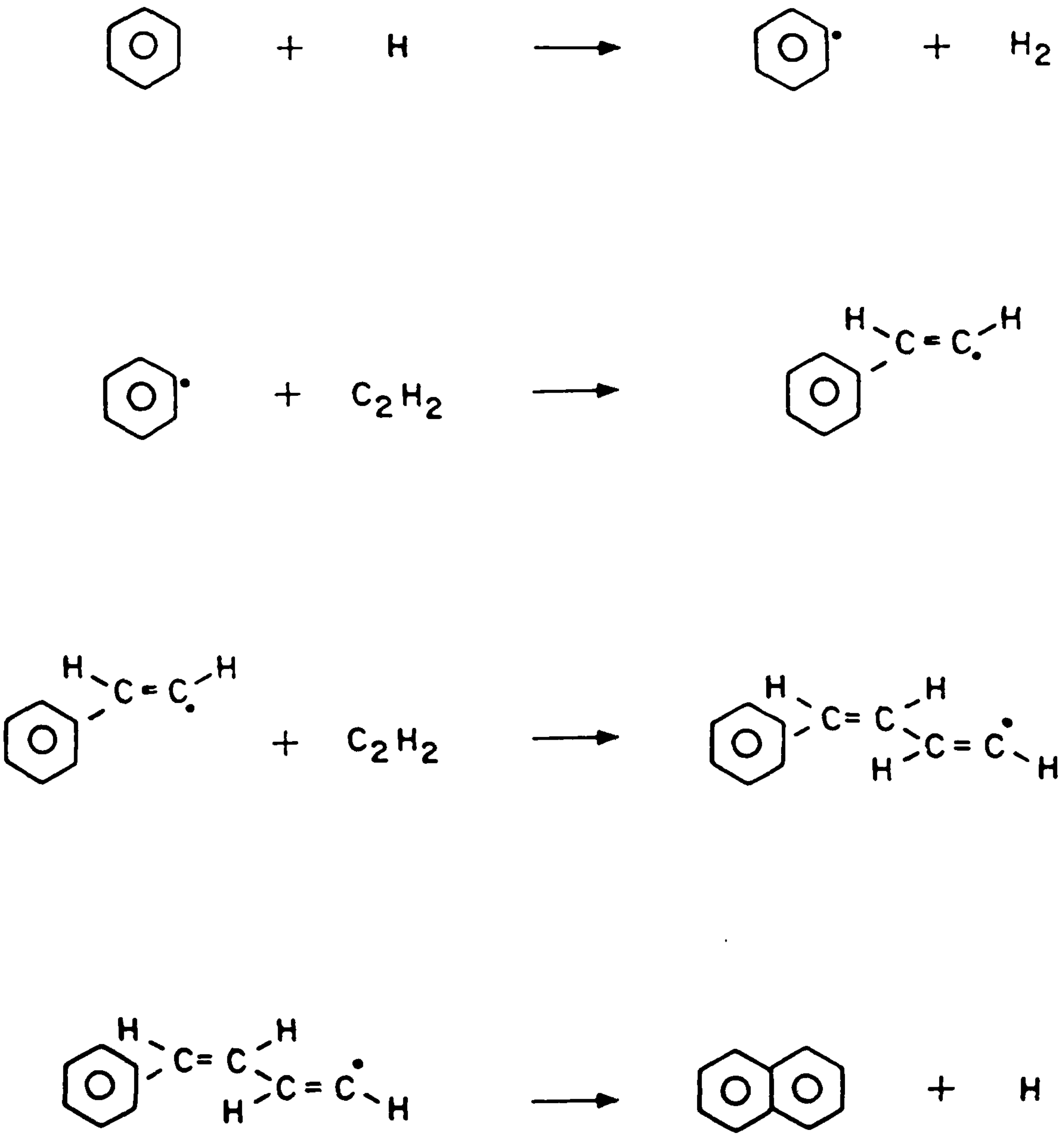
$k = A \exp(-E/RT)$

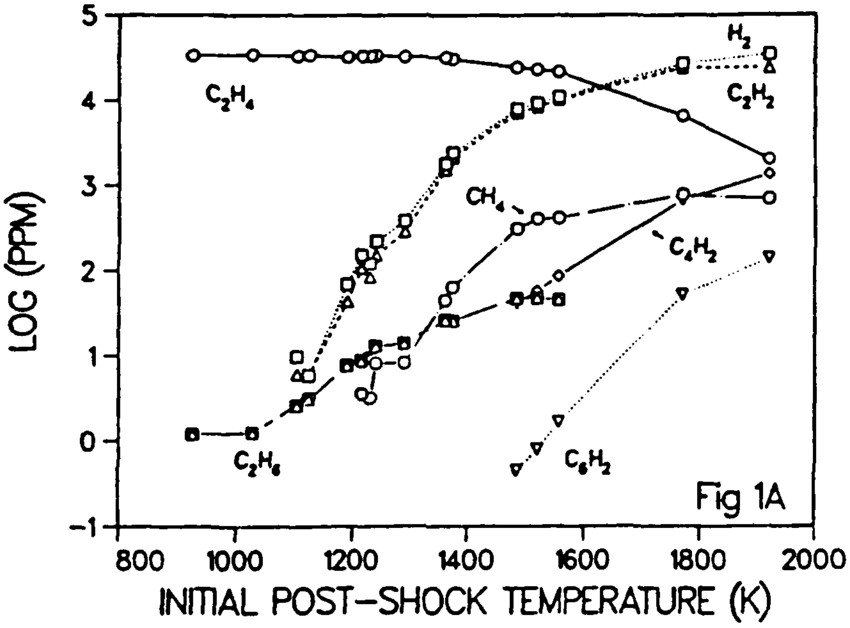
Units: A, cc, mole, sec

E, cal/mole/K

TABLE VI

Reactions Leading to
Formation of Polycyclic Hydrocarbons

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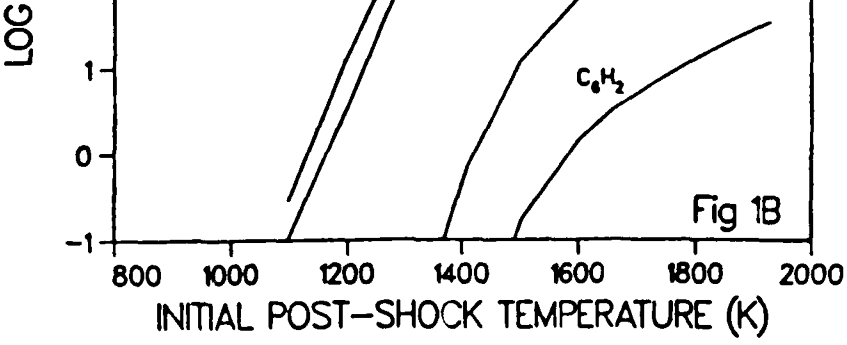
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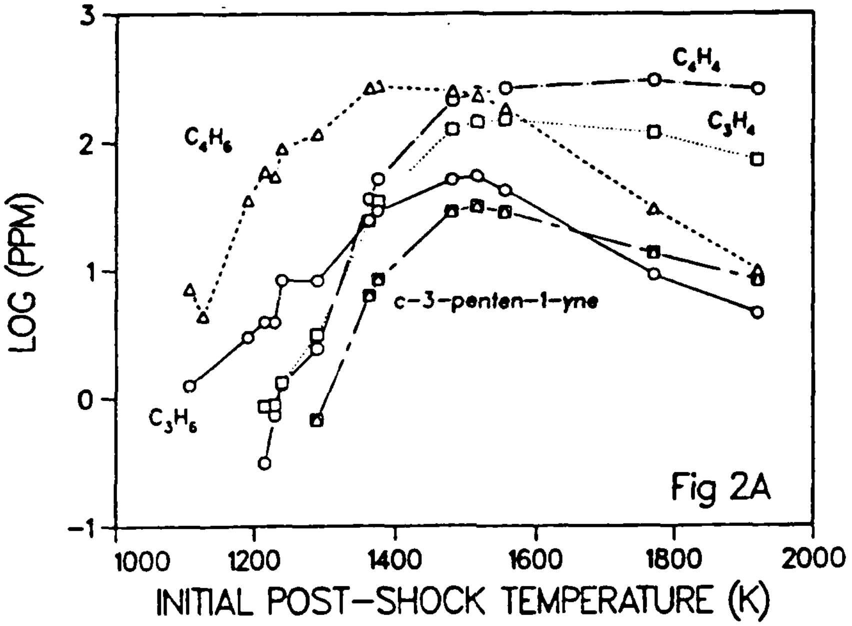
3.5% ETHENE PYROLYSIS, ALIPHATICS



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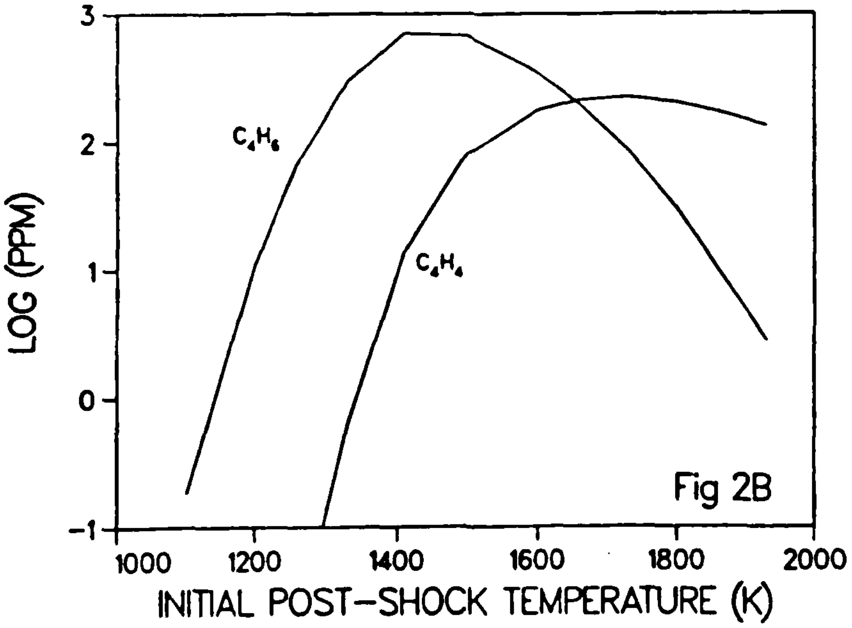
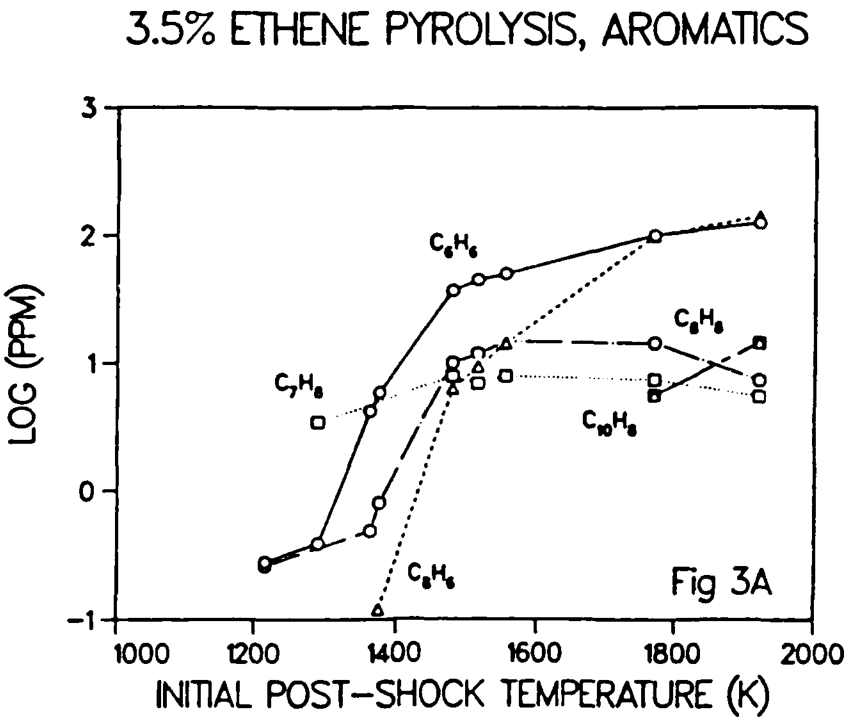
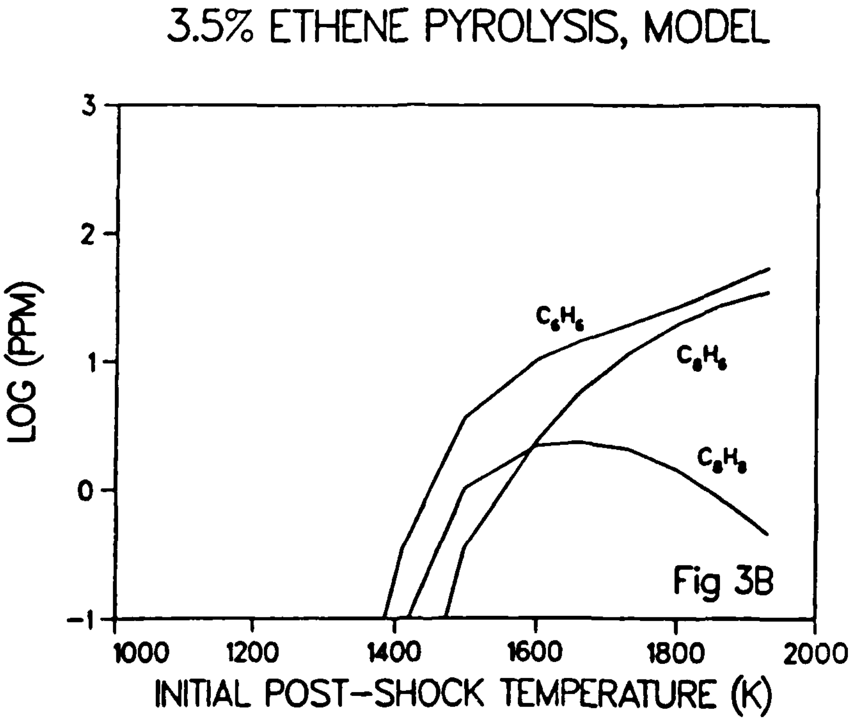
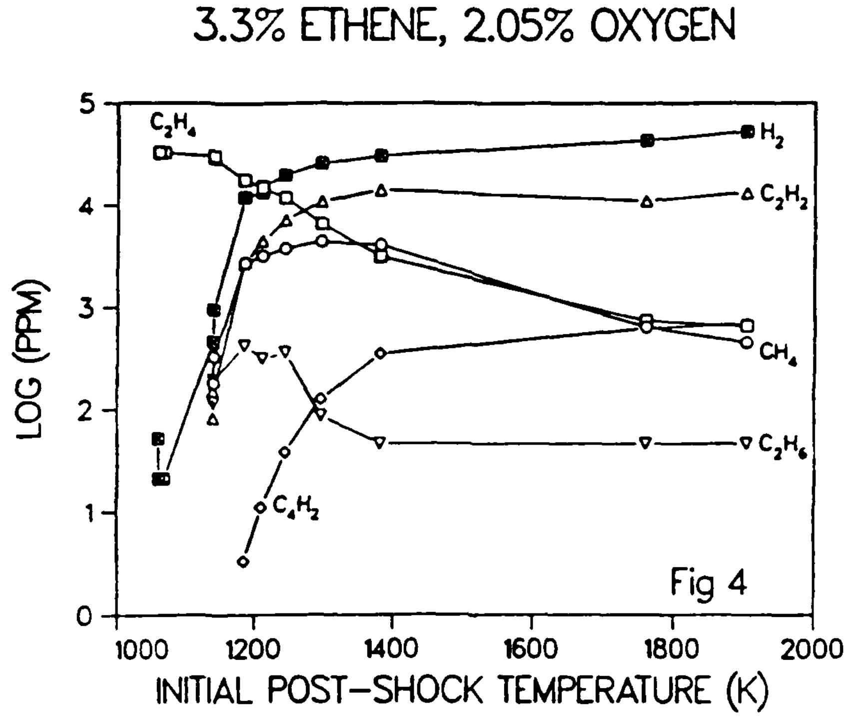


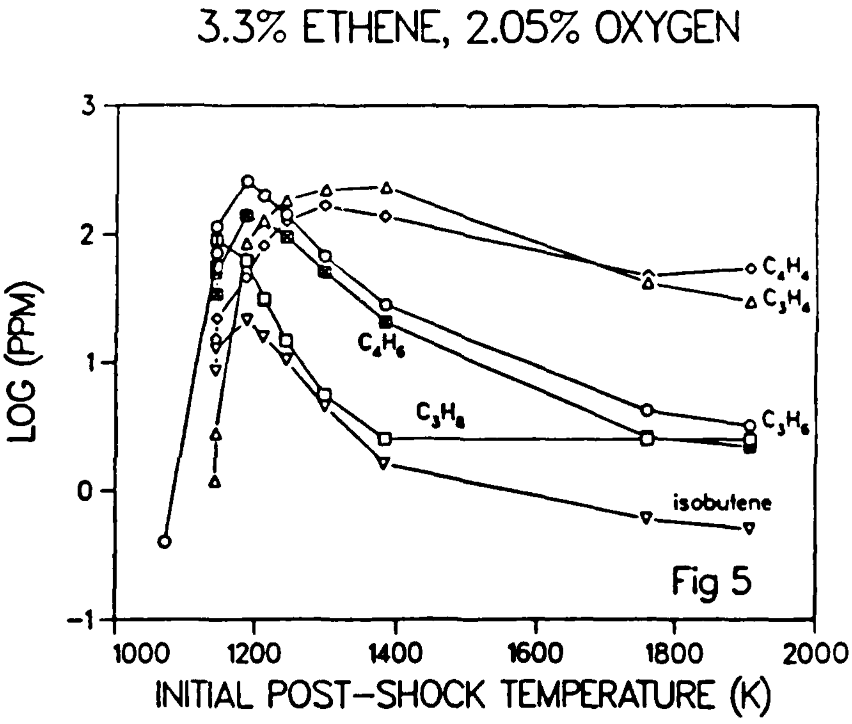

3.5% ETHENE PYROLYSIS, AROMATICS
LOG (PPM)
3
2
1
0
−1
1000
1200
1400
1600
1800
2000
INITIAL POST−SHOCK TEMPERATURE (K)
C_6H_6
C_8H_8
C_7H_8
$C_{10}H_8$
C_8H_6
Fig 3A


3.5% ETHENE PYROLYSIS, MODEL
LOG (PPM)
3
2
1
0
−1
1000
1200
1400
1600
1800
2000
INITIAL POST−SHOCK TEMPERATURE (K)
C_6H_6
C_8H_6
C_8H_8
Fig 3B



3.3% ETHENE, 2.05% OXYGEN

Fig 4



3.3% ETHENE, 2.05% OXYGEN

Fig 5

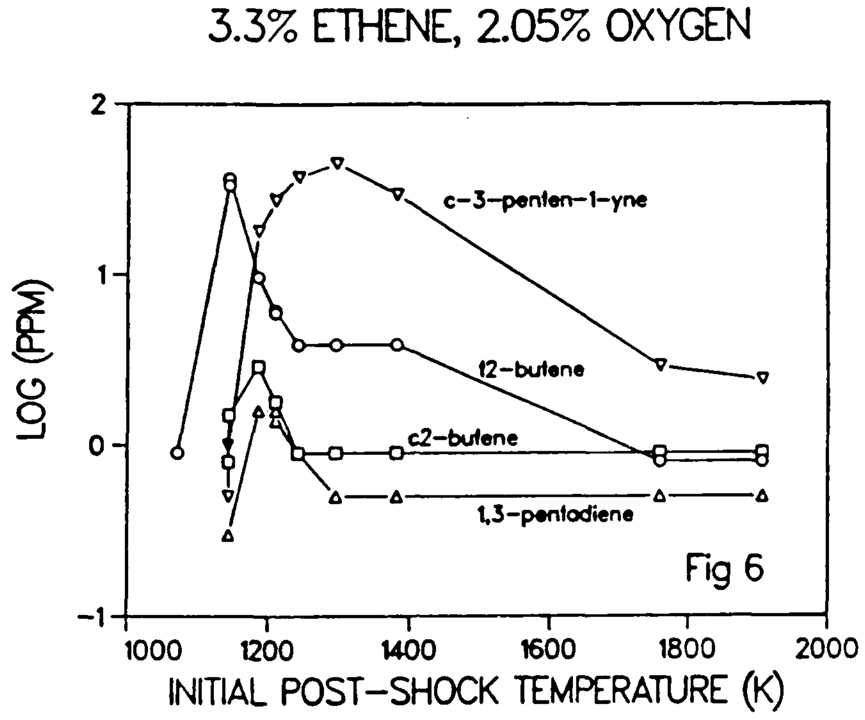

3.3% ETHENE, 2.05% OXYGEN
LOG (PPM)
2
1
0
−1
1000
1200
1400
1600
1800
2000
INITIAL POST−SHOCK TEMPERATURE (K)
c−3−penten−1−yne
t2−butene
c2−butene
1,3−pentodiene

Fig 6

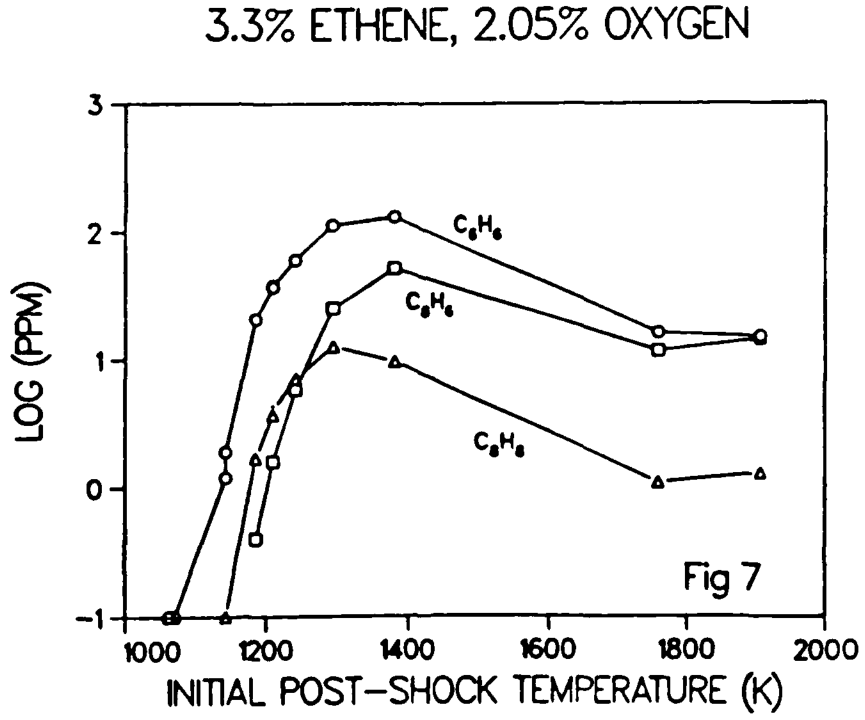
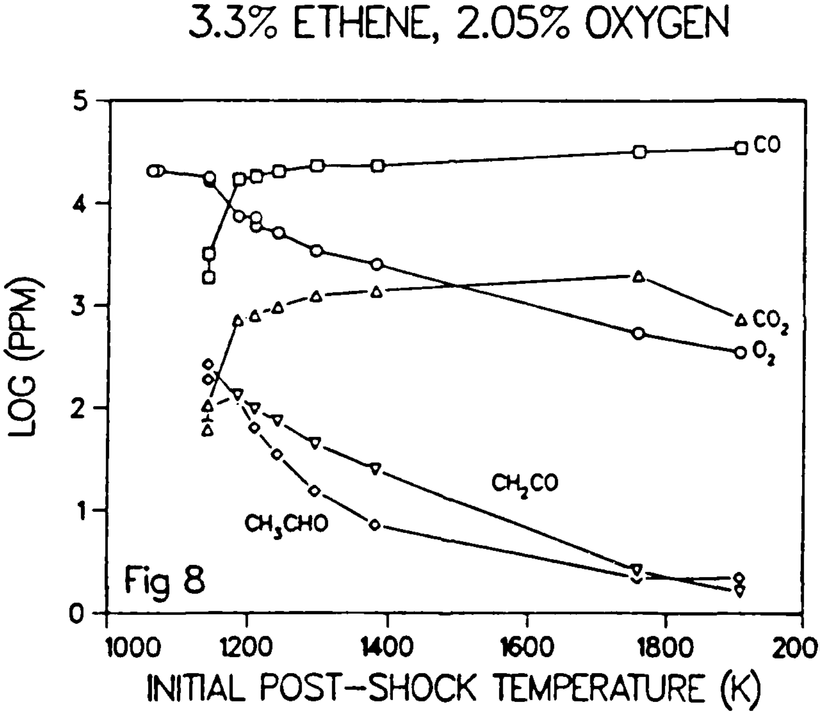

3.3% ETHENE, 2.05% OXYGEN
LOG (PPM)
3
2
1
0
−1
1000
1200
1400
1600
1800
2000
INITIAL POST−SHOCK TEMPERATURE (K)
C_6H_6
C_8H_6
C_8H_8

Fig 7



3.3% ETHENE, 2.05% OXYGEN

Fig 8

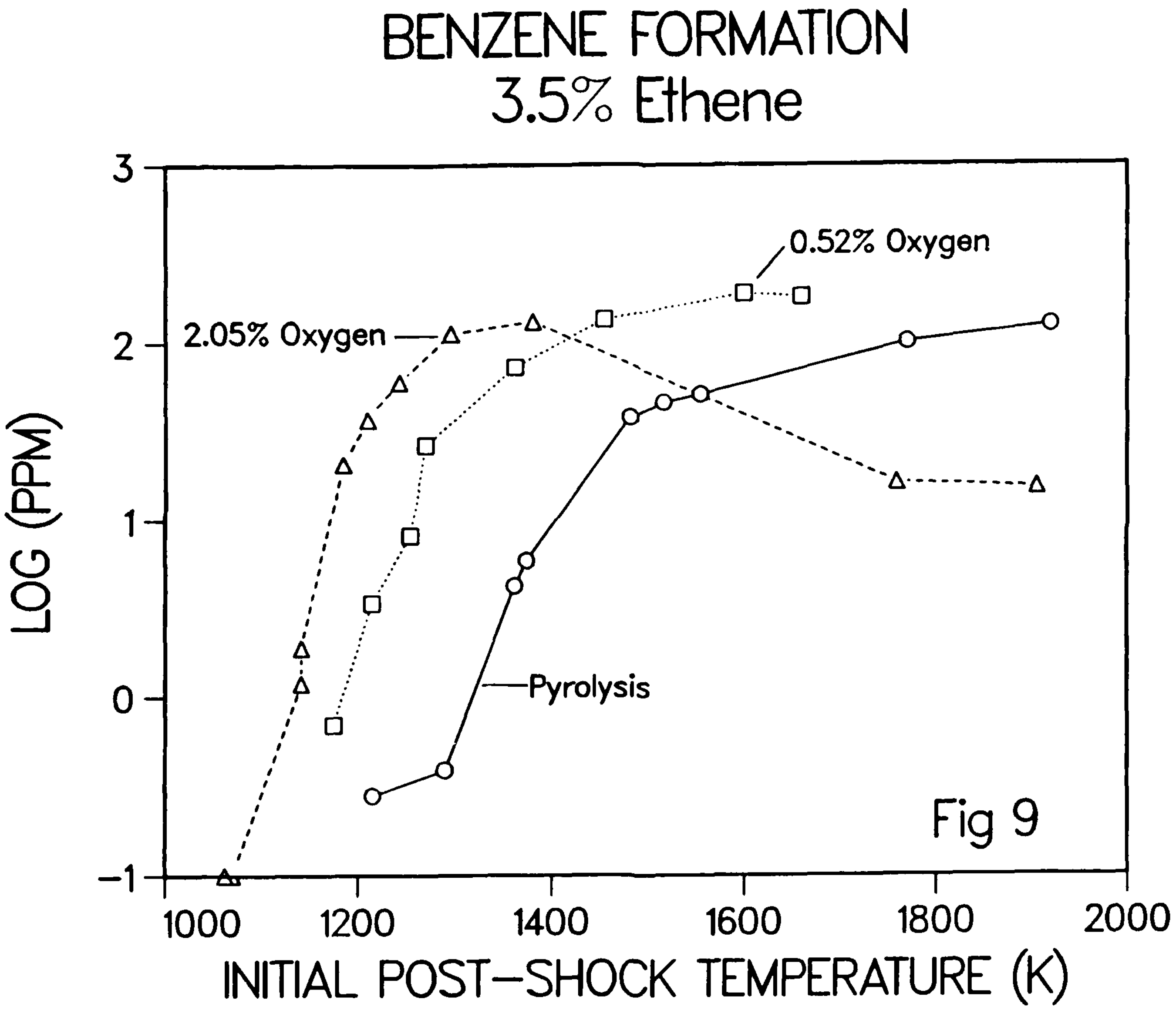

BENZENE FORMATION
3.5% Ethene
LOG (PPM)
3
2
1
0
−1
1000
1200
1400
1600
1800
2000
INITIAL POST−SHOCK TEMPERATURE (K)
0.52% Oxygen
2.05% Oxygen
Pyrolysis

Fig 9

PHENYLACETYLENE FORMATION
3.5% Ethene

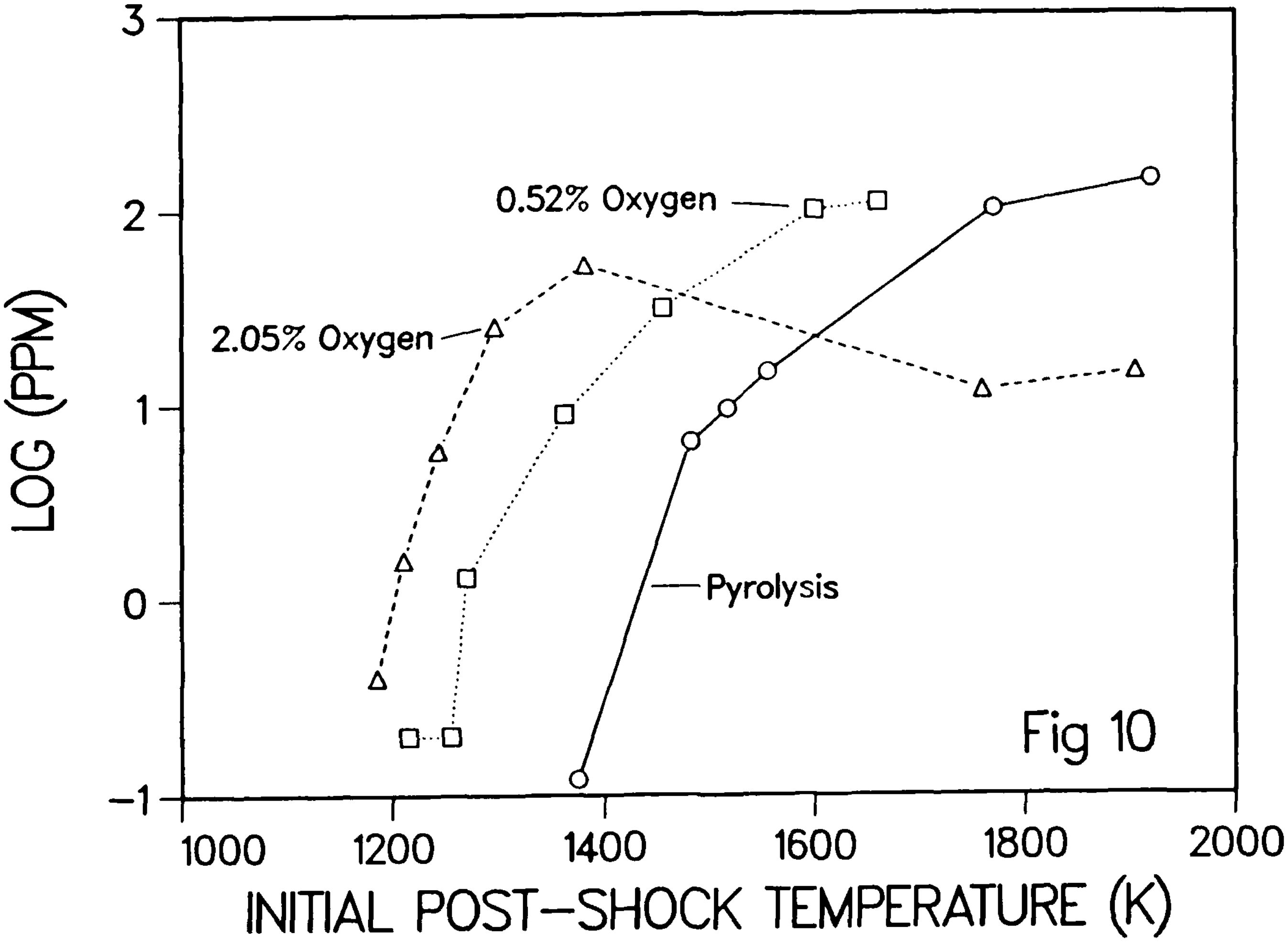


Fig 10

STYRENE FORMATION
3.5% Ethene

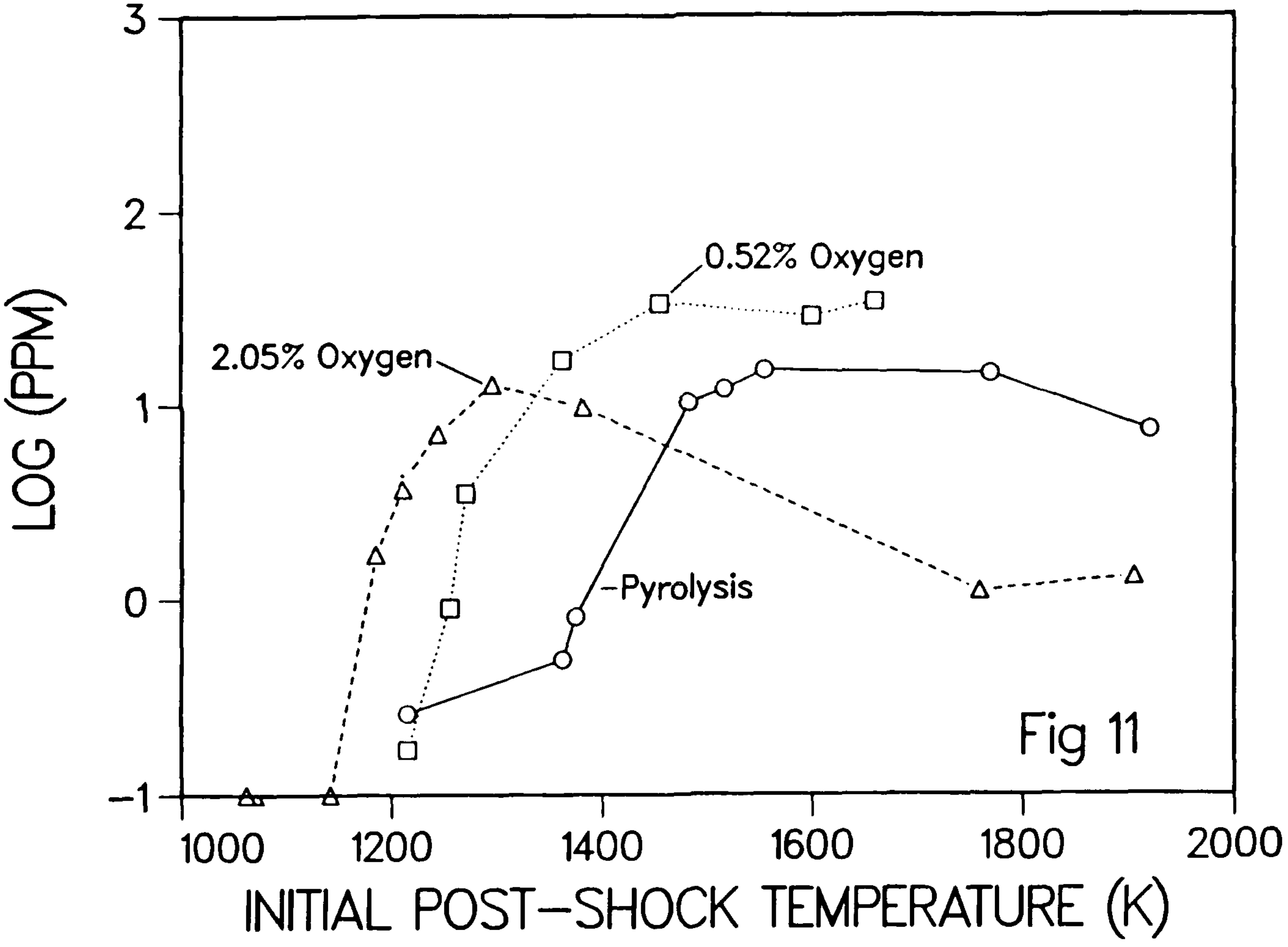


Fig 11

THE PYROLYSIS OF ACETYLENE INITIATED BY ACETONE

by

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Abstract

A detailed, chemical kinetic, radical-chain mechanism is used to model the pyrolysis of accetylene near 1000K. The assumption of a bimolecular initiation process is found to be inconsistent with thermochemistry. Since experimental evidence convinces the authors of the presence of a chain mechanism, alternative sources of initiation are considered. Acetone, a common impurity even in 'purified' acetylene was found to dominate radical initiation during the pyrolysis of acetylene near 1000K despite concentration levels only 0.1% that of acetylene. Modeling results compare favorably with the experimental results of Munson and Anderson for acetylene decay and the formation of products vinylacetylene, benzene, and ethylene. Rate constants for the following reactions are found to be

$$C_2H_3 + C_2H_3 \leftrightarrow C_4H_6 \qquad k_4 = 2.0 \times 10^{13}\ \mathrm{cc/mole/sec}$$

$$n - C_4H_5 \leftrightarrow C_4H_4 + H \qquad k_{32} = 1.6 \times 10^{14} \times e^{-(41.4\ \mathrm{kcal/mole/RT})}\ \mathrm{sec}^{-1}$$

$$n - C_4H_5 + C_2H_2 \rightarrow C_6H_6 + H \qquad k_{33} = 4.5 \times 10^{12} \times e^{-(10.\ \mathrm{kcal/mole/RT})}\mathrm{cc/mole/sec}$$

$$n - C_4H_5 + C_4H_4 \rightarrow C_8H_8 + H \qquad k_{35} = 1.2 \times 10^{13} \times e^{-(5.\ \mathrm{kcal/mole/RT})}\ \mathrm{cc/mole/sec}$$

to optimize the fit to the experimental data. A sensitivity analysis shows that the computed results were most sensitive to rate constants for these and a few other reactions.

By addition of high temperature reactions (involving ethynyl radicals), the mechanism was found to be consistent with experimental results using single-pulse shock tubes and the very high temperature study of Frank and Just. Calculations are quantitatively consistent with their experimental finding that acetone plays a negligible role at high temperature, low concentration conditions.

Introduction

Speculation on the mechanism of acetylene pyrolysis has occurred for many years. Experiments at low temperature (600 - 1200K) during the '50's and '60's resulted in a variety of suggestions including radical-chain processes and non-chain dimerizations involving diradical or electronically excited intermediates. During the '70's, a radical-chain mechanism was preferred[1-3] and initiation was usually believed to be due to

$$C_2H_2 + C_2H_2 \rightarrow n - C_4H_3 + H \qquad (1)$$

where n-C_4H_3 is the $HCCCH\dot{C}H$ radical. The low A-factor and activation energy used to describe the experimental data (e.g., $A = 2 \times 10^{12}$ cc/mole-sec, $E = 45.9$ kcal/mole, Ref. 1) were consistent with the type of reaction as well as thermochemistry widely in use at the time. However, the heat of formation of n-C_4H_3 is now believed to be close to 125 kcal/mole[4], much higher than the previously used value of 102 kcal/mole (equated to the early calculation for the $H\dot{C}CCCH_2$ radical by Duff and Bauer[5]). Thus, the endothermicity of Reaction 1 is about 68 kcal/mole and not 46 kcal/mole as previously believed. Attempts (at UTRC) to model acetylene pyrolysis with $E_1 \approx 68$ kcal/mole leads to an unacceptably high A-factor for this reaction. This result obviously raises serious doubt regarding the chain mechanism.

Furthermore, recent results[6,7] suggest that acetylene pyrolyzes, by first isomerizing to vinylidene (H_2CC:) which then inserts into a C-H bond of acetylene to form vinylacetylene directly. Duran, et al. interpreted experimental data to reach this conclusion while Kiefer argues this sequence is consistent with thermodynamics.

In our own analysis, we cannot disprove a non-chain dimerization; however, upon review of our own experimental data as well as that obtained by others we reach the unavoidable conclusion that a radical-chain process occurs. In attempts to model experimental data, we argue that thermal decomposition of acetone, a common impurity in acetylene, is quite probably responsible for initiating the radical-chain in laboratory studies of the pyrolysis of acetylene.

In this paper, evidence supporting a radical-chain will be presented, issues related to acetone-initiation are discussed, and modeling results are presented and compared to existing experimental data.

Evidence for Chain Mechanism

Palmer and Cullis' review article[8] cites results such as inhibition by radical scavengers, wall effects, and existence of an induction period as evidence that the thermal decomposition of acetylene is a radical process. Unfortunately, these observations cannot distinguish between diradical (non-chain) and monoradical (chain) mechanisms.

Evidence for a chain arises from the work of Callear and Smith[9] who investigated the reaction between acetylene and atomic hydrogen in a quartz vessel at 293K. Atomic hydrogen was generated by decomposing H_2 using a low-pressure mercury discharge lamp. Major products included ethene, 1,3-butadiene, benzene, and trans-1,3,5-hexatriene. To explain these products, Callear and Smith suggested a reaction mechanism similar to that used in the present study except that in the low temperature, hydrogen-rich investigation, C_2H_3, n-C_4H_5, and ℓ-C_6H_7 (1,3,5-hexatrien-1-yl) radicals formed principally C_2H_4, 1,3-C_4H_6, and 1,3,5-C_6H_8 rather than losing H-atoms to form C_2H_2, C_4H_4 and benzene. Some benzene was still formed at low temperatures presumably because of the high stability of the aromatic. If a chain process exists at room temperature, it should also occur at elevated temperatures.

At higher temperatures, there also is a multiplicity of products from the thermal decomposition of acetylene. Near 1000K, using 20% C_2H_2 in helium, Munson and Anderson[10] found vinylacetylene and also benzene, ethene, methane and hydrogen. Working at even higher temperatures, Ogura[3] detected the same products during pyrolysis in a single pulse shock tube and also diacetylene and traces of 1,3-butadiene, and C_3 and C_5-species. Under similar conditions but with a heated sampling system, Colket[11] detected the same species and benzene, phenylacetylene, and traces of naphthalene as well. Although the vinylidene mechanism apparently explains the overall decomposition rates of the reactant, it does not describe the variety of products that have been observed experimentally. Thus, contributions from a chain sequence are expected.

Further indications of a chain mechanism are provided by additional single-pulse shock tube data in Fig. 1. This figure compares vinylacetylene and benzene production from three different gases: (a) 2040 ppm biacetyl in argon, (b) 3.7% acetylene in argon and (c) a mixture of 3.55% acetylene and 1500 ppm biacetyl in argon. The production of C_4H_4 and C_6H_6 is substantially larger from the mixture than would be expected from purely additive considerations. Near 1100K, the mixture produces an order of magnitude greater C_4H_4 and C_6H_6 than are produced from acetylene or biacetyl. Since there is no reason to expect that biacetyl enhances the rate of the vinylidene mechanism, this enhancement must be a result of a chain mechanism initiated by biacetyl decomposition first into acetyl, then to methyl radicals. Mechanisms by which methyl radicals are converted to H-atoms (required for the acetylene chain) are discussed elsewhere in this manuscript. Methyl radical addition to acetylene and to subsequent adducts forms a variety of products, e.g., C_3H_4, C_4H_6, C_4H_8, etc., but the concentrations of these species are small relative to those of C_4H_4 and C_6H_6. There appears to be no facile method to produce vinylacetylene and benzene at the observed rates other than from the chain mechanism related to acetylene pyrolysis.

Finally, Ogura[3] shock-heated equimolar mixtures of C_2H_2/C_2D_2 diluted in argon. He found over 40% of the vinylacetylene in the form of the C_4H_3D and C_4HD_3 isotopes at temperatures as low as 1070K. It is highly unlikely that such significant scrambling can be accounted for by a vinylidene mechanism. Again a radical-chain sequence is favored.

In summary, (1) a radical-chain mechanism has been observed at room temperature; (2) acetylene pyrolysis produces a wide variety of products; (3) a large enhancement in the production of vinylacetylene and benzene is observed when acetylene is a co-pyrolyzed with biacetyl, and (4) significant scrambling was observed during pyrolysis of C_2H_2/C_2D_2 mixtures. Since these phenomena are either indicative of a chain mechanism or can only be explained by a chain mechanism, this analysis strongly supports the existence of a chain during acetylene pyrolysis at temperatures of 900-1400K. It does not exclude possible contributions of a vinylidene route or other non-chain mechanism, nor does it provide information on the relative contributions of the two mechanisms if they coexist. Nevertheless, since recent modeling efforts have focused on a non-chain mechanism, this work focuses solely on chain processes to examine whether or not acetylene decomposition and product formation can be described adequately.

Preliminary Modeling

For low temperature pyrolysis (900-1400K), Tanzawa and Gardiner[1] invoked bimolecular initiation followed by addition of H-atoms to C_2H_2 to form vinyl radicals. The proposed chain mechanism accounted quite well for the experimental results for acetylene decomposition. However, it did not describe the known production of benzene and higher molecular weight species, which together accounted for more than 50 percent of the decomposed acetylene (near 1000K). Frenklach and coworkers[12] extended this mechanism to describe formation of heavier species including PAH and soot formation during pyrolysis of acetylene at higher temperatures. Colket[11], subsequently, used a similar mechanism for comparison to experimental profiles of species with molecular weights up to 102.

An unsettling feature of these models is the rate expression for the initiation step (Reaction 1). Using a recent value[4] for the heat of formation of n-C_4H_3 of 124 kcal/mole, Reaction 1 is 68 kcal/mole endothermic. However, the activation energy used previously for this reaction is about 46 kcal/mole, significantly lower than its endothermicity. Hence, we attempted to model experimental data using $E_1 = 68$ kcal/mole. This value not only is required to satisfy thermochemistry but also is attractive when one performs a steady-state analysis on the simplified sequence presented in Table I. Such an analysis leads to

$$-\frac{d[C_2H_2]}{dt} = 2k_{3A}\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}}[C_2H_2]^2 + 2k_1[C_2H_2]^2 \qquad \text{Eq. A}$$

in agreement with the often quoted experimental observation of second order decomposition kinetics. (This sequence differs from that proposed by Tanzawa and Gardiner[1] in that vinyl recombination was found to dominate radical termination. In the earlier modeling[1] the high stability assumed for C_4H_3 led to its important role in termination and C_4H_3 + H dominated. Termination by vinyl recombination has also been suggested by Ogura[3].) Assuming a long chain, the second term in Eq. A can be ignored and the overall activation energy is $E_{ov} = E_{3A} + (E_1\text{-}E_4)/2$. Assuming $E_{3A} = 4$, $E_4 = 0$ kcal/mole and taking $E_1 = 68$, then $E_{ov} = 38$ kcal/mole which is in excellent agreement with measured values. The 'old' value for E_1 of 46 kcal/mole gives a steady-state E_{ov} of 27 kcal/mole, substantially lower than experimental results.

Despite the attractiveness of the 'updated' E_1, our attempts to model experimental results were not fully satisfying. Quite reasonable agreement could be obtained with both the decay profiles of acetylene and product formation as measured by Munson and Anderson[10]. The mechanism used was similar to that used by Colket[11] except that

$$k_1^{high} = 6 \times 10^{14} e^{(-68000\text{cal/mole}/RT)} \text{cc/mole/sec}$$

and

$$k_4 = 2 \times 10^{12} \text{cc/mole/sec.}$$

The first expression is denoted k_1^{high} since it is higher than the maximum value one would expect. The A-factor is obviously much too high for a bimolecular initiation of this type. The value of k_4, for vinyl-vinyl recombination, is more than five times lower than that typically used for this reaction. Consequently, these results must be viewed with caution.

Indications of Acetone Initiation

With concern about the above results yet with the evidence for the existence of a chain, possible initiation steps were re-examined. Of the likely possibilities

$$C_2H_2 \rightarrow C_2H + H - 128\text{kcal/mole}$$
$$C_2H_2 + C_2H_2 \rightarrow C_2H + C_2H_3 - 87\text{kcal/mole}$$
$$C_2H_2 + C_2H_2 \rightarrow i - C_4H_3 + H - 60\text{kcal/mole}$$

only the third has a sufficiently low endothermicity, yet it also would be expected to have a low A-factor in order to form the H_2CCCCH radical. This reaction remains a possibility and may contribute. Further consideration of the initiation problem led us to consider impurities as potential initiators. Acetone, stored in all acetylene bottles as an inhibitor, is a well-known impurity of acetylene and coelutes from tanks in concentrations of one to 20% that of acetylene[13]. When precautions are taken to reduce the concentration of impurities, acetone concentrations are typically decreased to approximately 0.1% of the acetylene concentration. Assuming that a radical initiation rate of $k_1^{high}\,[C_2H_2]^2$ is needed to produce sufficient radicals for acetylene pyrolysis, then this rate can be compared to the known[14] initiation by acetone.

$$CH_3COCH_3 \rightarrow CH_3 + CH_3CO \qquad (5)$$
$$CH_3CO \rightarrow CH_3 + CO \qquad (6)$$

Assuming $[acetone]/[C_2H_2] = 0.001$, one obtains

$$\frac{k_5[\mathrm{acetone}]}{k_1[C_2H_2]^2} = 0.0004 \times e^{(-4000.\mathrm{cal/mole/RT})}[C_2H_2]^{-1}$$

with Szwarc and Taylor's expression[14] for k_5 ($=2.4 \times 10^{15}$ exp(-72000 cal/mole/RT) sec^{-1}). At 20% C_2H_2 and 1000K (Munson and Anderson's conditions), this ratio is 22 while at $[C_2H_2] = 2.35 \times 10^{-5}$ mole/cc and 1200K (Ogura), the ratio is 3.2. Since this ratio is greater than one at both experimental conditions, radical initiation by thermal decomposition of acetone dominates over that of acetylene.

Considering that k_1^{high} is substantially higher than can be expected from thermodynamic arguments and that the radical initiation rate from acetone is higher than the required rate of initiation, it seems quite reasonable to expect that acetone plays a role in the initiation process. For reference, it is instructive to examine the ratio $k_5[\mathrm{acetone}]/k_1[C_2H_2]^2$ when k_1 is assigned the value determined by Tanzawa and Gardiner[1]. This ratio is then 0.13 and 0.12 for the previously discussed conditions. These values, in all probability, led to early conclusions that acetone initiation contributed negligibly to acetylene pyrolysis. This major difference in conclusions suggests a major difference in the two values of k_1 and reasons for this difference need to be examined.

The absolute value of k_1 determined by Tanzawa and Gardiner is nearly two orders of magnitude higher than that found in the present analysis. The principal reason for their higher value is believed to be a result of the low ΔH_f used for the n-C_4H_3 radical (~ 20 kcal/mole lower than that used in the present analysis). The resultant high stability of this radical as assumed in their model led to high rates of radical termination via n-C_4H_3 + H + M. This step played only a minor role in the present study; rather vinyl-vinyl recombination dominated termination. Thus radical termination was overestimated substantially in the earlier studies and the initiation rate was increased to compensate.

The important conclusion from this cursory analysis is that acetone decomposition is fast enough to influence the radical concentrations during acetylene pyrolysis.

Issues Raised by Acetone Initiation

Several critical issues must be raised if initiation by acetone contributes. First of all, a rapid mechanism for conversion of methyl radicals to H-atoms must be present; secondly, the 'well-known' second order behavior of acetylene must be addressed, specifically to see if this reaction order can be predicted and if not, why not; and thirdly, if acetone initiation dominates, then why is there such good experimental agreement (see Ref. 8) on acetylene decomposition from study to study when initial concentrations of acetone can be expected to vary.

It is readily shown that methyl radicals can be rapidly converted to H-atoms. A mechanism for conversion is shown in Table II. Rate constants were obtained from the literature where possible. The principal fate of methyl near 1000K will be its addition to acetylene (R7). According to a recent QRRK analysis[15] the resultant adduct should stabilize under these conditions. Using rate constants (in Table II and IV) and thermodynamic parameters nearly identical to those given by Dean and Westmoreland[15] (see Table VI) the rate of $CH_3CH\dot{C}H$ isomerization to allyl radical relative to its decomposition to methyl acetylene and H is approximately five. Due to the stability of allyl, its decomposition is slow and principally adds to acetylene to form C_5H_7 (R9). This linear radical can then either decompose to reactants (R(-8)) or form cyclopentadiene plus atomic hydrogen (R10). Thus, methyl radicals produced from acetone decomposition will be rapidly converted to H-atoms. Since the $k[\text{acetone}]/k_1[C_2H_2]^2$ ratios as previously calculated are significantly greater than one, production of H-atoms via acetone decomposition appears to be sufficiently fast to initiate the thermal decomposition of acetylene.

At higher temperatures, methyl radical addition to acetylene must compete with methyl recombination (R17), since the rapid decomposition of acetone quickly produces high concentrations of methyl. Also, methyl can extract hydrogen from acetylene (R16), since at high temperatures thermal energy is available to overcome the substantial endothermicity (~ 25 kcal/mole) of this reaction. In either high-temperature case, a variety of alternative sequences will again provide H-atoms.

The order, n, for the overall reaction as defined by

$$-\frac{d[C_2H_2]}{dt} = k_{ov}[C_2H_2]^n$$

is often cited as two. A steady-state analysis using reactions in Table I and Reactions 5-10 in Table II leads to

$$-\frac{d[C_2H_2]}{dt} = 2k_{3A}\left(\frac{2k_5}{k_4}\right)^{\frac{1}{2}}[C_2H_2][\text{acetone}]^{\frac{1}{2}}$$

or assuming $[\text{acetone}]/[C_2H_2] = 0.001$, then

$$-\frac{d[C_2H_2]}{dt} = 0.0894\, k_{3A}\left(\frac{k_5}{k_4}\right)^{\frac{1}{2}}[C_2H_2]^{1.5} \qquad \text{Eq. B}$$

This steady-state result that n=3/2 appears to be a major drawback of the present proposal regarding initiation by acetone. A review of the literature was performed in an attempt to find references in which the reaction order was determined or which provide data from which the order could be computed. A summary of reaction orders is presented in Table III. Although there is substantial variation in the reaction order, most values fall in the range of 1.5 to 2.0. The low temperature data from Silcocks[16] as well as the flow reactor data from Palmer and Dormish[17] were originally interpreted assuming simultaneous homogeneous and heterogeneous processes. Silcocks found the reaction orders to be two and one, respectively, while Palmer and Dormish found that this assumption was consistent with their data. An attempt has been made to reinterpret the latter experiments, with a resultant overall order ranging from 1.2 to 1.7. Munson and Anderson's low temperature experiments[10] exhibit significant scatter in plots of log(rate) vs. log$[C_2H_2]$ but the order appears to be 1.7 ± 0.2. Their higher temperature experiments clearly give $n = 1.5 \pm 0.1$. The results from Colket[11] of $n = 1.6 \pm 0.2$ are from comparison of single-pulse shock tube experiments at 4.9% (unpublished), 3.5% (Ref. 11) and 0.2% acetylene (unpublished). The order obtained by Ogura[3] is substantially higher than from other experiments. Results from Cullis and Franklin[18] at 983K give beautiful agreement with the assumption of a second order reaction. If indeed a chain mechanism controls the reaction, however, then Cullis and Franklin's data needs reinterpretation. They pyrolyzed pure acetylene at total pressures ranging from 96 to 402 torr. Under these conditions, some critical reactions, particularly $H + C_2H_2 \leftrightarrow C_2H_3$ can be expected to exhibit pressure dependence (see Warnatz[19]) and will lead to a net decrease in overall reaction rate with decreasing pressure. If pressure dependence is included, a preliminary analysis indicates that Cullis and Franklin's data are no longer inconsistent with the assumption of an overall reaction order of 1.5. Results from other authors listed in Table III do not support the 'well-known' reaction order of two.

Thus, with the exception of the very low temperature data of Silcocks and the value from Ogura, the assumption of an overall reaction order of 1.5 as suggested by acetone initiation is not unreasonable. In fact, the experimental data seem to support a value of 1.5 as well as or perhaps better than the order 2.

If acetone is the initiator, then why should experiments performed in many different laboratories, presumably with different initial acetone concentrations, all result in similar overall rate constants? This is a question which we could only partially address. A variety of purification techniques have been used. Often the level of impurities was not determined or not determined with sufficient accuracy. Based on our own experience, the work of Hamins, et al[13] and reported purity levels, we estimate that typical purified samples of acetylene contain about 0.1% acetone, with a total range of 0.05% to 0.2%. This variation of a factor of four leads to a factor of two variation in overall decomposition rates (due to the half-order dependence on acetone concentration). This variation in overall rates is within the measured experimental uncertainty.

Development of Kinetic Model

The kinetic model used in this analysis is based on (1) the initiation sequence as indicated in Table II largely using published rate constants and (2) an acetylene pyrolysis model as refined by Colket[11] to describe results obtained in a single-pulse shock tube. Model results (using a program based on CHEMKIN[20], LSODE[21] and isothermal, isobaric assumptions) were compared with the flow reactor data of Munson and Anderson[10]. The mechanism and rate constants used to model the flow reactor data are shown in Tables II and IV. Bimolecular initiation by acetylene (R1) was included in the model using a rate constant which can be expected to be an upper limit. In the modeling of the Munson and Anderson data, this reaction always had a negligible role. A few rate expressions have been modified in order to provide better fits to the flow reactor data. Selection of rate constants for modification was accomplished using a combination of a reaction pathway analysis (with computer programs developed at UTRC) and a sensitivity analysis using CHEMSEN[22]. For each rate expression modified, attempts were made to maintain consistency with the SPST modeling results by adjusting both the A-factor and the activation energy. In most cases this was possible since the flow reactor data were most dependent on kinetics over the range 900-1000K, whereas for the SPST results, the range was 1200-1500K. In the case of the competitive sinks for the n-C_4H_5 radical,

$$n - C_4H_5 \leftrightarrow H + C_4H_4 \quad (32)$$
$$n - C_4H_5 + C_2H_2 \rightarrow C_6H_6 + H \quad (33)$$

this was not possible, but an attempt was made instead to maintain the ratio of rate constants as determined in modeling the SPST data. Reaction 33 has been simplified from the previous 3-step reversible sequence involving intermediate formation of ℓ-C_6H_7 and c-C_6H_7, since a QRRK analysis by Westmoreland[23] indicates that at the conditions of the present study, the reaction rapidly proceeds as

$$C_2H_2 + n - C_4H_5 \rightarrow \ell - C_6H_7^* \rightarrow c - C_6H_7^* \rightarrow C_6H_6 + H$$

.

Modeling results near 1000K using the irreversible one-step or the three-step reversible sequence were virtually indistinguishable.

Other differences between the present and previous model include rate expressions for H-atom extraction by phenyl or vinyl from vinylacetylene. These were equated to the expression for vinyl plus 1,3-butadiene suggested by Kiefer, et al.[24]. Model results showed little sensitivity to rate constants for these reactions. Vinyl-vinyl recombination (R4) was taken to be 2×10^{13} cc/mole/sec based on a fit to the Munson and Anderson data. Rate constants for other alkyl radical terminations were assumed to be equal. The selected value was 5×10^{12} cc/mole-sec. After Frenklach, et al.[12], the two isomers, n-C_4H_3 and i-C_4H_3 were included; however, there is no ready sink for i-C_4H_3 at the low temperatures of the Munson and Anderson study. To resolve this problem, two reactions were included:

$$n - C_4H_3 \leftrightarrow i - C_4H_3 \quad (61)$$
$$i - C_4H_3 + C_4H_4 \rightarrow C_8H_6 + H \quad (66)$$

The first of these was found to be negligible near 1000K. The second was the dominant sink for i-C_4H_3 while affecting phenylacetylene slightly. The first reaction was assigned a rate constant similar to a value[25] for the i-C_3H_7 ↔ n-C_3H_7 isomerization, although an activation energy close to the strain energy in cyclopropene was used. The second reaction has been proposed[26] as an alternative mechanism for forming phenyl acetylene. It is a multistep process requiring a 1,4 H-atom shift, cyclization, and loss of an H-atom and was assigned a rate expression identical to that of Reaction 4 which requires a similar transformation. Neglecting the back reaction is justified since the reverse process is slow at these temperatures. A QRRK analysis[27] has been performed for Reaction 66 and indicates that near 1000K approximately 50% of the C_4H_4–i-C_4H_3 adducts will go directly to products prior to stabilization to intermediates. Therefore elimination of the intermediate steps is reasonable.

A third possible sink for i-C_4H_3 not included in the modeling is the addition of i-C_4H_3 to acetylene, cyclization to form a five-membered ring and then isomerization to phenyl.

Third body effects have been assumed to be small for this analysis. The greatest deviation from this assumption will occur for the H-atom addition to acetylene. Fall-off curves given by Warnatz[19] indicate that the k/k_∞ for this reaction is approximately 0.5 at one atmosphere of argon and 1000K.

In the present study, 20% of the gas is acetylene, a more efficient third body, suggesting the k/k_∞ is larger than 0.5; therefore, neglecting pressure effects is believed to result in only a small error. A reduction of k_2 by a factor of two results in a reduction of the overall decomposition rate of about 5-10%.

Some modeling was also performed for comparison to shock tube results. For these calculations, the kinetic mechanism was expanded to include ethynyl and related radicals (see Table V).

Thermodynamic values are reported in Table VI and are the same as those used previously[11], except for those of the C_4H_3 isomers, phenyl radical and the C_8-species which were obtained from Stein[4]. The latter are identical to those used in the study by Frenklach, et al[11].

Kinetic Model vs. Theory

In Figs. 2 to 5, calculations of acetylene, benzene, vinylacetylene, and ethene are compared to experimental profiles as measured by Munson and Anderson[10] in a flow reactor. For these calculations it was assumed that the acetone/acetylene ratio was 0.001. Overall the agreement is quite satisfactory. Benzene is overpredicted at long times for the highest temperature run, presumably because of the conversion of benzene to higher molecular weight species. Vinylacetylene is underpredicted at the low temperatures. Hydrogen, not shown, is underpredicted by about a factor of five to ten. Although substantial methane formation was observed, a model for methane formation was not included. Methane produced from methyl directly or via odd-carbon species derived from acetone could only account for a very small portion of the methane observed. Heterogeneous processes seem the most likely source of methane although gas-phase reactions are possible. For example, consider addition of the i-C_4H_5 radical ($H_2CCH\dot{C}CH_2$) to acetylene followed by cyclization to a *five-membered ring* and isomerization to methylcyclopentadienyl. Subsequent reactions involving methylcyclopentadienyl may then form methyl radicals and/or methane. The i-C_4H_5 radical is generally ignored in kinetic modeling but may play a significant role since it should be formed readily via H-addition to vinylacetylene.

The formation of polyaromatic hydrocarbons is not included in the present model. Modeling results for acetylene, benzene, and vinylacetylene[28] fit the experimental data almost perfectly for the Munson and Anderson data of 1073K when formation of polyaromatic hydrocarbons are included. There is relatively little change to the model predictions for the lower temperature runs.

Model calculations have also been compared to data obtained in a single-pulse shock tube by Colket[11,28] at 3.5% and 4.9% acetylene in five and eight atmospheres of argon, respectively. Experimental procedures for the unpublished 4.9% data were similar to those previously described[11]. The acetone concentrations were equated to the measured values, that is, 0.1% and 0.2% the concentration of acetylene for the 3.5% and 4.9% data,, respectively. Calculations were performed using a shock tube code modified to account for quenching processes. Again satisfactory agreement (comparable to that achieved in Ref. 11) is obtained for most species, including the minor products, styrene and ethylene. The main descrepancy is that the model underpredicts product formation at low temperatures. Of particular interest is Fig. 6 in which only odd-carbon products derivable from the impurity acetone are shown for the 4.9% series of runs. Also plotted is the sum of the concentrations of acetone plus half of all species containing an odd number of carbons. Acetone produces two methyl radicals, each of which could produce an odd-carbon species. The fact that this sum is essentially constant over the range of temperature of experiments lends strong support to a major thesis of this work; i.e., acetone produces methyl radicals which convert to H-atoms via addition to acetylenes, whereas ethane formation via methyl recombination is small compared to methyl addition to acetylene. Model predictions are not shown in Fig. 6 since prediction of the odd-carbon products is generally poor. This limitation is probably a direct result of the fact that there is very little experimental data on these species, and many of the rate constants in Table II were estimated.

Ogura also obtained single-pulse shock tube data at 5% acetylene in about two atmospheres of argon. Model predictions are compared to the Ogura[3] data in Fig. 7. for vinylacetylene, diacetylene and hydrogen. Again comparison between experiments and theory seem quite satisfactory. For the model calculations, dwell times of one millisecond were assumed and quenching rates comparable to those measured by Colket[11] were used. The acetone/acetylene ratio was assumed to be 0.001. Attempts to fit Ogura's experimental profiles of methane, methylacetylene, allene, and ethylene for experiments with 10% acetylene in argon were also made. The agreement was good for methane and satisfactory for ethylene except at low temperatures when the model significantly underpredicted the experimental data. The model overpredicts the C_3-hydrocarbons by about a factor of two to three. This difference does not seem unreasonable considering the general lack of knowledge regarding pyrolysis of odd-carbon, acetylenic species.

Vinylidene vs. Chain

Perhaps the most significant pieces of experimental evidence against a radical chain-mechanism are the results by Hou and Anderson[29] and more recently by Duran, et al[6]. The earlier study involved a molecular beam, mass spectrometric analysis of acetylene pyrolysis products from a flow reactor near 1000K. The usefulness of their facility was 'proved' by its ability to detect methyl radicals during pyrolysis of tetramethyl lead and di-t-butylperoxide. They detected no radicals during acetylene pyrolysis. Calculations for their experimental conditions indicate that during acetylene pyrolysis their total radical concentrations always were substantially less than one part per million. It appears unlikely that their facility had the sensitivities to observe species at such low concentrations, whereas methyl radicals readily produced from the test compounds would be expected to achieve substantial concentrations. We think that these early experiments do not disprove a radical-chain mechanism.

Recent pyrolysis experiments by Duran, et al[6]. were also performed in a flow reactor with mass spectrometric results. Additions of benzene and toluene showed respectively, no inhibition and an acceleration. The acceleration, unexplained by the vinylidene mechanism, is easily explained via chain processes since initiation via toluene ($C_7H_8 \rightarrow C_7H_7 + H$) using any of the recently proposed rate expressions (see Ref. 30-31 and citations contained therein) can be shown to be substantially faster than initiation by acetone. In addition, Duran observed a variety of vinyl benzenes when benzene and acetylene were copyrolyzed. They interpreted these results as evidence for insertion of the carbene (vinylidene) into the benzene ring. Alternatively, these vinylbenzenes may also be the result of the displacement ($C_2H_3 + C_6H_6 \rightarrow H + C_6H_5C_2H_3$), which is similar to the known[32] methyl-substitution in the benzene-toluene system. Copyrolysis of toluene and acetylene produced principally a species at mass 118, interpreted to be methyl styrene. Instead this species may be phenyl propene formed by acetylene addition to the stable benzyl radical. Consequently, we question their conclusion of proof for the vinylidene mechanism.

Overall Reaction Order and Activation Energy

Reaction order was determined from model predictions by varying the initial concentration (while holding temperature constant at 973 K). Plots of log $(d[C_2H_2]/dt)_0$ vs. log $[C_2H_2]_0$ yielded an overall reaction order of 1.43±.10. The initial rate $d[C_2H_2]/dt]_0$ was taken to be the value immediately after a short induction period (~0.2 seconds at 20% acetylene, 873 K). Reaction orders were also determined from plots of predicted log ($d[C_2H_2]/dt$) vs. $[C_2H_2]$ as a funtion of time over the temperature range 873 to 1073 K. These calculations resulted in a reaction order of 1.43, 1.66, and 1.67 at 973, 1023, and 1073K respectively. These values are consistent with the overall order of 1.5 obtained from the steady-state analysis. Assuming this latter value, an overall rate expression was determined using the model prediction for Munson and Anderson's conditions. The rate expression determined was:

$$\left.\frac{d[C_2H_2]}{dt}\right)_{\text{overall}} = 10^{11} e^{-(40600\ \text{cal/mole/RT})} [C_2H_2]^{1.5}\ (\text{cc/mole})^{\frac{1}{2}} \sec^{-1}$$

at 873 - 1073 K. This expression can be compared to that obtained from the simplified steady-state expression (sss), Eq. B. Equating k_{3A} to k_3 and using other rates from Tables II and IV, this simpilied expression becomes

$$\left.\frac{d[C_2H_2]}{dt}\right)^{\text{sss}}_{\text{overall}} = 3.4 \times 10^{11} e^{-(40000\ \text{cal/mole/RT})} [C_2H_2]^{1.5}\ (\text{cc/mole})^{\frac{1}{2}} \sec^{-1}$$

The lower A-factor from the detailed model is due to a combination of the reverse of R3, alternative termination reactions (e.g., R54), and the fact that some acetone decomposes via a chain process rather than R5 (see Reactions 21-23 in Table II).

Higher Temperature Modeling

Preliminary modeling has been performed for shock tube conditions at higher temperatures. The scenario regarding initiation, termination, fate of acetone and methyl radicals changes somewhat. The changes include a greater fraction of acetone decomposing via radical attack. This leads to the production of ketene which also is an effective radical initiator. The resulting sequence,

$$\begin{array}{rcll}
H + CH_3COCH_3 & \leftrightarrow & CH_2COCH_3 + H_2 & (22a) \\
CH_2COCH_3 & \leftrightarrow & CH_2CO + CH_3 & (22b) \\
CH_2CO & \leftrightarrow & CH_2 + CO & (24) \\
CH_2 + C_2H_2 & \leftrightarrow & C_3H_3 + H & (28) \\
C_3H_3 + C_3H_3 & \leftrightarrow & C_6H_6 & (29)
\end{array}$$

leads to the net production of only one methyl radical (the H-atom is regenerated) compared to the two radicals from initiation directly through acetone decomposition (Reaction 5). This sequence is very dependent on the uncertain high temperature chemistry of methylene (CH_2) and propargyl (C_3H_3) radicals. Besides recombination, the latter can add to acetylene to form a C_5H_5 radical whose stability is enhanced by resonance. Other potential complicating features are that some species formed as by-products of acetone decomposition, e.g. cyclopentadienes, have weak C-H bonds because of the resonantly-enhanced stability of the hydrocarbon radical (in this case cyclopentadienyl). Consequently, even though acetone may be destroyed early during reaction, some of the products will continue to provide radicals and maintain the decomposition of acetylene. At high temperatures, vinyl recombination no longer dominates radical termination. Methyl radicals and radical adducts formed by addition to acetylene contribute to chain termination.

At very high temperatures (>2000K), a significantly different story emerges. Acetone decomposes within a few nanoseconds to methyl radicals which rapidly equilibrate with ethane in the recombination reaction. Eventually, methyl is converted to two H-atoms via the sequence Reaction 18,20, but the amount of H-atoms is small compared to H-atom production from pure acetylene pyrolysis as initiated by cleavage of the C_2H-H bond[33]. In fact our calculations are consistent with the results of Frank and Just[33] who found that 'purified' and unpurified acetylene produced the same H-atom profiles at 50ppm acetylene and 2400K. In contrast, near 2000K they found that high concentration runs require purification. Again this result is identical to our calculations. In fact, our model predicts that the accelerated rate they observe at 1800-2000K for the initiation rate can be explained by the presence of small amounts of acetone (~0.1% in acetylene)

Sensitivity and Reaction Pathway Analyses

A sensitivity analysis has been performed using CHEMSEN for the isobaric, isothermal conditions of Munson and Anderson. Results of these calculations are reproduced in Table VII for 973 K after 10% decomposition for the six reactions most sensitive to the computed results for each of the five species listed in Table VII. Rate constants for several of these reactions were determined in this work. Also, a reaction pathway analysis was performed using programs developed at UTRC. Reactant decay and product formation as determined using this analysis are described below.

Acetylene was calculated to decay principally by three reactions:

$$\begin{aligned} H + C_2H_2 &\leftrightarrow C_2H_3 && (2) \\ C_2H_3 + C_2H_2 &\leftrightarrow n - C_4H_5 && (3) \\ n - C_4H_5 + C_2H_2 &\rightarrow C_6H_6 + H && (33) \end{aligned}$$

The net rates of the first two are essentially equal whereas the rate of the third is slower because of the decay of n-C_4H_5 to vinylacetylene. Vinylacetylene is formed almost entirely by H-atom elimination from n-C_4H_5 (Reaction 32). Its decay is due predominantly to:

$$n - C_4H_5 + C_4H_4 \leftrightarrow C_8H_8 + H \qquad (35)$$

which inturn forms styrene, although H-atom abstraction from vinylacetylene by phenyl or vinyl (R41-42, 64-65) also contributes to vinylacetylene decay. The formation of benzene is from n-C_4H_5 addition to acetylene (R33). As the reaction proceeds, additional benzene is produced by phenyl (from R38) abstracting H-atoms from molecular hydrogen, vinylacetylene or ethene. Ethene arises mainly from H-atom attack on styrene (R38) although some is produced by abstraction of H-atoms from hydrogen and vinylacetylene by vinyl radicals (R47 and R65). According to the proposed model, which underpredicts hydrogen by a factor of five to ten, hydrogen is formed by H-atom attack on styrene (R36).

Discussions of Rate Constants and Uncertainties

In order to fit the Munson and Anderson data, values of four rate constants have been modified from values previously proposed. The related reactions are

$$C_2H_3 + C_2H_3 \leftrightarrow C_4H_6 \qquad (4)$$

$$n - C_4H_5 \leftrightarrow C_4H_4 + H \qquad (32)$$

$$n - C_4H_5 + C_2H_2 \rightarrow C_6H_6 + H \qquad (33)$$

$$n - C_4H_5 + C_4H_4 \rightarrow C_8H_8 + H \qquad (35)$$

k_4, the rate constant for vinyl-vinyl recombination, was selected to be 2×10^{13} cc/mole/sec in this work. This value although slightly high is consistent with rate coefficients for recombination of other low molecular weight hydrocarbons (see Ref 34). The value used here is about 50% larger than the expression suggested by Ebert, et al[35]. The rate constant for R32 was based on the thermochemical estimate by Weissman and Benson[38] but the A-factor was increased by 60% to enhance the fit to experimental data. Equilibrium calculations give a reverse rate constant of about 8×10^{12} cc/mole/sec at 1000K. This value is about a factor of five higher than the H + C_2H_2 reaction. Errors in the thermochemistry and possible contributions from reactions involving vinylidene may be the cause of the high rates for R32 and R(-32) as required by this analysis. At 1000K, the irreversible rate constant, k_{33}, is about a factor of four[36], two[11,23], and one and one-half[37] lower than values previously proposed. The major difference of this work is the high activation energy (10kcal/mole) compared to other evaluations: 3.7[37], 4.9(from a fit to reported[23] calculations, 6.9[36], and 9[11]. Due to this difference, the extrapolated value from the present work is essentially identical to other values[23,37] near 1200-1300K. $k_{35} = 1.1 \times 10^{13} e^{-5000/RT}$ as used in this study is substantially lower than the high value suggested by Colket[11] but is about four times larger than the value reported by Cole, et al.[37]. As discussed previously, the i-C_4H_5 radical may play a role or C_4H_4-C_4H_4 reactions may contribute.

Rate constants as determined in this work are generally within a factor of four of other values recently proposed and experimental data for these reactions is extremely limited: usually, rate expressions have been estimated or determined from detailed modeling. Consequently, we believe that the evaluations of rate constants in this study are very reasonable and lend strong support for the general thesis of this paper regarding the importance of acetone.

Uncertainties in the analysis include possible contributions due to reactions involving vinylidene and related species. As discussed previously, we are unable to disprove the existence of such mechanisms. Due to the generally good agreement between the modeling (without invoking such mechanisms) and experimental data, we believe that contributions due to these reactions are negligible; instead, the chain mechanism seems to dominate in most cases. It is possible that the vinylidene mechanism contributes to vinylacetylene production at 873K (see Fig. 3) when the chain underpredicts the experimental data. Other uncertainties are related to the lack of a model for methane formation at low temperatures. At 973K, Munson and Anderson found that about 1.2% of the initial carbon was converted to methane. Often it is suggested that this methane formation is catalytic. An alternative and speculative mechanism, described in this paper but not included in the model involves the intermediate formation of the i-C_4H_5 radical. It may be formed by H-atom addition to vinylacetylene or isomerization of the excited n-C_4H_5 radical after its formation by vinyl addition to acetylene. The formation of excited radicals via radical additions to acetylenes is another area of uncertainty in the proposed model. A limited number of QRRK[15] calculations have been performed and indicate that these effects should be included at elevated temperatures. An example, is the system

$$
\begin{aligned}
C_2H_3 + C_2H_2 &\leftrightarrow n - C_4H_5^{\bullet} \\
n - C_4H_5^{\bullet} &\leftrightarrow n - C_4H_5 \\
n - C_4H_5^{\bullet} &\leftrightarrow C_4H_4 + H \\
n - C_4H_5^{\bullet} &\leftrightarrow i - C_4H_5
\end{aligned}
$$

but for simplicity, these effects have not been included in the present analysis.

Significant uncertainties exist in the kinetics and mechanisms related to the odd-carbon, acetylenic species. This belief is based on the facts that very little experimental data or estimates on such species exist; large uncertainties exist in the thermodynamics of the odd-carbon radicals; and predictions of profiles of odd-carbon species, although qualitative are not quantitatively accurate. Despite these drawbacks, the major conclusion of this paper, that is that acetylene pyrolysis is initiated by a small amount of acetone, should not be altered.

Conclusions

The major conclusion of this study is that the pyrolysis of pure acetylene has not been investigated at temperatures below 2000K. The very high C-H bond strengths in acetylene prevent a rapid initiation of radicals; instead very low concentrations of impurities are the source of radicals which initiate and sustain a chain decomposition. Acetone, a contaminant present in kinetic studies of acetylene pyrolysis has been shown to dominate radical initiation. The overall reaction rate determined both from a simple steady-state analysis and detailed chemical kinetic modeling has an activation energy near 40 kcal/mole and a reaction order near 1.5. The overall activation energy is consistent with previous experiments while the reacion order is lower than the usually assumed value of two. A detailed review of the literature shows in fact minimal support for a reaction order of two while experiments are reasonably consistent with an order of 1.5. A few rate constants have been selected to provide a fit to the Munson and Anderson data. Values of these rate constants are in general consistent with values previously published. The modeling makes no attempt to include reactions involving the vinylidene radical. Although there is no proof against mechanisms involving this carbene, there appears now to be ample evidence in support of a chain mechanism; firstly, experimental evidence from a wide variety of sources and conditions support the presence of a chain, and secondly, a mechanism initiated by thermal decomposition of acetone adequately describes experimental results. Vinylidene-related mechanisms may contribute to acetylene pyrolysis but we believe that a chain mechanism dominates all acetylene pyrolysis above 900K.

Acknowledgements

This work has been supported in part by the Air Force Office of Scientific Research under Contract No. F49620-85-C-0012. The authors are indebted to Dr. Julian Tishkoff, AFOSR contract monitor, for his support. We thank Prof. J. Mackie from the Univ. of Sydney for many fruitful discussions and Prof. J. Kiefer from the Univ. of Illinois for his many challenging questions related to this research. Thanks are given to Dr. A. Dean of Exxon and Prof. J. Bozzelli of New Jersey Institute of Technology for their QRRK calculations of the $C_4H_4 + i - C_4H_3$ system. The able assistance of G. Deske and H. Hollick in the preparation of the manuscript and figures is gratefully acknowledged.

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TABLE I

Simplified Reaction Sequence For Low Temperature Pyrolysis Of Pure Acetylene

$C_2H_2 + C_2H_2 \leftrightarrow n - C_4H_3 + H$ (1)

$H + C_2H_2 \leftrightarrow C_2H_3$ (2)

$C_2H_3 + C_2H_2 \leftrightarrow C_4H_4 + H$ (3a)

$C_2H_3 + C_2H_3 \leftrightarrow C_4H_6$ (4)

TABLE II
PROPOSED SET OF REACTIONS AND RATE COEFFICIENTS FOR INITIATION BY ACETONE

$\log k = \log A + n\log T - E/R/T/2.303$ *

	Reactions	Forward Rate Constant			Reverse Rate Constant			
		logA	n	E	logA	n	E	Ref
5	CH3COCH3=CH3CO+CH3	14.38	0.0	72.0	11.55	0.0	-5.6	14
6	CH3CO=CH3+CO	12.48	0.0	16.7	10.68	0.0	4.6	a
7	CH3+C2H2=CH3CHCH	11.79	0.0	7.7	12.87	0.0	33.9	38
8	CH3CHCH=C3H5	13.15	0.0	36.0	14.10	0.0	57.4	15
9	C3H5+C2H2=C5H7	12.00	0.0	8.0	13.11	0.0	20.1	est
10	C5H7-C-C5H6+H	10.30	0.0	5.0	0.00	0.0	0.0	est
11	H+C3H4=CH3CHCH	12.76	0.0	3.1	12.52	0.0	38.2	39
12	H+ALLENE=C3H5	12.60	0.0	2.7	13.13	0.0	60.9	39
13	2C3H5=C3H6+C3H4	12.70	0.0	0.0	13.20	0.0	30.5	est
14	C3H5+C2H3=C5H8	12.70	0.0	0.0	15.62	0.0	82.5	est
15	C3H5+H=C3H6	13.60	0.0	0.0	14.81	0.0	87.0	est
16	CH3+C2H2=CH4+C2H	12.40	0.0	35.0	13.11	0.0	15.1	est
17	2CH3=C2H6	14.38	-.4	0.0	16.31	0.0	87.1	a
18	2CH3=C2H5+H	14.90	0.0	26.5	16.92	0.0	16.3	a
19	C2H6+CH3=C2H5+CH4	-0.26	4.0	8.3	14.71	0.0	25.1	a
20	C2H5=C2H4+H	13.30	0.0	39.7	12.50	0.0	1.9	a
21	CH3+CH3COCH3-CH4+CH2CO+CH3	11.60	0.0	9.7	0.00	0.0	0.0	40
22	H+CH3COCH3-H2+CH2CO+CH3	13.28	0.0	6.4	0.00	0.0	0.0	39
23	C2H3+CH3COCH3-C2H4+CH2CO+CH3	12.48	0.0	6.4	0.00	0.0	0.0	est
24	CH2CO=CH2+CO	14.00	0.0	71.0	11.65	0.0	-4.4	c
25	CH3+H=CH2+H2	14.86	0.0	15.1	14.09	0.0	10.1	41
26	CH3+CH2=C2H4+H	13.30	0.0	0.0	15.89	0.0	61.3	41
27	2CH2=C2H2+H2	13.30	0.0	0.0	15.65	0.0	128.7	41
28	CH2+C2H2=C3H3+H	12.26	0.0	0.0	13.36	0.0	11.5	a
29	2C3H3-C6H6	12.70	0.0	0.0	0.00	0.0	0.0	est
30	CH2CO+H=CH3+CO	12.85	0.0	3.0	11.87	0.0	37.0	a
31	CH2CO+CH3=C2H5+CO	12.30	0.0	3.0	13.34	0.0	26.7	est

* NOTES: Units for A: cc,moles,sec.
Units for E: kcal/mole.
"=" represents forward and reverse directions included in model.
"-" represents forward direction only included in model.
PW indicates rate evaluted from the present work.
a indicates rate constants from Ref. 19.
c rate constant a factor of three lower from that reported in Ref. 19.
est estimate based on thermodynamics and/or analogous reactions.

TABLE III

Experimental Overall Reaction Orders

	Apparatus	Temp (K)	Order (n)
Silcocks[16]	static reactor	625-745	1(het.),2(hom.)
Cullis and Franklin[18]	static reactor	983	2
Munson and Anderson[10]	flow reactor	873,923 973-1073	1.7±0.2 1.5±0.1
Palmer and Dormish[17]	flow reactor	1333-1528	1(het.),2(hom.) [1.2 to 1.7]*
Ogura[3]	SPST	1000-1670	(~2.3)
Colket[28]	SPST	1100-1400	1.6±0.2
Aten and Greene[42]	shock tube	1400-2500	1.72±0.1
Cundall, et al[43]	shock tube	1500-2500	1**
Gay, et al[44]	shock tube	1600-2400	not 2
Towell and Martin[45]	flow reactor	1220-1400	1.5**

* reevaluated in present study

** overall order for formation of products

TABLE IV
PROPOSED SET OF REACTIONS AND RATE COEFFICIENTS FOR ACETYLENE PYROLYSIS AT LOW AND INTERMEDIATE TEMPERTURES

$\log k = \log A + n \log T - E/R/T/2.303$ *

	Reactions	Forward Rate Constant			Reverse Rate Constant			
		logA	n	E	logA	n	E	Ref
1	2C2H2=n-C4H3+H	13.00	0.0	67.0	12.48	0.0	-2.0	est
2	H+C2H2=C2H3	12.74	0.0	2.5	13.01	0.0	43.7	49
3	C2H3+C2H2=n-C4H5	12.04	0.0	4.0	13.88	0.0	38.4	11
4	2C2H3=C4H6	13.30	0.0	0.0	16.71	0.0	101.1	pw
32	n-C4H5=C4H4+H	14.20	0.0	41.4	13.60	0.0	3.0	pw
33	n-C4H5+C2H2-C6H6+H	12.65	0.0	10.0	0.00	0.0	0.0	pw
34	C2H3+C4H4-C6H6+H	11.60	0.0	0.0	0.00	0.0	0.0	b
35	C4H4+n-C4H5-C8H8+H	13.08	0.0	5.0	0.00	0.0	0.0	pw
36	C8H8+H=C8H7+H2	14.60	0.0	7.0	13.65	0.0	12.0	11
37	C8H7=C8H6+H	12.85	0.0	45.0	12.95	0.0	0.7	est
38	C2H4+C6H5=C8H8+H	11.27	0.0	2.1	12.38	0.0	1.6	d
39	C6H6+H=C6H5+H2	14.40	0.0	16.0	12.69	0.0	9.8	a
40	C2H2+C6H5=C8H6+H	12.00	0.0	4.0	13.88	0.0	6.0	b
41	C2H3+C4H4=C2H4+n-C4H3	13.30	0.0	14.5	13.23	0.0	13.4	24
42	C4H4+C6H5=C6H6+n-C4H3	13.30	0.0	14.5	13.60	0.0	18.9	24
43	L-C6H5=n-C4H3+C2H2	14.00	0.0	36.0	11.69	0.0	1.0	11
44	C6H5=L-C6H5	13.54	0.0	65.0	9.91	0.0	1.1	11
45	C2H3+C6H6=C2H4+C6H5	13.30	0.0	14.5	12.94	0.0	9.1	e
46	C2H3+H=C2H4	13.60	0.0	0.0	15.55	0.0	105.1	est
47	C2H4+H=C2H3+H2	14.84	0.0	14.5	13.49	0.0	13.8	a
48	C2H3+H=H2+C2H2	13.00	0.0	0.0	13.34	0.0	63.1	a
49	C4H4+H=n-C4H3+H2	13.90	0.0	14.5	12.49	0.0	12.7	a
50	C6H6=C6H5+H	15.70	0.0	107.9	13.39	0.0	-2.6	47
51	C6H5+C6H6=C12H10+H	11.80	0.0	11.0	13.04	0.0	8.7	b
52	2n-C4H5=C8H10	12.70	0.0	0.0	16.92	0.0	106.9	est
53	n-C4H5+H=C4H6	13.60	0.0	0.0	15.44	0.0	107.9	est
54	n-C4H5+C2H3=C6H8	12.70	0.0	0.0	16.33	0.0	104.0	est
55	C4H6+H=n-C4H5+H2	14.00	0.0	14.5	12.76	0.0	10.9	24
56	C4H6+C2H3=n-C4H5+C2H4	13.30	0.0	14.5	13.41	0.0	11.7	e
57	C6H5+C2H3=C8H8	12.70	0.0	0.0	15.76	0.0	104.5	est
58	i-C4H3+H2=C2H2+C2H3	10.70	0.0	20.0	10.58	0.0	17.8	11
59	i-C4H3=C4H2+H	12.00	0.0	49.0	12.05	0.0	0.6	11
60	n-C4H3=C4H2+H	12.60	0.0	40.0	12.95	0.0	-0.4	11
61	n-C4H3=i-C4H3	13.00	0.0	53.0	13.30	0.0	61.0	est
62	i-C4H3+H=C4H2+H2	13.00	0.0	0.0	13.65	0.0	56.0	11
63	C4H4+H=i-C4H3+H2	14.49	0.0	14.5	13.38	0.0	20.7	11
64	C6H5+C4H4=C6H6+i-C4H3	13.30	0.0	14.5	13.90	0.0	26.9	e
65	C2H3+C4H4=C2H4+i-C4H3	13.30	0.0	14.5	13.54	0.0	21.4	e
66	C4H4+i-C4H3-C8H6+H	11.60	0.0	0.0	0.00	0.0	0.0	est
67	H2+M=2H+M	12.35	-.5	92.5	9.98	0.0	-13.1	a

* NOTES: see notes for Table II

b see citations in Ref. 11. (Reverse rate constants may differ slightly due to differences in the thermodynamics and the temperature range of the fit for the reverse rate.)

d rate constant divided by 2 from that cited in Ref. 11.

e see text

TABLE V
PROPOSED SET OF REACTIONS AND RATE COEFFICIENTS FOR HIGH TEMPERATURE ACETYLENE PYROLYSIS

$\log k = \log A + n\log T - E/R/T/2.303$ *

	Reactions	Forward Rate Constant			Reverse Rate Constant			
		logA	n	E	logA	n	E	Ref
68	C2H2+M=C2H+H+M	16.62	0.0	107.0	15.21	0.0	-18.2	b
69	C2H+C4H4=C2H2+i-C4H3	13.60	0.0	0.0	13.29	0.0	27.0	b
70	n-C4H3=C2H2+C2H	14.30	0.0	57.0	13.42	0.0	0.8	11
71	n-C4H3+H=C4H2+H2	12.00	0.0	0.0	12.95	0.0	64.0	11
72	i-C4H3+H=C4H4	13.78	0.0	0.0	15.49	0.0	98.2	est
73	C2H+H2=H+C2H2	12.85	0.0	0.0	13.65	0.0	20.8	b
74	C2H+C2H2=C4H2+H	13.60	0.0	0.0	14.84	0.0	15.8	b
75	C4H2=C4H+H	14.89	0.0	120.0	13.25	0.0	1.9	b
76	C2H+C4H2=C6H2+H	13.60	0.0	0.0	15.04	0.0	15.5	b
77	C4H+C2H2=C6H2+H	13.30	0.0	0.0	14.97	0.0	8.5	11
78	C6H2=C6H+H	14.89	0.0	120.0	13.02	0.0	5.2	b
79	C4H+H2=H+C4H2	13.30	0.0	0.0	14.34	0.0	13.8	b
80	C6H+H2=H+C6H2	13.30	0.0	0.0	14.56	0.0	10.5	b
81	C2H+C6H6=C6H5+C2H2	13.30	0.0	0.0	12.40	0.0	14.7	b
82	C4H+C6H6=C6H5+C4H2	13.30	0.0	0.0	12.63	0.0	7.6	b
83	C2H3+C4H2=C4H4+C2H	13.48	0.0	23.0	13.47	0.0	3.1	11
84	C4H4=C2H+C2H3	16.00	0.0	105.0	13.37	0.0	-16.2	11

* NOTES: Units for A: cc,moles,sec.
Units for E: kcal/mole.
"=" represents forward and reverse directions included in model.
"-" represents forward direction only included in model.
PW indicates rate evaluted from the present work.
b see footnote b in Table IV.
est estimate based on thermodynamics and/or analogous reactions.

TABLE VI

SELECTED THERMODYNAMICS AT 300K

SYMBOL	NAME/structure	S° eu	ΔH_f kcal/mole
$C_{12}H_{10}$	biphenyl	93.6	43.6
C_8H_{10}	octatetraene	90.4	53.2
C_8H_8	styrene	82.6	35.3
C_8H_7	$C_6H_5\dot{C}CH_2$	83.8	83.2
C_8H_6	phenylacetylene	76.4	75.2
C_6H_8	hexatriene	79.4	39.6
C_6H_6	benzene	65.2	19.8
C_6H_5	phenyl	69.1	78.2
C_6H_2	triacetylene	71.1	169.7
C_6H	C_6H	74.3	233.2
C_4H_6	1,3-butadiene	66.6	26.1
n-C_4H_5	$H_2CHCH\dot{C}H$	69.1	82.5
C_4H_4	vinylacetylene	66.1	69.4
i-C_4H_3	$HCC\dot{C}CH_2$	68.1	116.1
n-C_4H_3	$HCCCH\dot{C}H$	69.4	124.1
C_4H_2	diacetylene	59.9	111.7
C_4H	C_4H	62.8	179.0
C_2H_3	vinyl	54.5	65.7
C_2H	ethynyl	49.6	128.5
C_5H_8	1,4-pentadiene	76.6	18.7
C_5H_7	1,4-pentadien-1-yl	79.3	78.2
c-C_5H_6	cyclopentadiene	64.6	32.0
CH_3CO	acetyl	62.0	-6.0
C_2H_5	ethyl	54.6	26.4
CH_3CHCH	$CH_3CH\dot{C}H$	67.5	61.6
C_3H_5	allyl	62.1	39.4
C_3H_4	methylacetylene	59.3	44.4
C_3H_3	propargyl	60.0	81.5
CH_2	methylene	46.4	92.4
CH_2CO	ketene	57.8	-12.4

note: Thermodynamics of species not listed in this table are essentially identical to those listed in Ref. 25.

TABLE VII

Normalized Sensitivity Coefficients

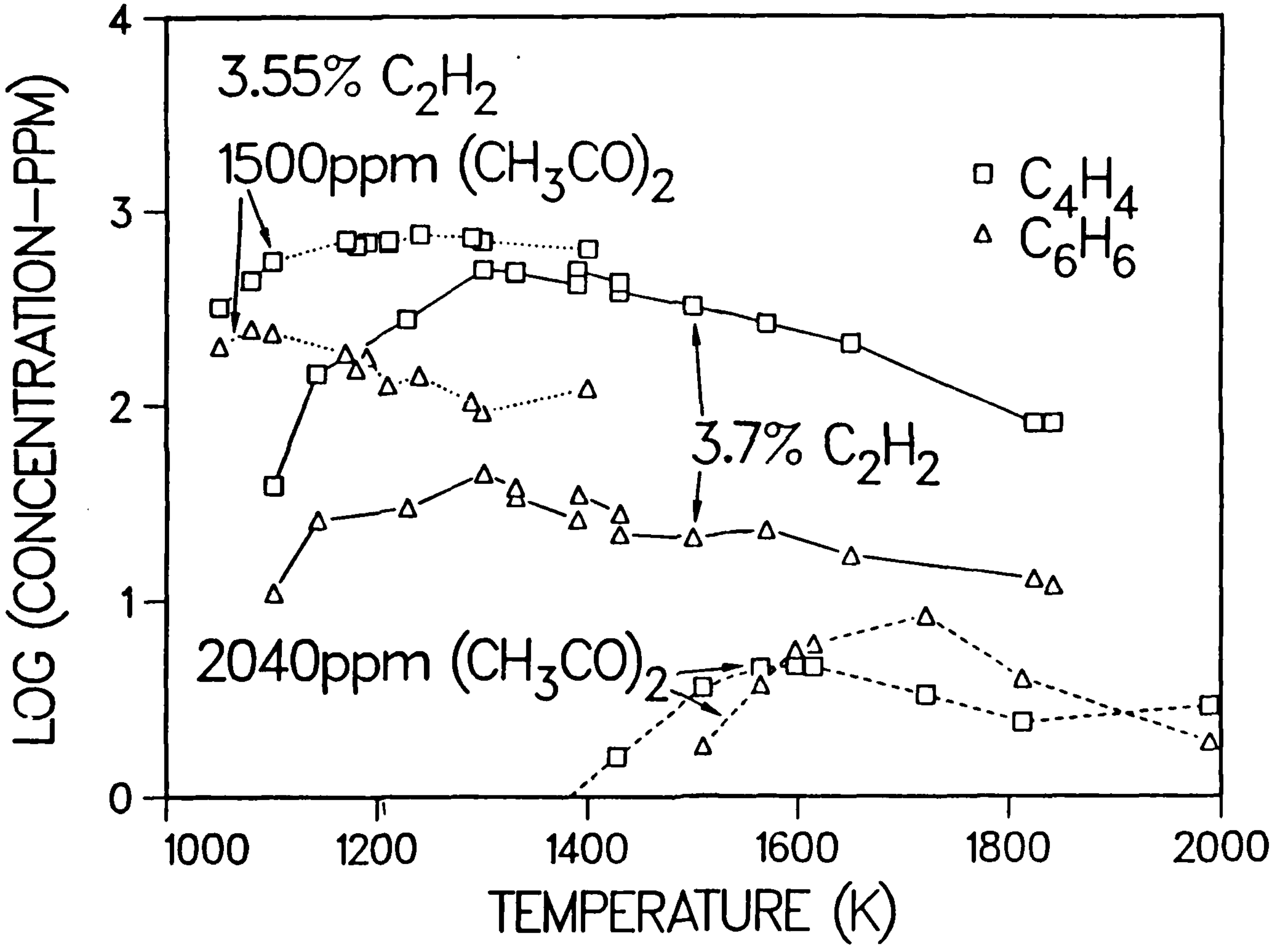
$$\frac{dy}{dk} \times \frac{k}{y}^{*}$$

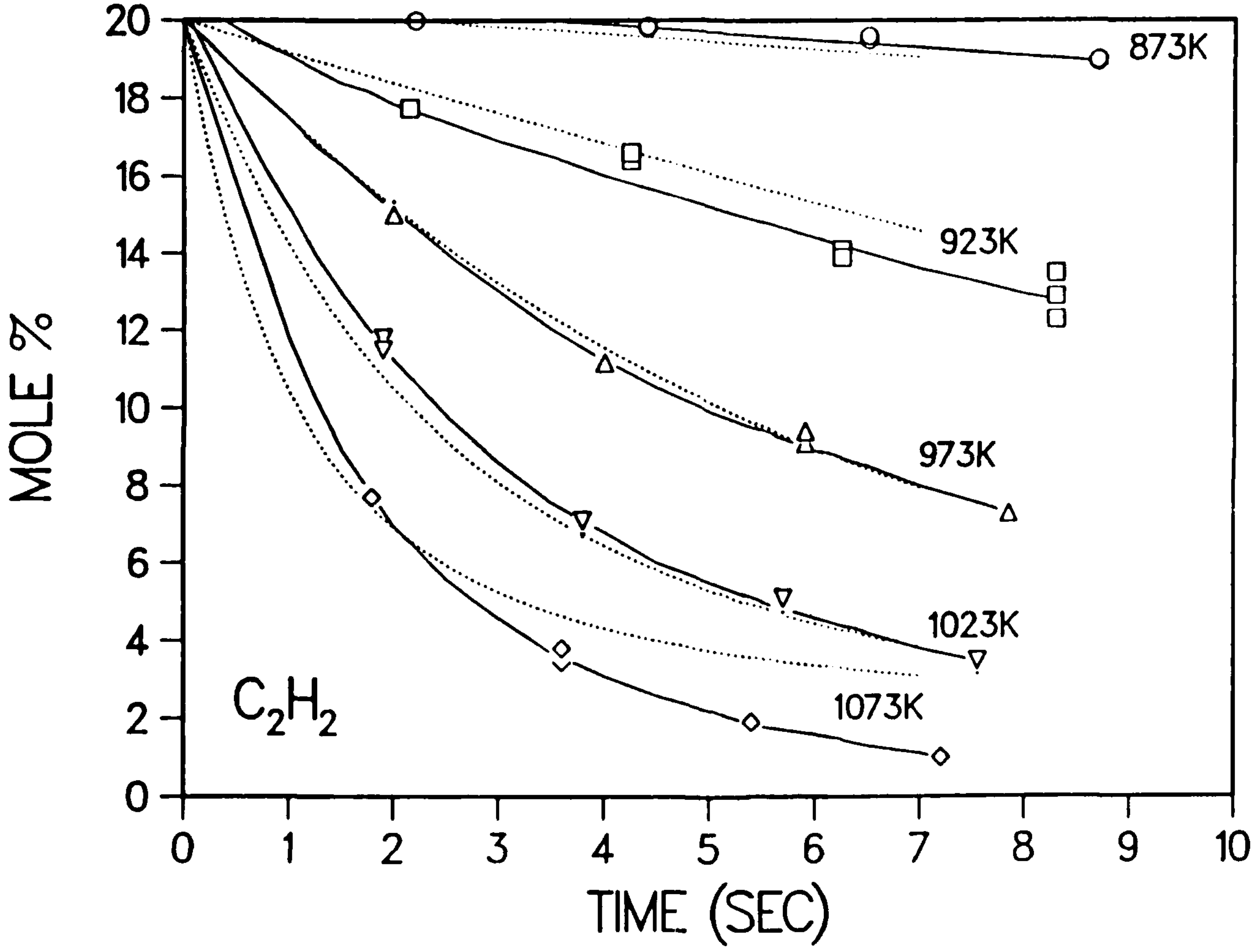
	C_2H_2	C_2H_4	C_4H_4	C_6H_6	H_2
2) $H + C_2H_2 \leftrightarrow C_2H_3$	-0.014	0.06	0.13	0.09	-0.52
3) $C_2H_3 + C_2H_2 \leftrightarrow n\text{-}C_4H_5$	-0.030	0.10	0.18	0.21	0.61
4) $C_2H_3 + C_2H_3 \leftrightarrow C_4H_6$	0.025	-0.42	-0.11	-0.23	-0.55
5) $CH_3COCH_3 \leftrightarrow CH_3 + CH_3CO$	-0.050	0.85	0.22	0.47	1.11
23) $C_2H_3 + CH_3COCH_3 \rightarrow C_2H_4 + CH_2CO + CH_3$	-	0.20	-0.01	-0.01	-0.02
32) $n\text{-}C_4H_5 \leftrightarrow C_4H_4 + H$	-0.020	0.35	0.68	-0.14	0.64
33) $n\text{-}C_4H_5 + C_2H_2 \rightarrow C_6H_6 + H$	-0.035	0.13	-0.13	0.73	-0.04
34) $C_2H_3 + C_4H_4 \rightarrow C_6H_6 + H$	-	-0.02	-0.12	0.10	-0.01
35) $n\text{-}C_4H_5 + C_4H_4 \rightarrow C_8H_8 + H$	-	-0.01	-0.30	-0.10	0.54
36) $C_8H_8 + H \leftrightarrow C_8H_7 + H_2$	-	-0.08	-0.02	-0.04	0.54
41) $C_2H_3 + C_4H_4 \leftrightarrow C_2H_4 + n\text{-}C_4H_3$	-	0.18	-	-	-
45) $C_2H_3 + C_6H_6 \leftrightarrow C_2H_4 + C_6H_5$	-	0.22	-	-	-

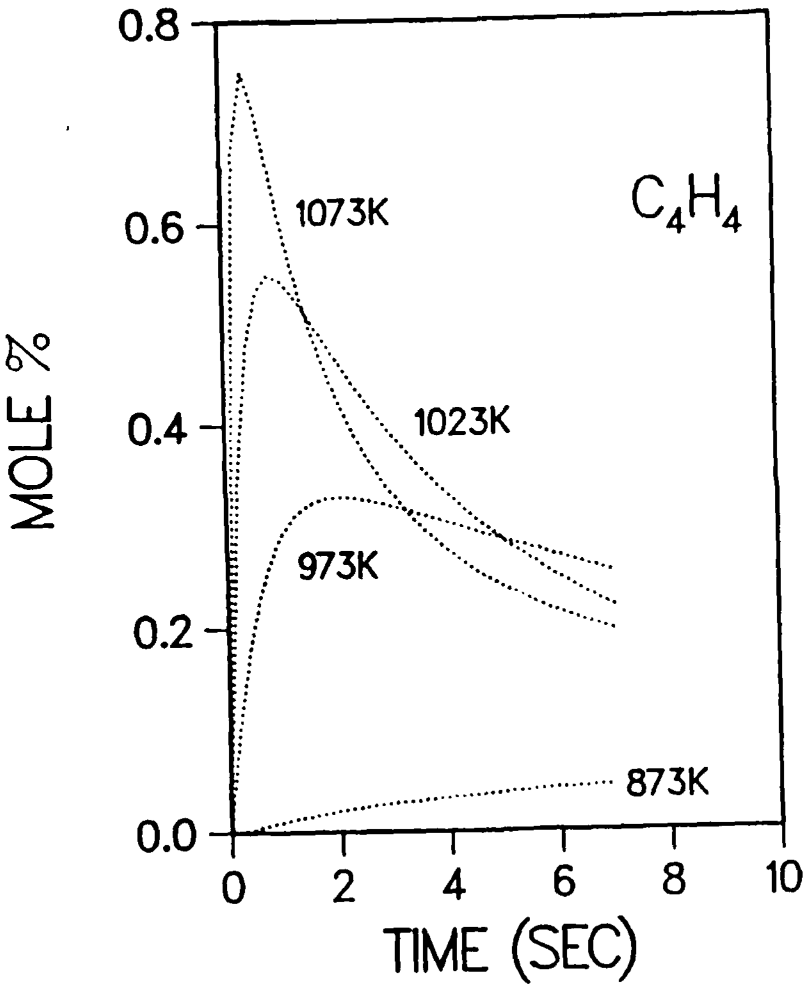
* As calculated by CHEMSEN at 10% decomposition of acetylene, 973K, 20% acetylene in one atmosphere of argon.

LIST OF FIGURES

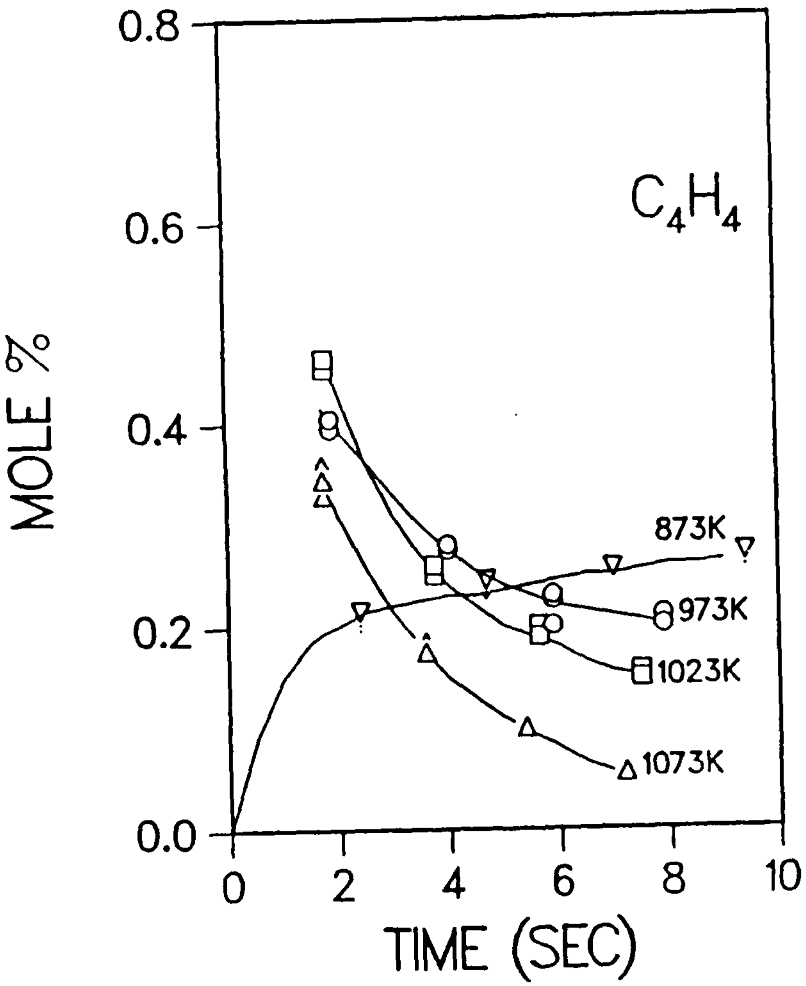
1. Comparison of Production of Vinylacetylene and Benzene in a Single-Pulse Shock Tube. 3.7% acetylene, 2040ppm biacetyl, 3.55% acetylene/1500ppm biacetyl. Squares - vinylacetylene, triangles - benzene. Total pressure ~ eight atmospheres, dwell times ~ 500-700 microseconds.
2. Comparison of Data and Model Predictions of Acetylene Decay. Symbols and aolid lines are data and best fits from Munson and Anderson. Dotted lines are model predictions from the present study.
3. Comparison of Data and Model Predictions of Vinylacetylene Formation and Decay. (see caption of Fig. 2.)
4. Comparison of Data and Model Predictions of Benzene Formation. (see caption of Fig. 2.)
5. Comparison of Data and Model Predictions of Ethylene Formation. (see caption of Fig. 2.)
6. Single-pulse shock tube data for 4.9% acetylene, 100ppm acetone in eight atmospheres of argon. Only odd-carbon species are shown including acetone, allene plus methyl acetylene, four C_5-species (one of two dominant peaks idendified as cylcopentadiene), and toluene. Top line is molar sum of the acetone concentration and one-half of all the odd-carbon species.
7. Comparison of Data and Model for Vinylacetylene, Diacetylene, and Hydrogen for Pyrolysis of Five Percent Acetylene. Single-pulse shock tube data is from Ogura. Solid Lines are model predictions.


3.55% C_2H_2
1500ppm $(CH_3CO)_2$
C_4H_4
C_6H_6
3.7% C_2H_2
2040ppm $(CH_3CO)_2$
LOG (CONCENTRATION–PPM)
0
1
2
3
4
1000
1200
1400
1600
1800
2000
TEMPERATURE (K)

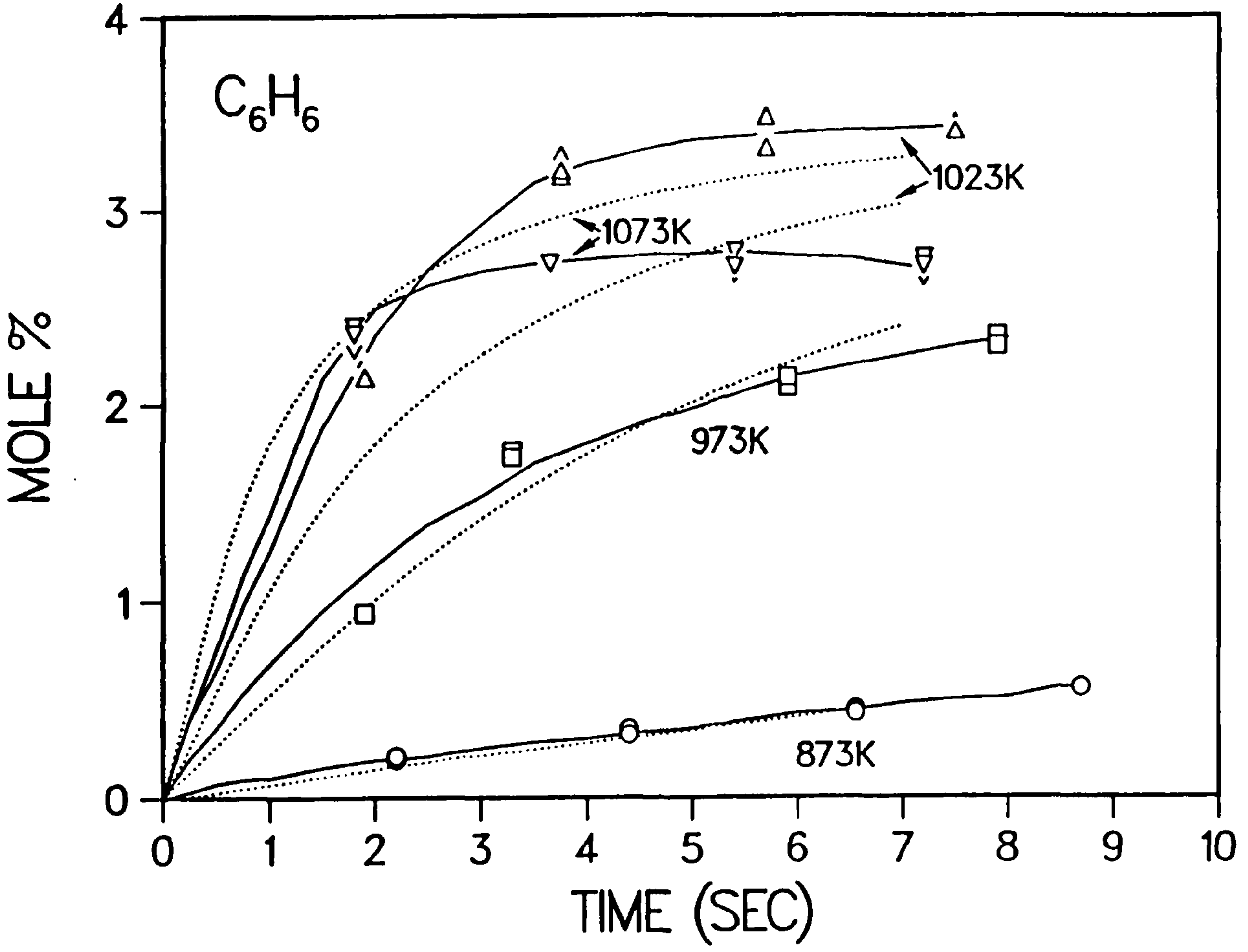

20
18
16
14
12
10
8
6
4
2
0
MOLE %
0
1
2
3
4
5
6
7
8
9
10
TIME (SEC)
873K
923K
973K
1023K
1073K
C_2H_2



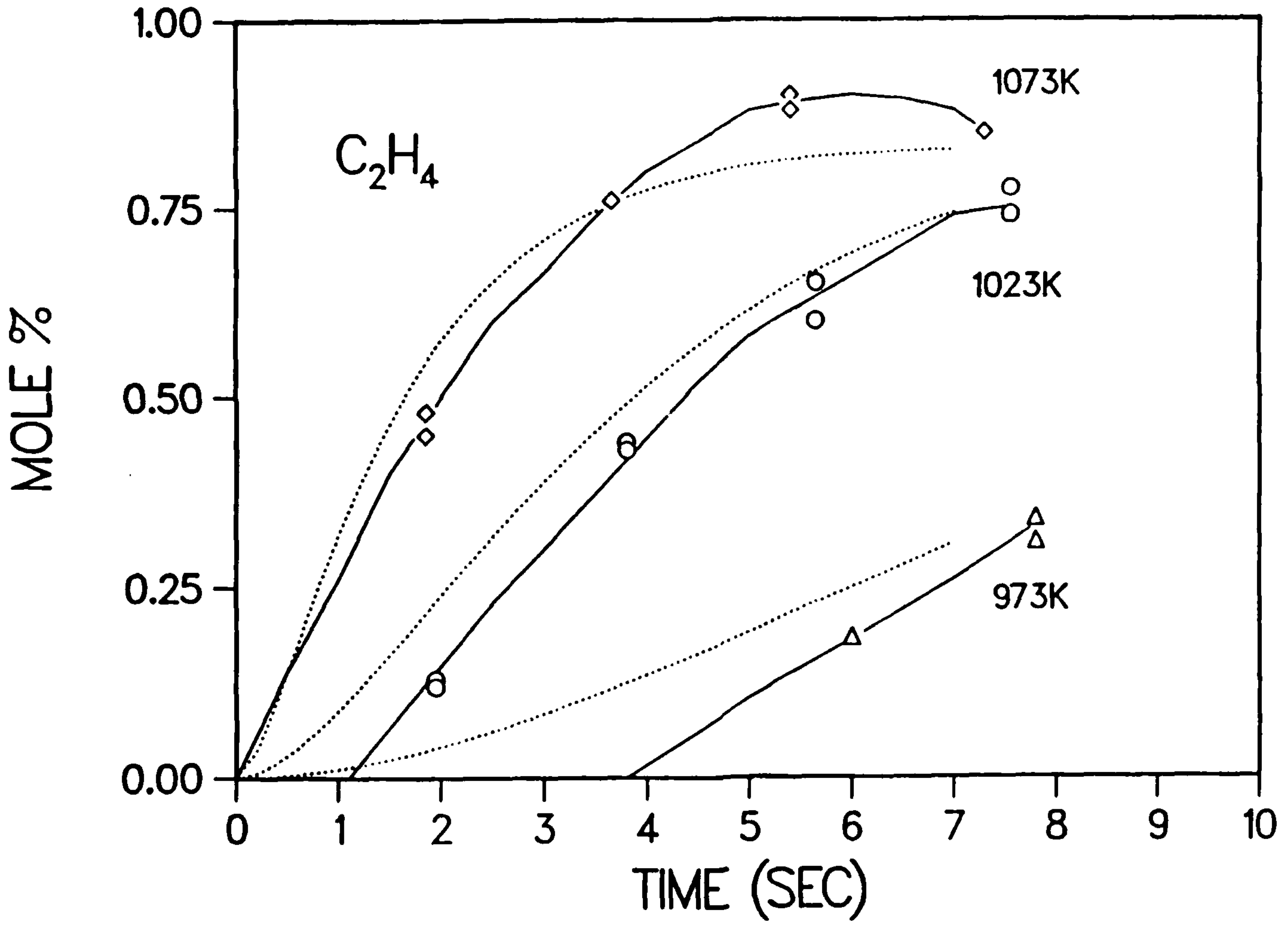
C_4H_4
MOLE %
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
TIME (SEC)
1073K
1023K
973K
873K

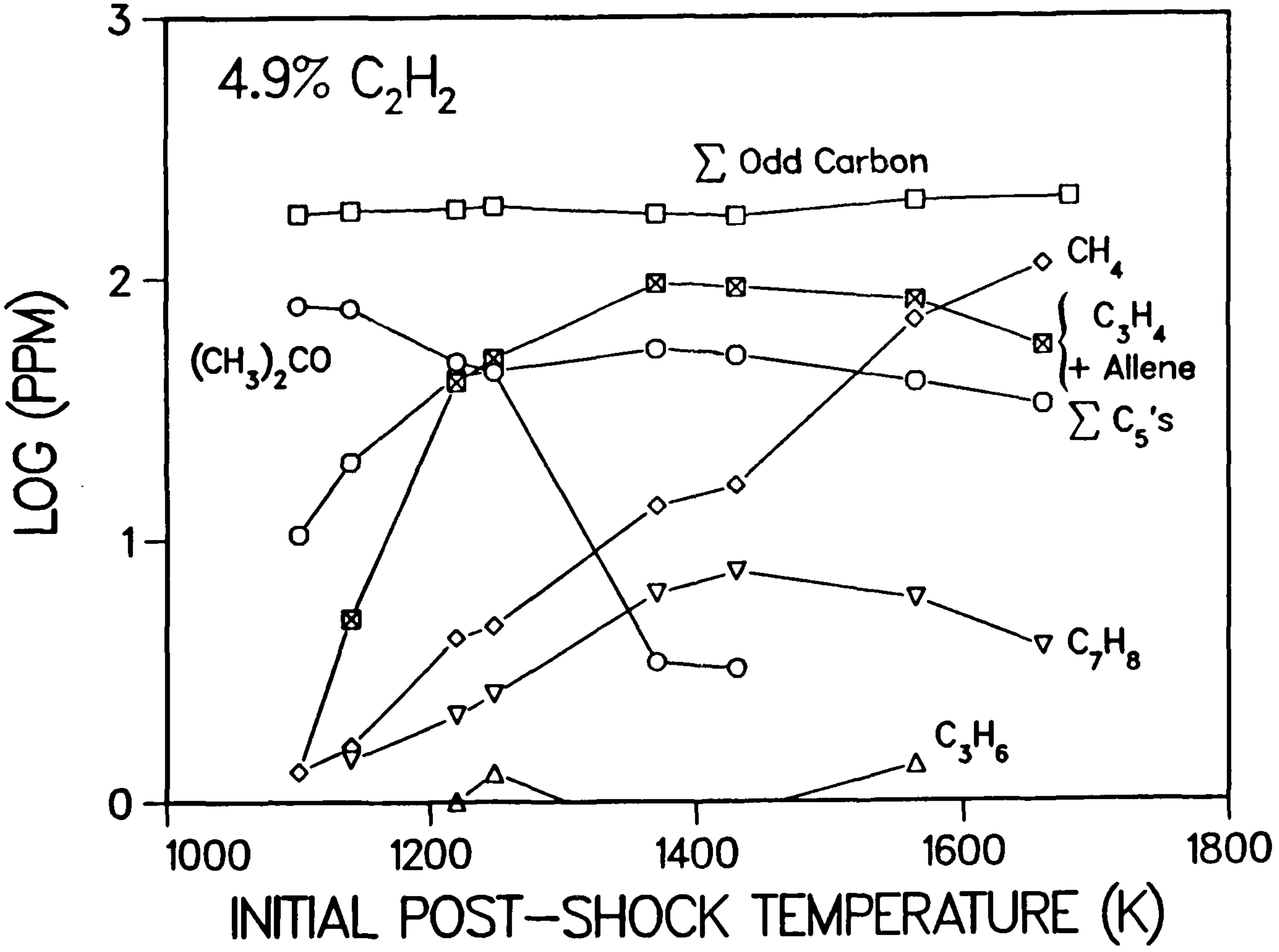


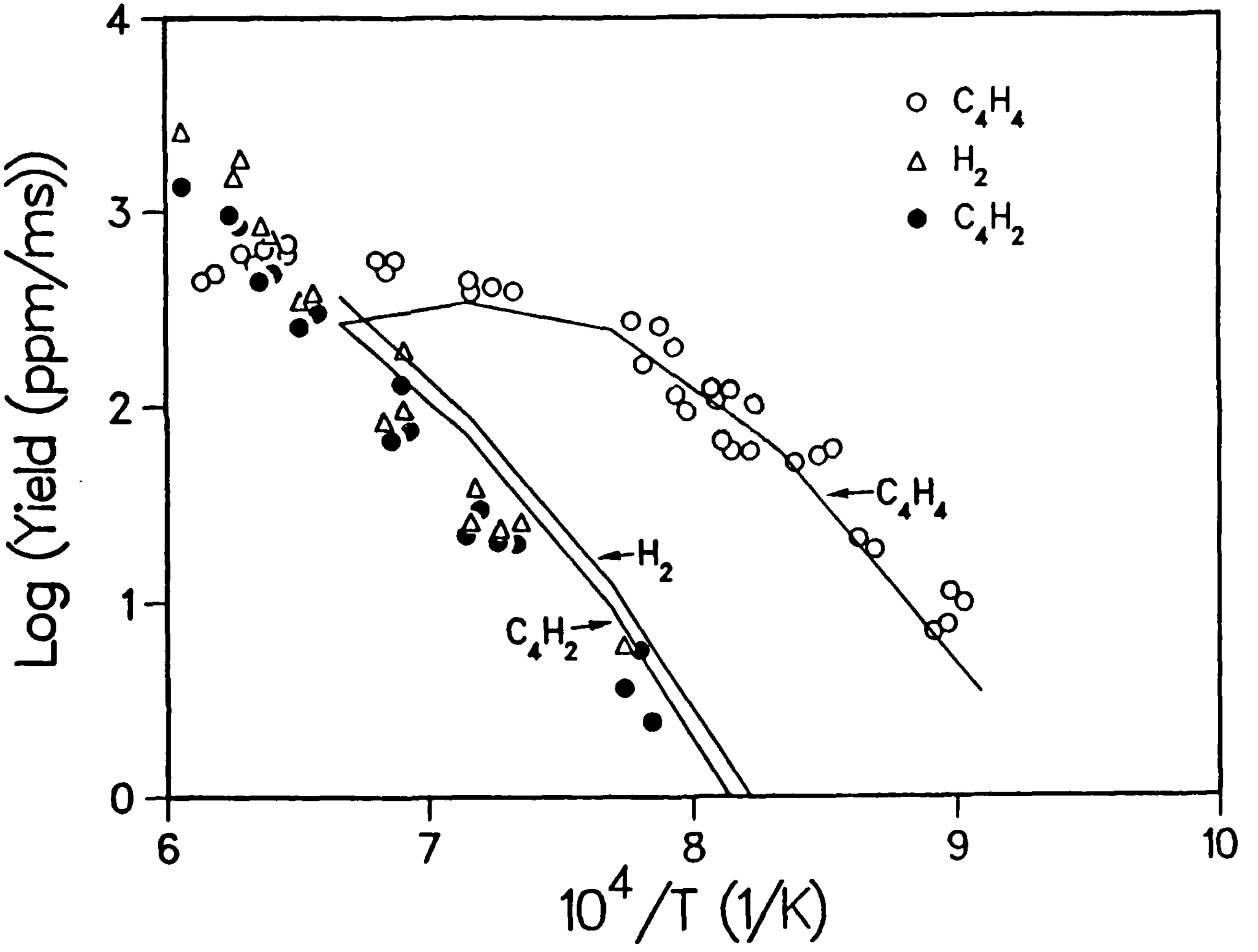
C_4H_4
MOLE %
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
TIME (SEC)
873K
973K
1023K
1073K



C_6H_6
1023K
1073K
973K
873K
MOLE %
TIME (SEC)
0
1
2
3
4
0
1
2
3
4
5
6
7
8
9
10


C$_2$H$_4$
1073K
1023K
973K
MOLE %
1.00
0.75
0.50
0.25
0.00
0
1
2
3
4
5
6
7
8
9
10
TIME (SEC)


4.9% C_2H_2
$\sum$ Odd Carbon
CH_4
C_3H_4 + Allene
$\sum C_5$'s
$(CH_3)_2CO$
C_7H_8
C_3H_6
LOG (PPM)
0
1
2
3
1000
1200
1400
1600
1800
INITIAL POST-SHOCK TEMPERATURE (K)


Log (Yield (ppm/ms))
4
3
2
1
0
6
7
8
9
10
$10^4/T$ (1/K)
○ C_4H_4
△ H_2
● C_4H_2
C_4H_4
H_2
C_4H_2

APPENDIX B

SOME THOUGHTS ON MODELING PRE-PARTICLE CHEMISTRY

by
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Within the last decade, pre-particle kinetics has been identified[1-3] as an important step in soot formation. This chemistry limits particle inception rates which in turn limits the total number of soot particles. Since the number of particles limit the total surface area available for surface growth and since particle sizes are typically limited to 300 to 500Å, the initial chemistry leading to soot inception limits both the rate of growth (i.e., mass addition) and the total amount of soot formed in a given environment. This very important conclusion has led to a substantial effort directed towards understanding pre-particle chemistry and, more generally, the pyrolysis of hydrocarbons. Chemistry involving neutral species has been a focus of this research since recent results[4-5] indicate that ions play at most a minor role. This approach[6] seems quite reasonable until such time as non-ionic reactions can be shown to be insufficient for prediction of particle inception rates.

Research in pre-particle kinetics has resulted in the identification of several possible mechanisms for the formation of a single aromatic ring. These reactions involve addition of radical intermediates to acetylenic (and sometimes olefinic) compounds. Many of these are summarized in Table I where only initial reactants and forward rate constants are reported. Typically, these reactions include the formation of a linear adduct followed by cyclization, and loss (or addition) of an H-atom. Energetics of some of these reactions have been described recently[7].

Table I presents a wide range of possibilities for ring formation. Generally, for a given fuel and temperature range, a particular sequence will dominate. For example, during pyrolysis of allene, the C_3 reactions are most important; in 1,3-butadiene flames, reactions involving the butadienyl radical dominate; and during acetylene pyrolysis, steps involving radical addition to acetylene are the fastest. Temperature is also important. At low temperatures (<1500K) during acetylene pyrolysis[8], rings are formed principally via $n-C_4H_5$ addition to acetylene yet at higher temperatures $n-C_4H_3$ addition to acetylene dominates. The temperature dependence of mechanistic pathways to rings is simply explained by the temperature dependence of radical concentrations. At low temperatures, $n-C_4H_5$ is formed rapidly via H-atom addition to acetylene to form vinyl which then adds to acetylene; whereas at high temperatures, the favored H-atom abstration from acetylene forms ethenyl (C_2H) which then adds to acetylene thereby forming $n-C_4H_3$. In a similar matter, fuel dependence of mechanisms is explained by the principal species present during pyrolysis or oxidation. The net conclusion is that there is no unique pathway to ring formation.

This conclusion is discouraging when considering that formation of the first ring is only the first step in a comprehensive model for soot formation. The potential complexity of such a model could be overwhelming. Consider, as an example, the first attempt at detailed modeling[9] which included 619 reversible reactions to describe soot formation during pyrolysis of acetylene. In subsequent publications[10-11], the reaction complexity has increased further in order to include additional fuels and oxidation steps. Hopefully, there is a way to simplify such models. In fact, there is some evidence supporting such an expectation in flames or during oxidation. During acetylene oxidation in a shock tube[10], the dominant sequence for ring formation was found to be

$$H + C_2H_2 \leftrightarrow C_2H_3$$
$$C_2H_3 + C_2H_2 \leftrightarrow n - C_4H_5$$
$$n - C_4H_5 + C_2H_2 \leftrightarrow \ell - C_6H_7$$
$$\ell - C_6H_7 \leftrightarrow c - C_6H_7$$
$$c - C_6H_7 \leftrightarrow C_6H_6 + H$$

Recent measurements[12] on a methane/air diffusion flame are consistent with this conclusion. Other encouraging results have been obtained on premixed flames. For example, by controlling temperature while using a wide range of fuels, sooting points were correlated independent of fuel structure[13]. Thus, it is probable that, in each of these flames with different fuels, soot is formed by the same mechanism. Similar conclusions were obtained[14] when soot formed in a lightly-sooting, ethylene premixed flame was found to be essentially identical to that formed in a flame in which a portion of the ethylene fuel was substituted with toluene. Toluene is normally considered to enhance significantly soot-forming characteristics. In diffusion flames and in heavily sooting premixed flames, soot formation is dependent on the structure of the fuel. However, such fuel-dependent soot formation may simply be an enhancement of the underlying fuel-independent soot formation mechanism. This acceleration may arise principally from an enhancement in the initial rate of ring formation while mechanisms related to the growth of PAH's, soot inception, or soot growth, etc., remain unchanged. There is some encouragement to assume this optimistic viewpoint. Recently, sooting tendencies for several fuels have been correlated[15] with benzene production as measured using a time-of-flight mass spectrometer coupled to a shock tube. Recent measurements in a single-pulse shock tube are consistent with this observation. Thus, the influence of fuel structure on soot formation may lie (in the first order) in the propensity of a given fuel to initiate the formation of aromatic rings. If this is true, then fuel-type effects can be simulated in a soot model by including reactions (specific to the particular fuel) for the formation of aromatics with one (or possibly two) ring(s). The remainder of the model would be an 'underlying' mechanism which is similar to that occurring in other flame or pyrolytic systems. This approach is similar to that utilized in the extension of the acetylene model[9] to other fuels and to oxidation[10-11].

Conversion of identifiable hydrocarbon species into nascent soot particles is a research topic of which very little is presently known. Due to our inability to measure dynamically and quantitatively species/particles in size ranges of 5-20Å, it seems unlikely that speculative models can be confirmed experimentally, at least for the near future. Consequently, we will have to rely on thought experiments and computer modeling to test out various theories of soot inception. Recent proposals include condensation of high boiling point compounds[16] and formation of concentric, imperfect spheres consisting of carbon atoms bonded in pentagonal and hexagonal configurations[17]. Some authors[10] have avoided the uncertainty of nucleation by simply allowing large poly-nuclear aromatics to continue growing by sequential addition of acetylene (and H-atom abstractions). In this model there is no upper limit to size. Other authors[2,18] have suggested that nucleation occurs by collision of two (or three) pre-particle species, thus forming a three-dimensional aggregate. Data on particle inception rates[18] have then been used to estimate that these pre-particle species are relatively small polycyclic aromatics comparable in size to pyrene. This proposal although yet to be proven is obviously attractive due to the potential of simplifying an otherwise extremely complex system.

Is it, or will it be possible to construct a comprehensive model for pre-particle kinetics and soot formation? Based on the above analysis, the author has increased hope that such a task can be accomplished. In summary, the reasons for this optimism include:

(1) the probable existence of an 'underlying' mechanism for pre-particle chemistry which for flames is independent of fuel;

(2) the hope that fuel-type dependence may be limited to enhancement/suppression of the formation of the first one or two rings;

(3) the fact that a mechanism has been proposed[10] which offers a starting or reference point for revised models of pre-particle chemistry; and

(4) the existence of several reasonable proposals for soot inception, i.e., conversion of gas-phase species into solid particles.

Much remains to be done including obtaining new data on thermochemistry, kinetics, and mechanisms. In addition, methods for conversion of a detailed chemical kinetics model and a model describing growth/ dynamics/ agglomeration/ and oxidation into a form usable to designers of engines must still be determined.

ACKNOWLEDGEMENTS

This work has been supported in part by the Air Force Office of Scientific Research under Contract No. F49620-85-C-0012. The author is indebted to Dr. Julian Tishkoff, AFOSR contract monitor, for his support and to those referenced below for their publications and for many valuable discussions with the author.

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TABLE I

Recent Proposals for the Formation of the First Aromatic Ring

Initial Reactants	Forward Rate Constant[1] A	E	Reference
$CH_3 + RH...$	-	-	Benson
$n - C_4H_3 + C_2H_2$	$5.0*10^{11}$	0.0	Colket(1987)
	$1.0*10^{13}$	0.0	Frenklach, et al.(1985)
	$7.5*10^{11}$	5.4	Westmoreland[2](1986)
$n - C_4H_5 + C_2H_2$	$6.5*10^{12}$	9.0	Colket(1987)
	$3.2*10^{11}$	3.7	Cole, et al.(1983)
	$6.7*10^{11}$	4.9	Westmoreland[2](1986)
	$1.0*10^{13}$	0.0	Frenklach, et al.(1985)
	$4.0*10^{12}$	6.9	Weissman and Benson(1984)
$n - C_4H_5 + C_4H_4$	$3.2*10^{11}$	0.6	Cole, et al.(1983)
	$7.9*10^{13}$	3.0	Colket(1987)
$n - C_4H_5 + C_3H_4$	$3.2*10^{11}$	3.7	Cole, et al.(1983)
$n - C_4H_5 + C_4H_2$	$3.2*10^{11}$	1.8	Cole, et al.(1983)
$C_2H_3 + C_4H_6$	$3.2*10^{11}$	3.0	Weissman and Benson(1984)
$C_2H_3 + C_4H_4$	$4.0*10^{11}$	0.0	Colket(1987)
$C_3H_3 + C_3H_4$	$2.2*10^{11}$	2.0	Wu and Kern(1987)
$C_3H_3 + C_3H_3$	$3.0*10^{11}$	0.0	Wu and Kern(1987)

1. k=Aexp(-E/RT) cm^3/moles/sec (E in kcal/mole)
2. Fit for one atmosphere, 500<T<1500K

APPENDIX C

Kinetic Mechanism for Pyrolysis of Acetylene Near 1000K

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INTRODUCTION

Recently a mechanism for acetylene pyrolysis was proposed to describe experimental data obtained from a single-pulse shock tube (1) over the temperature range of 1100 to 2000K. The kinetic mechanism is similar to those proposed previously (2,3) and includes mechanisms to describe formation of vinylacetylene, benzene, and phenylacetylene. Subsequently, a subset of this mechanism was modified and used (4) to match decay profiles of acetylene as well as product formation for pyrolysis data obtained in a flow reactor (5) at temperatures of 873 to 1173K.

It is the objective of this study: (a) to extend the mechanism (4) to include formation of higher molecular weight species, with a detailed discussion of growth from one to two rings; (b) to discuss the possible role of the 'odd' radical, i-C_4H_3; (c) to discuss some uncertainties with modeling PAH formation.

Description of Model

The kinetic model used in this study is listed in Table I and contains 89 reactions and 43 species. CHEMKIN and LSODE were used for integration of the rate equations. For modeling of the flow reactor data, constant temperature and pressure conditions were imposed whereas, for the shock tube data, a shock tube code modified (1) to simulate quenching in a single-pulse shock tube was utilized.

Thermodynamic parameters (except for those of vinyl radicals) are the same as those used and reported previously (1) for the lower molecular weight species. Parameters for species with molecular weights above 100 AMU were obtained from Stein (6) and are believed to be identical to those used in Frenklach, et. al. (3) Reference data for vinyl radicals and heavier species are reported in Table II. Stein's thermodynamic data for vinyl radicals were adopted since his heat of formation (68.4 kcal/mole) is higher than that used by Colket (1) (65.7 kcal/mole) and is closer to some recent determinations. In addition, Stein's reference value for entropy is higher (by 2 eu) than that used by Colket. Fortunately, the differences in values are nearly offset when determining equilibrium constants ($\ln K_{eq} = -(\Delta H - T\Delta S)/RT$) and changes in chemical kinetic modeling results are minimal.

The chemical kinetic model differs from that used previously (4) in that C_2H, C_4H_2, C_4H, i-C_4H_3, C_6H_2 and C_6H and associated reactions were included. In addition, species and reactions related to formation of polycyclic aromatics were also added. Of particular note is a modification in the dominant bimolecular initiation step. Previously the reaction

$$C_2H_2 + C_2H_2 \rightleftharpoons n\text{-}C_4H_3 + H$$

was used with a rate constant of log (k/sec^{-1}) = 14.54 - 68000/4.58T. In the present study the reaction

$$C_2H_2 + C_2H_2 \rightleftharpoons i\text{-}C_4H_3 + H$$

which has a lower endothermicity was employed with a rate of log (k/sec^{-1}) = 14.54-60500/4.58T. This larger rate constant for initiation is required to counterbalance termination steps omitted previously.

Formation of Fused Rings

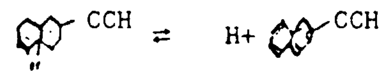
This work was guided substantially by the significant contributions of Bittner, Howard, and Palmer (7) and of Frenklach, et. al (3). An important conclusion of the former work is that ring growth is dominated by addition of aryl radicals to triple bonds, followed by addition of acetylene to the resultant vinyllic (aromatic) radical, cyclization, and loss of an H-atom.

i.e.,

$$\dot{\phi} + C_4H_2 \rightleftharpoons \phi CH\dot{C}CCH$$

$$\phi CH\dot{C}CCH + C_2H_2 \rightleftharpoons \phi CHC(CCH)CH\dot{C}H$$

$\phi CHC(CCH)CH\dot{C}H \rightleftharpoons$



Other than reverse processes, the main competitive process which can inhibit ring growth is the thermal decomposition of the vinyllic adducts (i.e., loss of H-atoms). Bittner, et. al, reached specific conclusions regarding the importance of the thermal decomposition of the vinyllic adduct relative to its addition to acetylene. However, these conclusions may have to be re-examined, since calculations were based on low pressure flame conditions rather than those of a high pressure combustor.

Frenklach, et. al, included at least six separate reaction sequences for growth from a single to a fused ring. One reaction sequence, however, was found to dominate although a second played a minor, but contributing role. The second (minor) reaction sequence is comparable to that proposed by Bittner, et. al (see above) although phenyl radicals add to acetylene, rather than diacetylene. The dominant reaction sequence was found to be initiated by H-atom abstraction from the ortho position on phenylacetylene, followed by acetylene addition and cyclization.

$$\dot{\phi}CCH + C_2H_2 \rightleftharpoons \phi(CCH)CH\dot{C}H$$

$\phi(CCH)CH\dot{C}H \rightleftharpoons$

The resultant aryl radical can subsequently add to triple bonds to continue growth to higher order polycyclic aromatics. Due to the lack of experimental rate data for reactions involving abstraction, addition, cyclization, or ring fracturing of polycyclic aromatics, Frenklach, et. al, selected generic rate constants for classes of reaction.

Rate constants for reactions involving aromatic species as listed in Table I were selected using the same technique of Frenklach, et. al, i.e., rate constants for a class of reactions are equated. Previously (3), values for several of these classes were assigned since experimental data was sparse. In this study, we have where possible updated the reaction rate data to be consistent with recently available determinations.

Predictions from the model (at 973K, 20% acetylene, and one atmosphere) are compared to the data from Munson and Anderson (5) in Fig. 1 for acetylene decay and production of benzene. In Fig. 2, predictions of production of styrene, naphthalene, and phenanthrene are shown. Although there is no experimental data from Munson and Anderson for these species, the final concentration of naphthalene is similar to other results (8) near 1000-1100K. The predicted value for styrene is about a factor of ten high.

Initially, only the dominant and minor mechanism (as identified by Frenklach, et. al) were included in the reaction sequence, specifically Mechanisms I and II:

$$\text{I} \qquad \phi C_2H + R \rightleftharpoons \dot{\phi}C_2H + RH \qquad \text{(A)}$$

$$\dot{\phi}C_2H + C_2H_2 \rightleftharpoons \phi(C_2H)CH\dot{C}H$$

$$\phi(C_2H)CH\dot{C}H \rightleftharpoons A2$$

and

$$\text{II} \qquad \phi C_2H + H \rightleftharpoons \phi CH\dot{C}H \qquad \text{(B)}$$

$$\dot{\phi} + C_2H_2 \rightleftharpoons \phi CH\dot{C}H \qquad \text{(C)}$$

$$\phi CH\dot{C}H + C_2H_2 \rightleftharpoons \phi CHCHCH\dot{C}H$$

$$\phi CHCHCH\dot{C}H \rightleftharpoons A2H + H$$

where A2 represents the 1-naphthyl radical and A2H, naphthalene.

The net contribution of the second sequence to the formation of A2H (or A2) dominates over that of the first by several orders of magnitude. For the specific conditions considered in this study, this fact can be easily explained.

At the low temperature (≃1000K) and the high initial concentrations of acetylene, forward reaction rates can be shown to dominate. Ignoring the contribution of Reaction C and taking the radical, R, in Reaction A to be an H-atom, then the relative rate is simply the rate of H-atom abstraction from the ring by H-atoms relative to the rate of H-atom addition to the acetylenic group in phenylacetylene. The value (9) of k ($C_6H_6 + H \rightarrow C_6H_5 + H_2$)

at 1000K is about 10^{10} cc/mole-sec. The rate constant for H-atom addition to acetylene, according to Ellul, et. al (10), extrapolates to 2 x 10^{12} cc/mole-sec at 1000K. Using these rate constants as estimates for k_A and k_B, respectively, Mechanism II is approximately 200 times faster than the first. The dominance of the Mechanism II becomes more apparent when the contribution of Reaction C is considered, since Reaction C is two to three orders of magnitude faster than Reaction B. Consequently, the second sequence is more than four orders of magnitude faster than the first. This is opposite to the trend observed by Frenklach, et. al. This strong discrepancy can be explained by a combination of (a) the higher temperatures of their study which enhance thermal decomposition of the radical adducts; (b) the lower partial pressures of acetylene in their study (40 torr vs. 150 torr in this study) which reduce the rate of radical addition to acetylene; and (c) the use by Frenklach of a high, temperature independent rate constant for Reaction A (with R as H-atom). Their rate constant was selected to be 10^{14} cc/mole-sec whereas, Kiefer, et. al's expression (9) gives 1.6 x 10^{12} cc/mole-sec at 1600 K.

Consequently, a reanalysis of dominant reactions occurring in a practical device should be performed for the specific ambient conditions. A preliminary analysis of the kinetic model indicates that the Mechanism II will dominate at temperatures of 1500-1700K for high pressure combustors, in which local acetylene concentrations may be at least an order of magnitude larger than considered in this and and previous studies.

Also found to contribute a minor but significant role at 973K are the overall reactions

$$\dot{\phi} + C_4H_4 \rightarrow A2H + H$$

and

$$\phi C_2H + i\text{-}C_4H_3 \rightarrow A2C_2H + H$$

both of which require H-atom shifts prior to cyclization. The second of these could be part of a very attractive sequence (as shown in Fig. 4) depending on the concentration of i-C_4H_3 radicals.

Role of i-C_4H_3

It is recognized that thermochemistry plays a significant role in the ability to model the above processes. Frenklach, et al. (11) have demonstrated quantitatively that uncertainties in thermochemistry drastically affect computed results. An interesting and possibly important thermochemical aspect of acetylene pyrolysis is due to the rather large difference between the heats of formation of the two isomers of C_4H_3, i.e., HCCCH$\dot{C}$H and HCC$\dot{C}$CH$_2$. The separation in this work was taken to be 10 kcal/mole, although Stein (6) and Bittner (12) give 8 and 15 kcal/mole, respectively. Due to its relative stability, the isomer with the unpaired electron on the secondary carbon atom (i-C_4H_3) becomes a dominant radical in the acetylene system. The situation is exacerbated if an isomerization step (i-$C_4H_3 \rightleftarrows$ n-C_4H_3) is not included. Depending on temperature, the concentration of i-C_4H_3 is two to three orders of magnitude higher than that of its isomer and an order higher than that of the vinyl radical. Consequently, it is logical that i-C_4H_3 plays a significant role in termination, and quite possibly in ring formation and growth.

The importance of this radical to chain termination or to ring formation and growth is dependent critically on (a) the thermodynamics of the C_4H_3 isomers; (b) the isomeration rate (equated in this work to a rate suggested (13) for the i-propyl $\rightleftarrows$ n-propyl isomeration); and (c) rate constants for reactions forming and destroying i-C_4H_3. Reactions which dominate formation of i-C_4H_3 include H-atom abstraction from vinylacetylene by phenyl, vinyl and H-atoms. The principal destruction mechanism in the present study is the isomerization to n-C_4H_3.

Uncertainties

Significant uncertainties in both rate constants and mechanisms still exist. The initiation step in acetylene pyrolysis has been a matter of unresolved dscussion for nearly thirty years. There is perhaps just as much uncertainty in the termination step(s). In this work, recombination of C_2H_3 + C_2H_3, H + C_2H_3, i-C_4H_3 + i-C_4H_3, and H + i-C_4H_3 all contributed to termination, yet there is essentially no data available on the absolute value of their rate constants (although some information on reverse reactions is available). The addition of H-atoms to acetylene is critically important to this mechanism, yet there is no data on this reaction near or above 1000K. Rate constants for reactions of similar types have been equated in this work; however, changes in rate constants depending on molecular size may be quite significant. Molecular and ionic processes have been ignored in the present study; however, there is as yet no proof against their occurrence. It is believed, however, that due to the reasonable agreement between the present model and experiments, contributions due to such reactions are perhaps small.

Conclusions

A chemical kinetic model, revised to include growth of aromatic rings predicts profiles of acetylene decay and formation of benzene, vinylacetylene, ethane, and hydrogen which are in agreement with experimental flow reactor results near 1000K. In addition the model predicts the formation of styrene, phenylacetylene, naphthalene and other fused rings. An analysis of the detailed model indicates that the dominant route for growth from a single to a fused ring is due to addition of phenyl radicals to two acetylenes. Addition of phenyl to vinylacetylene was proposed and may play a significant role depending on pressure and relative concentrations. Uncertainties associated with the role of the i-C_4H_3 radical were discussed and a mechanism involving sequential addition of i-C_4H_3 to phenylacetylene and the resultant products was proposed as a conceptually attractive mechanism for ring growth. Uncertainties related to the heat of formation and rate of isomerization to n-C_4H_3 prevent quantitative predictions as to the importance of such a mechanism.

Acknowledgements

This work has been supported by the Air Force Office of Scientific Research (AFSC) under Contract No. F49620-85-C-0012. The United States government is authorized to reproduce and distribute reprints for governmental purposes, notwithstanding any copyright notation herein.

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TABLE I
REACTIONS FOR ACETYLENE PYROLYSIS NEAR 1000K
$\log k = \log A + n\log T - E/R/T/2.303$ *

	Reactions	Forward Rate Constant			Reverse Rate Constant		
		logA	n	E	logA	n	E
1	2C2H2=i-C4H3+H	14.54	0.0	60.5	13.49	0.0	0.2
2	H+C2H2=C2H3	12.92	0.0	2.7	12.96	0.0	41.6
3	C2H3+C2H2=n-C4H5	12.88	0.0	8.0	14.86	0.0	44.1
4	n-C4H5=C4H4+H	13.00	0.0	33.0	12.39	0.0	-5.4
5	n-C4H5+C2H2=ℓ-C6H7	12.18	0.0	5.0	14.25	0.0	41.0
6	c-C6H7=ℓ-C6H7	14.48	0.0	50.0	11.36	0.0	0.4
7	C6H6+H=c-C6H7	13.60	0.0	4.3	13.12	0.0	24.6
8	C2H3+C4H4-C6H6+H	11.60	0.0	0.0	0.00	0.0	0.0
9	C4H4+n-C4H5-A1C2H3+H	13.50	0.0	5.0	0.00	0.0	0.0
10	A1C2H3+H=A1C2H2S+H2	14.00	0.0	14.5	13.09	0.0	19.7
11	C2H4+C6H5=A1C2H3+H	11.57	0.0	2.1	12.92	0.0	1.4
12	C6H6+H=C6H5+H2	14.40	0.0	16.0	12.39	0.0	9.5
13	C2H2+C6H5=A1C2H2	12.00	0.0	4.0	13.72	0.0	42.2
14	C2H3+C4H4=C2H4+n-C4H3	13.00	0.0	10.0	13.09	0.0	9.5
15	C4H4+C6H5=C6H6+n-C4H3	12.48	0.0	0.0	13.04	0.0	3.1
16	ℓ-C6H5=n-C4H3+C2H2	13.40	0.0	36.1	11.11	0.0	0.0
17	C6H5=ℓ-C6H5	13.54	0.0	65.0	10.25	0.0	1.7
18	C2H3+C6H6=C2H4+C6H5	13.48	0.0	13.0	13.00	0.0	9.3
19	2C2H3=C4H6	13.40	0.0	0.0	17.15	0.0	104.9
20	C4H4=n-C4H3+H	15.00	0.0	100.0	12.91	0.0	-7.9
21	C6H6=C6H5+H	15.70	0.0	107.9	13.05	0.0	-3.2
22	n-C4H5+H=C4H4+H2	13.00	0.0	0.0	12.99	0.0	66.0
23	n-C4H5+H=C4H6	13.00	0.0	0.0	14.84	0.0	107.9
24	n-C4H5+n-C4H3=2C4H4	12.70	0.0	0.0	14.18	0.0	69.5
25	n-C4H5+C2H3=C4H4+C2H4	12.00	0.0	0.0	13.57	0.0	69.0
26	C2H3+H=C2H4	12.85	0.0	0.0	15.00	0.0	107.2
27	C6H5+C2H3=A1C2H3	12.60	0.0	0.0	16.11	0.0	106.5
28	C2H3+H=H2+C2H2	13.00	0.0	0.0	13.57	0.0	65.5
29	C2H4+H=C2H3+H2	14.84	0.0	14.5	13.30	0.0	11.7
30	C4H4+H=n-C4H3+H2	13.90	0.0	14.5	12.42	0.0	11.0
31	C4H6+H=n-C4H5+H2	14.00	0.0	14.5	12.76	0.0	10.9
32	C4H6+C2H3=n-C4H5+C2H4	13.18	0.0	10.0	13.52	0.0	9.5
33	C6H5+C6H6=C12H10+H	11.80	0.0	11.0	13.38	0.0	9.2
34	C2H4+M=C2H3+H+M	16.16	0.0	81.8	14.01	0.0	-25.4
35	2i-C4H3=C4H4+C4H2	11.00	0.0	0.0	14.35	0.0	47.8
36	i-C4H3+H2=C2H2+C2H3	10.70	0.0	20.0	11.18	0.0	14.8
37	C4H4=i-C4H3+H	15.20	0.0	95.0	12.72	0.0	-2.1
38	C2H+C4H4=C2H2+i-C4H3	13.60	0.0	0.0	12.48	0.0	27.9
39	n-C4H3=C2H2+C2H	14.30	0.0	57.0	13.56	0.0	3.0
40	i-C4H3=C4H2+H	12.00	0.0	49.0	12.86	0.0	-0.2
41	n-C4H3=C4H2+H	12.60	0.0	40.0	13.04	0.0	1.4
42	n-C4H3=i-C4H3	13.00	0.0	35.0	12.58	0.0	45.7
43	i-C4H3+H=C4H2+H2	13.00	0.0	0.0	14.47	0.0	55.2
44	n-C4H3+H=C4H2+H2	12.48	0.0	0.0	13.53	0.0	65.9

* NOTES: Units for A: cc,moles,sec., Units for E: kcal/mole.
= represents forward and reverse directions included in model.
\- represents forward direction only included in model.

(CONTINUED NEXT PAGE)

TABLE I (continued)
REACTIONS FOR ACETYLENE PYROLYSIS NEAR 1000K

logk = logA + nlogT - E/R/T/2.303 *

	Reactions	Forward Rate Constant			Reverse Rate Constant		
		logA	n	E	logA	n	E
45	C4H4+H=i-C4H3+H2	14.49	0.0	14.5	12.62	0.0	21.9
46	C6H5+C4H4=C6H6+i-C4H3	12.18	0.0	0.0	12.31	0.0	13.8
47	C2H3+C4H4=C2H4+i-C4H3	12.70	0.0	10.0	12.36	0.0	20.2
48	C4H4=C2H+C2H3	15.70	0.0	115.0	12.93	0.0	-7.8
49	H2+M=2H+M	12.35	-.5	92.5	11.74	-.5	-11.9
50	C2H2+M=C2H+H+M	16.62	0.0	107.0	15.25	0.0	-17.9
51	C2H+H2=H+C2H2	12.85	0.0	0.0	13.60	0.0	20.5
52	C2H+C2H2=C4H2+H	13.60	0.0	0.0	14.78	0.0	15.4
53	C2H+C4H2=C6H2+H	13.60	0.0	0.0	14.97	0.0	15.1
54	C4H+C2H2=C6H2+H	13.30	0.0	0.0	14.91	0.0	8.1
55	C4H+H2=H+C4H2	13.30	0.0	0.0	14.30	0.0	13.5
56	C6H+H2=H+C6H2	13.30	0.0	0.0	14.53	0.0	10.3
57	C2H+C6H6=C6H5+C2H2	13.30	0.0	0.0	12.05	0.0	14.1
58	C4H+C6H6=C6H5+C4H2	13.30	0.0	0.0	12.29	0.0	7.0
59	C2H3+C4H2=C4H4+C2H	13.48	0.0	23.0	13.70	0.0	5.4
60	2C6H5=C12H10	12.48	0.0	0.0	16.57	0.0	108.3
61	C2H+C4H4=C2H2+n-C4H3	13.60	0.0	0.0	12.91	0.0	17.2
62	A1C2H3+H=A1C2H2+H2	14.50	0.0	14.5	13.29	0.0	11.7
63	A1C2H2S=A1C2H+H	13.00	0.0	45.0	13.11	0.0	0.8
64	A1C2H2=A1C2H+H	12.30	0.0	37.0	12.71	0.0	0.8
65	A1C2H2+C2H2=A1C4H4	12.88	0.0	8.0	14.81	0.0	44.5
66	A1C4H4=A2H+H	10.00	0.0	0.0	13.32	0.0	18.5
67	C6H5+C4H4=A2H+H	11.60	0.0	0.0	17.14	0.0	56.4
68	A1C2H+C2H3=A1C2HP+C2H4	13.70	0.0	13.0	14.02	0.0	10.5
69	A1C2H+H=A1C2HP+H2	14.40	0.0	16.0	13.18	0.0	10.7
70	A1C2H+C2H=A1C2HP+C2H2	13.30	0.0	0.0	12.85	0.0	15.2
71	A1C2H+i-C4H3-A2C2H+H	11.60	0.0	0.0	0.00	0.0	0.0
72	A1C2H+C2H3-A2H+H	11.60	0.0	0.0	0.00	0.0	0.0
73	A1C2HP+C4H4=A1C2H+i-C4H3	12.18	0.0	0.0	11.51	0.0	12.6
74	A1C2HP+C2H2=A1C2HV	12.30	0.0	4.0	13.70	0.0	41.8
75	A1C2HV=A2	11.00	0.0	0.0	14.14	0.0	53.4
76	A2C2H2=A2C2H+H	12.30	0.0	37.0	12.71	0.0	0.8
77	A2+C2H2-A2R5+H	12.30	0.0	4.0	0.00	0.0	0.0
78	A2C2H2+C2H2=A2C4H4	12.88	0.0	8.0	14.81	0.0	44.5
79	A2C4H4=A3H+H	10.00	0.0	0.0	13.32	0.0	20.7
80	A2H+H=A2+H2	14.40	0.0	16.0	12.88	0.0	10.7
81	A2H+H=A2P+H2	14.40	0.0	16.0	12.88	0.0	10.7
82	C2H3+A2H=C2H4+A2	13.70	0.0	13.0	13.72	0.0	10.5
83	C2H3+A2H=C2H4+A2P	13.70	0.0	13.0	13.72	0.0	10.5
84	A2P+C2H2=A2C2H2	12.30	0.0	4.0	13.70	0.0	41.8
85	A2C2H+H=A2C2HX+H2	14.40	0.0	16.0	13.49	0.0	10.7
86	A2C2H+C2H3=A2C2HX+C2H4	13.70	0.0	13.0	14.33	0.0	10.5
87	A2C2HX+C2H2-A3	12.30	0.0	4.0	0.00	0.0	0.0
88	A3+C2H2-A4H+H	12.30	0.0	4.0	0.00	0.0	0.0
89	A3H+H=A3+H2	14.40	0.0	16.0	13.18	0.0	10.7

* NOTES: Units for A: cc,moles,sec., Units for E: kcal/mole.

= represents forward and reverse directions included in model.

\- represents forward direction only included in model.

TABLE II
Selected Thermodynamics at 300K
(from Stein(6))

Species	Identification	Heat of Formation (kcal/mole)	Entropy (eu)
C2H3	vinyl	68.4	56.5
A1C2H3	styrene	35.3	82.6
A1C2H2	A1CH$\dot{C}$H	91.2	85.2
A1C2H2S	A1$\dot{C}$CH2	83.2	83.8
A1C2H	phenylacetylene	75.2	76.4
A1C2HP	$\dot{A}$1C2H	133.6	79.0
A1C2HV	A1(C2H)CH$\dot{C}$H	146.6	95.1
A1C4H4	A1CHCHCH$\dot{C}$H	104.7	98.0
A2	1-naphthyl	94.4	83.6
A2P	2-naphthyl	94.4	83.6
A2H	naphthalene	36.1	79.7
A2C2H	2-naphthylacetylene	91.5	90.9
A2C2H2	A2CH$\dot{C}$H	107.4	99.7
A2C2HX	$\dot{A}$2C2H	149.9	92.1
A2C4H4	A2CHCHCH$\dot{C}$H	121.0	112.5
A2R5	acenaphthylene	61.7	87.2
A3	phenanthrenyl	108.5	96.8
A3H	phenanthrene	50.1	94.2
A4H	pyrene	55.2	96.5

FIG. 1 MODEL PREDICTIONS vs. DATA OF REF. 5
C2H2 and C6H6 Concentrations at 973K

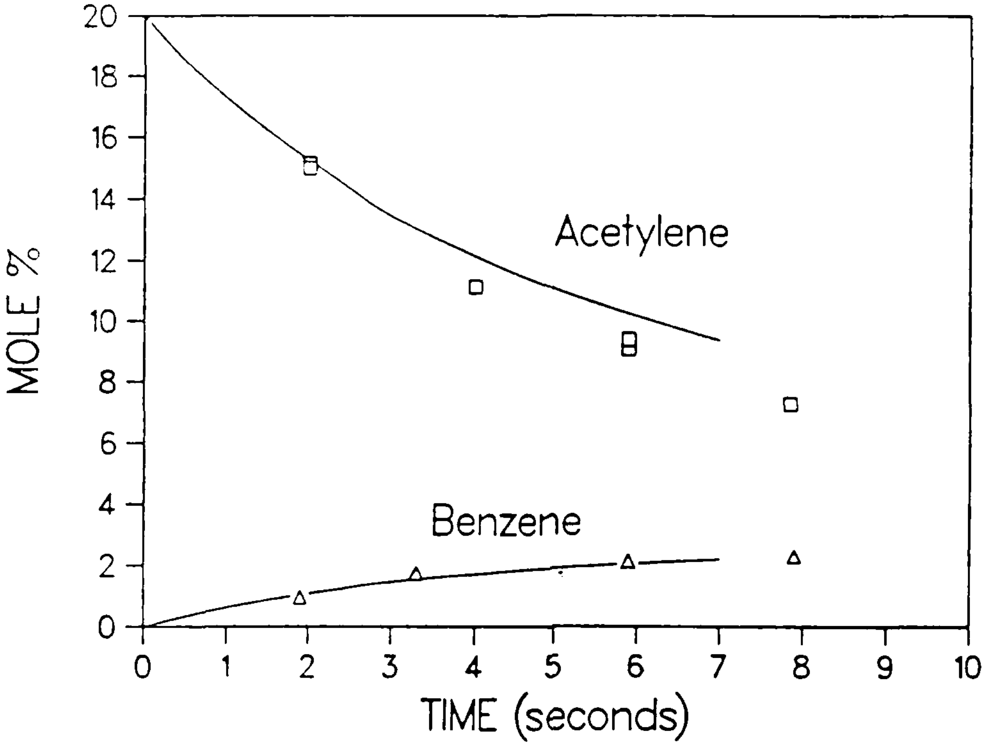
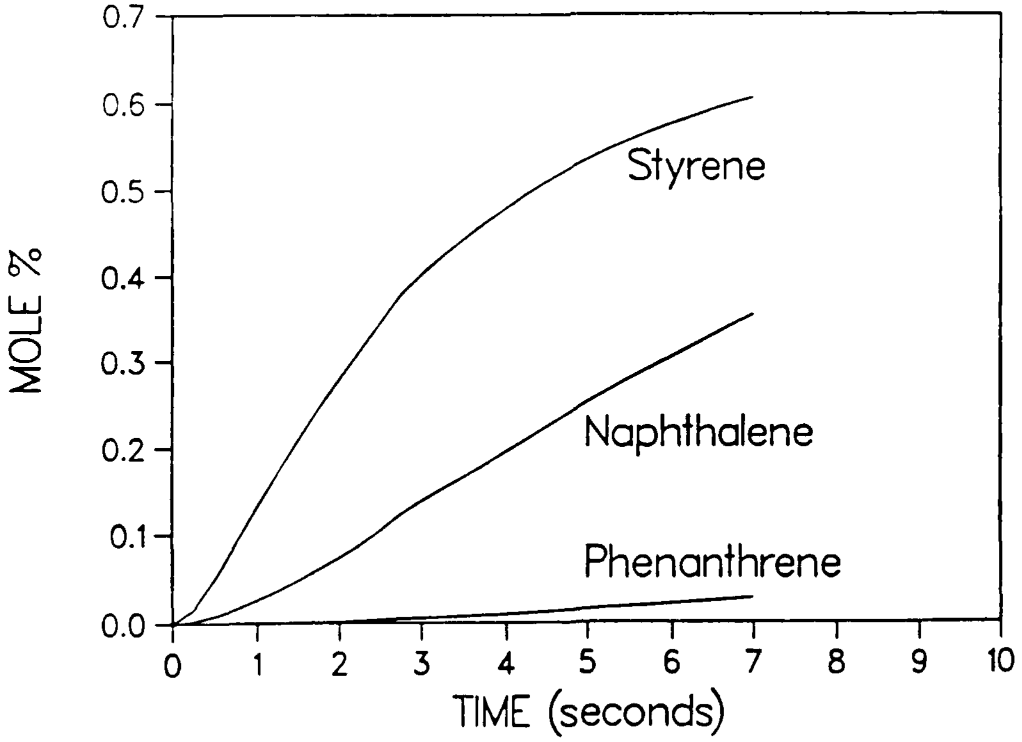


FIG. 2 PYROLYSIS OF 20% ACETYLENE AT 973K
Formation of Aromatic Products (predictions)



RING GROWTH BY SEQUENTIAL ADDITION OF i-C_4H_3

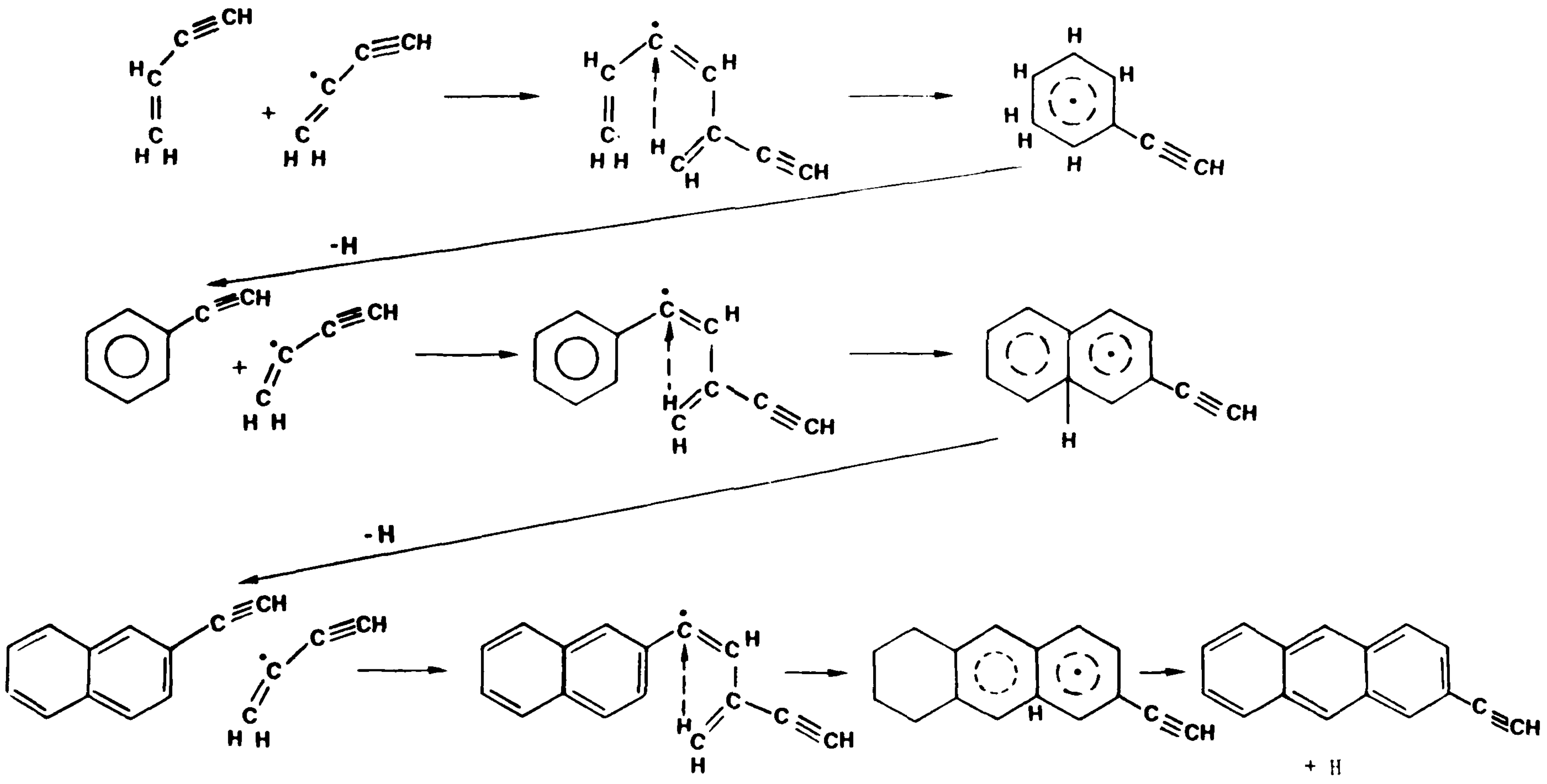


FIG 3

87-4-89-1

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MASTER Proof Set

THE PYROLYSIS OF ACETYLENE AND VINYLACETYLENE IN A SINGLE-PULSE SHOCK TUBE

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Acetylene and vinylacetylene have been pyrolyzed in a single-pulse shock tube for the temperature range 1100 to 2400°K, at total pressures of approximately eight atmospheres and for dwell times of approximately 700 microseconds. Initial concentrations of the hydrocarbon in argon ranged from about 100 ppm to 4%. Gas samples were collected and analyzed using gas chromatography for hydrogen, and C_1 to C_{10}-hydrocarbons. The data from the pyrolysis of acetylene exhibit substantial production of vinylacetylene, benzene, and phenylacetylene, but agree well with a detailed chemical kinetic model. Data from vinylacetylene pyrolysis and thermochemical arguments suggest a chain mechanism by which H adds to vinylacetylene and the resultant adduct decomposes to acetylene and a vinyl radical. Rate constants for the reverse steps of those occurring during vinylacetylene and benzene pyrolysis have been calculated using thermodynamics and forward rate constants. These reverse rate constants assist in describing the production of vinylacetylene, benzene, and phenylacetylene during acetylene pyrolysis.

Four separate reaction mechanisms for the initial formation of aromatic rings have been identified. The relative importance of each step depends on the ambient temperature and relative concentrations. *Overall* steps can be written as

$$C_2H_2 + n\text{-}C_4H_5 \rightarrow C_6H_6 + H$$
$$C_2H_2 + n\text{-}C_4H_3 \rightarrow C_6H_5$$
$$C_4H_4 + n\text{-}C_4H\cdot \rightarrow C_6H_5C_2H_3 + H$$
$$C_4H_4 + C_2H_3 \rightarrow C_6H_6 + H$$

Introduction

Glassman[1] has convincingly argued that the chemistry of fuel pyrolysis plays an important role in sooting diffusion flames. Some pyrolysis steps may be rate-limiting for the production of incipient soot particles, and therefore the total amount of soot.[2] Armed with this information, many research programs have begun to identify the rate-limiting processes. For example, Bittner and Howard,[3] and Bockhorn, et al.[4] have provided experimental confirmation of a variety of high molecular weight polycyclic aromatics present in rich flames. Cole, et al.[5] and Weissman and Benson[6] have suggested mechanisms with rates consistent with thermochemical analysis and experimental data for the production of single-ring aromatics. Frenklach, et al.[7] has modeled soot formation from acetylene pyrolysis in shock tubes using a detailed chemical mechanism. The mechanism includes production of aromatic rings and continual growth of polycylic aromatics. Qualitative success has been obtained in this substantial effort despite the lack of confirming experimental data describing profiles of intermediates for confirmation/support of the proposed model.

It is the objective of the present work to extend these earlier works in order to help elucidate pyrolysis steps and chemical mechanisms related to the formation and break-up of aromatic rings. A single-pulse shock tube[8,9] was selected for this study, not only because shock tubes are one of the few devices capable of generating conditions of importance to soot formation in diffusion flames, but also to extend the information on soot production already generated through optical studies in shock tubes.[10–13]

Preliminary versions of the modeling work have been described separately for acetylene[14] and vinylacetylene.[15] The present work combines the earlier models, including a recent one for benzene pyrolysis,[16] into one model which satisfactorily describes both decomposition (of the parent hydrocarbons) and product forma-

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101-2

tion. Required revisions include slight adjustments to rate constants and to assumed thermodynamic parameters.

Description of Facilities

The SPST used in this program is 285 cm long and has a diameter of 3.8 cm (i.d.). The driver is 88 cm in length and can be turned by shortening its length in 3.8 cm increments; the driven section is 197 cm long. An 11.7 liter "dump tank" is located in the driver (lower pressure) section 30 cm downstream of the diaphragm. Pressure profiles were determined using Kistler pressure transducers located 15.25 and 2.50 cm from the end wall. Arrival times were measured to within one microsecond using digitized pressure traces. Calculated quench rates are typically 10^5 K/sec or higher in the rarefaction wave. Starting pressures prior to filling are 0.2μ and leak rates are less than 1μ/min. Post-shock temperatures were calculated based on the measured incident shock velocity and normal shock wave equations.

The procedures for performing an experiment are similar to those described by Tsang,[17] except for an automated sampling system. The sample is collected at the endwall of the shock tube using 0.045 inch i.d. tubing heated to over 85°C. Approximately 30 milliseconds after the gas has been shock heated and cooled, a solenoid valve opens to the evacuated sample cell and then closes after 300 milliseconds. The sample storage vessel is all stainless steel with an internal volume of 25 cc.

The sampling volume is directly coupled to a low volume (<3cc), heated inlet system of a Hewlett Packard 5880 A gas chromatograph. Valves, detectors and software integration routines as described previously[14] enable this system to provide automatic quantitative detection of hydrogen and hydrocarbon species up to C_{10}-hydrocarbons. Based on repeated injections of calibrated samples, overall accuracies are estimated to be three percent. Calibration gases were stored in stainless steel cylinders with degreased valves and were heated to approximately 60°C prior to injection.

Argon (99.999% pure) was obtained from Matheson and was the principal diluent. Compressed acetylene, also from Matheson, contained about 1 to 2% acetone (added for stability) depending on bottle conditions. Acetylene was purified by repeated freezing and thawing at liquid N_2 temperatures and retaining only the middle 50%. Final samples still contained 0.1 to 0.2% acetone. Vinylacetylene was obtained from Wiley Organics and contained an unidentified hydrocarbon with a concentration of approximately 8000 ppm.

Model Description

Detailed chemical kinetic calculations have been performed using CHEMKIN,[18] LSODE,[19] and a version of a shock tube code originally developed by Mitchell and Kee[20] but modified to include quenching effects in an SPST. Quenching rates are determined using experimental pressure traces, assuming adiabatic expansion, and using the equation

$$\frac{dT}{dt} = \frac{T}{P}\frac{\gamma-1}{\gamma}\frac{dP}{dt}.$$

Calculated quenching rates vary as a function of shock strength and time. Initial quenching rates are as high as 2×10^6K/sec for shocks producing initial post-shock temperatures of 2000°K, but only 25% of that rate for shocks producing reflected shock temperatures near 1200°K.

The chemical kinetic model used in this work is reproduced in Table I and is based on proposed mechanisms for the pyrolysis of acetylene[21] and ethene.[22] The reaction set includes the identification of the C_4H_3 isomers following Frenklach, et al.[7] The radicals are denoted n-C_4H_3 for the (normal) isomer with the unpaired electron on the terminal vinylic carbon and i-C_4H_3 for the (iso)isomer with the radical site on the interior carbon atom. n-C_4H_5 (radical on end carbon) was the only C_4H_5 isomer considered in this work. Also, the mechanism includes the forward and reverse processes of the predominant path for decomposition of benzene, i.e.,

$C_6H_6 + H \rightleftarrows C_6H_5 + H_2$ (39)
$C_6H_5 \rightleftarrows \ell\text{-}C_6H_5$ (56)
$\ell\text{-}C_6H_5 \rightleftarrows n\text{-}C_4H_3 + C_2H_2$ (55)

where ℓ-C_6H_5 has been suggested[16] to be the 1-hexyne-3,5-dien-6-yl radical. The rate constants (R55,R56) have been revised slightly from the previous work[16] in order to be consistent with the reverse processes.

As required, thermodynamic estimates of some species were made using group additivity techniques.[23] Otherwise, data from readily available sources were used.[24,25] Both estimates of rate parameters and those calculated using equilibrium constants are dependent on the selected thermodynamics. Of particular concern during the present research is the apparent uncertainty in the heat of formation of

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TABLE I
Proposed Set of Reactions and Rate Coefficients

$\log k = \log A + n\log T - E/RT/2.303$ *

	Reactions	Forward Rate Constant			Reverse Rate Constant			
		logA	n	E	logA	n	E	Ref
1	C2H4 + M=C2H3 + H + M	16.16	0.0	81.8	14.24	0.0	−23.0	22
2	C2H4 + H =C2H3 + H2	14.84	0.0	14.5	13.53	0.0	14.0	21
3	H + C2H2=C2H3	12.74	0.0	2.5	13.01	0.0	43.8	21
4	C2H3 + H=H2 + C2H2	13.00	0.0	0.0	13.34	0.0	63.2	21
5	H2 + M=2H + M	12.35	−.5	92.5	11.74	−.5	−11.9	21
6	C2H2 + M=C2H + H + M	16.62	0.0	107.0	15.25	0.0	−17.9	21
7	2C2H2=n−C4H3 + H	12.30	0.0	45.9	11.67	0.0	−25.0	21
8	i−C4H3 + H2=C2H2 + C2H3	10.70	0.0	20.0	11.41	0.0	17.1	PW*
9	C4H4=i−C4H3 + H	15.20	0.0	85.0	12.72	0.0	−12.1	PW
10	C4H4=n−C4H3 + H	15.00	0.0	100.0	12.93	0.0	−7.7	PW
11	C2H + C4H4=C2H2 + i−C4H3	13.60	0.0	0.0	12.48	0.0	27.9	21
12	n−C4H3=C2H2 + C2H	14.30	0.0	57.0	13.56	0.0	3.0	PW
13	i−C4H3=C4H2 + H	12.00	0.0	49.0	12.86	0.0	−0.2	PW
14	n−C4H3=C4H2 + H	12.60	0.0	40.0	13.04	0.0	1.4	PW
15	n−C4H3 + H=i−C4H3 + H	13.48	0.0	0.0	13.06	0.0	10.7	PW
16	i−C4H3 + H=C4H2 + H2	13.00	0.0	0.0	14.47	0.0	55.2	PW
17	n−C4H3 + H=C4H2 + H2	13.00	0.0	0.0	14.05	0.0	65.9	PW
18	C4H4 + H=i−C4H3 + H2	14.49	0.0	14.5	12.62	0.0	21.9	26,PW
19	C4H4 + H=n−C4H3 + H2	13.90	0.0	14.5	12.45	0.0	11.2	26,PW
20	C2H3 + C2H2=n−C4H5	12.04	0.0	4.0	13.79	0.0	37.7	PW
21	C2H + H2=H + C2H2	12.85	0.0	0.0	13.60	0.0	20.5	22
22	C2H + C2H2=C4H2 + H	13.60	0.0	0.0	14.78	0.0	15.4	21
23	C4H2=C4H + H	14.89	0.0	120.0	13.28	0.0	2.1	22
24	C2H + C4H2=C6H2 + H	13.60	0.0	0.0	14.97	0.0	15.1	21
25	C4H + C2H2=C6H2 + H	13.30	0.0	0.0	14.91	0.0	8.1	21,PW
26	C6H2=C6H + H	14.89	0.0	120.0	13.05	0.0	5.3	22
27	C4H + H2=H + C4H2	13.30	0.0	0.0	14.30	0.0	13.5	22
28	C6H + H2=H + C6H2	13.30	0.0	0.0	14.53	0.0	10.3	22
29	C2H + H=C2 + H2	12.00	0.0	23.0	11.55	0.0	3.8	PW
30	C2H + M=C2 + H + M	16.67	0.0	124.0	15.61	0.0	0.4	36
31	C4H4 + C6H5=C6H6 + n−C4H3	12.00	0.0	0.0	12.56	0.0	3.1	PW
32	C4H4 + C6H5=C6H6 + i−C4H3	12.00	0.0	0.0	12.14	0.0	13.8	PW
33	C2H + C6H6=C6H5 + C2H2	13.30	0.0	0.0	12.05	0.0	14.1	34
34	C4H + C6H6=C6H5 + C4H2	13.30	0.0	0.0	12.29	0.0	7.0	34
35	C2H3 + C4H2=C4H4 + C2H	13.48	0.0	23.0	13.46	0.0	3.1	PW*
36	C2H3 + C4H4=C2H4 + n−C4H3	11.70	0.0	16.3	11.55	0.0	13.4	35,PW
37	C2H3 + C4H4=C2H4 + i−C4H3	11.70	0.0	16.3	11.13	0.0	24.1	35,PW
38	C6H6=C6H5 + H	16.18	0.0	107.9	13.55	0.0	−3.0	16
39	C6H6 + H=C6H5 + H2	14.40	0.0	16.0	12.39	0.0	9.5	34
40	2C6H5=C12H10	12.48	0.0	0.0	16.57	0.0	108.3	17
41	C6H5 + C6H6=C12H10 + H	11.80	0.0	11.0	13.27	0.0	8.4	37
42	n−C4H3 + C6H5−C10H8	13.00	0.0	0.0	0.00	0.0	0.0	PW
43	C2H2 + C6H5=C8H6 + H	12.00	0.0	4.0	13.50	0.0	3.1	38,PW
44	C2H4 + C6H5=C8H8 + H	11.57	0.0	2.1	12.99	0.0	1.6	38
45	C2H3 + C4H4−C6H6 + H	11.60	0.0	0.0	0.00	0.0	0.0	PW
46	n−C4H5=C4H4 + H	14.00	0.0	41.4	13.42	0.0	3.2	6
47	n−C4H5 + C2H2=*l*−C6H7	12.81	0.0	9.0	14.80	0.0	44.4	6,PW
48	n−C4H5 + H=C4H4 + H2	13.00	0.0	0.0	13.03	0.0	66.2	PW
49	C4H6 + H=n−C4H5 + H2	14.00	0.0	14.5	12.80	0.0	11.2	26,PW
50	C6H6 + C2H=C8H6 + H	12.00	0.0	0.0	12.25	0.0	13.2	PW
51	C4H4=C2H + C2H3	16.00	0.0	105.0	13.46	0.0	−15.5	PW

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TABLE I (Continued)

Reactions	Forward Rate Constant logA	 n	 E	Reverse Rate Constant logA	 n	 E	Ref
52 C4H4 + n-C4H5-C8H8 + H	13.90	0.0	3.0	0.00	0.0	0.0	PW
53 C8H8 + H-C8H6 + H + H2	14.60	0.0	7.0	0.00	0.0	0.0	PW
54 C6H5 + C2H3=C8H8	13.00	0.0	0.0	16.34	0.0	104.4	PW
55 *l*-C6H5=n-C4H3 + C2H2	14.00	0.0	36.0	11.71	0.0	-0.1	PW
56 C6H5=*l*-C6H5	13.54	0.0	65.0	10.22	0.0	1.4	PW
57 C6H6 + H=c-C6H7	13.60	0.0	4.3	13.12	0.0	24.6	PW
58 c-C6H7=*l*-C6H7	14.48	0.0	50.0	11.36	0.0	0.4	PW

*NOTES: Units for A: cc,moles,sec.
Units for E: kcal/mole.
"=" *represents forward and reverse directions included in model.*
"-" represents forward direction only included in model.
PW indicates rate evaluted from the present work.

vinyl[26,27] and related (e.g. n-C_4H_3 and n-C_4H_5) radicals. Uncertainties in the heats of formation and entropies of these radicals directly translate into errors in proposed rate constants. Thermodynamic parameters at room temperature for species included in this work are presented in Table II.

Results and Discussion

Several series of runs of the pyrolysis of acetylene and vinylacetylene have been completed. Each series represents approximately 10 to 15 separate experiments and each experiment in a series has the same initial concentration in argon. For each run, a chemical analysis is performed of final product distribution. Initial post-shock temperatures for runs from a given series typically range from 1100 to 2400°K. Detailed chemical kinetic model calculations have been performed for most series and the numerical results for selected series are compared to the experimental data in Figs. 1,3–5. Mass balance data were presented previously.[14] A detailed discussion of the experimental data and kinetic mechanism follows.

Acetylene

The decomposition of 3.7% acetylene in argon and production of the major species, i.e. C_4H_2, H_2, and C_6H_2, agree well with existing kinetic models. As seen in Fig. 1, vinylacetylene (VA), benzene and phenylacetylene are also observed and may play a critical role in the growth and production of polycyclic aromatics. The bimolecular reaction $2C_2H_2 \rightarrow C_4H_4$ is thought to occur at low temperatures. Extrapolation of low temperature rate constants provided quantitative agreement with the experimental profile. In addition, the activation energy for this process (~40 kcal/mole) is in reasonable agreement with the assumption of intermediate formation of the C_4H_4 diradical, which is approximately 35 to

TABLE II
Selected Thermodynamics at 300K

Species	*Heat of Formation* (kcal/mole)	*Entropy*
$C_{12}H_{10}$	43.6	93.7
$C_{10}H_8$	36.0	79.5
C_8H_6	78.3	79.6
$l-C_6H_7$	97.4	81.8
$c-C_6H_7$	49.9	72.1
C_6H_6	19.9	65.2
C_6H_5	78.5	69.4
$l-C_6H_5$	139.2	80.0
C_6H_2	169.7	71.1
C_6H	233.2	74.3
C_4H_6	26.1	66.6
$n-C_4H_5$	82.5	69.1
C_4H_4	69.4	66.1
$n-C_4H_3$	125.1	68.7
$i-C_4H_3$	115.2	71.6
C_4H_2	111.7	59.9
C_4H	179.0	62.8
C_2H_4	12.6	52.4
C_2H_3	65.7	54.5
C_2H_2	54.2	48.1
C_2H	128.5	49.6
C_2	200.2	47.7

43 kcal more energetic than two molecules of acetylene.[28] Unfortunately, this mechanism does not provide a plausible, parallel path for the formation of benzene; yet the similarity in profiles of benzene and VA strongly suggest a parallel mechanism. Stein[29] suggested an alternative chain process initiated by H-atom addition to acetylene to form VA, i.e.,

$$C_2H_2(+ H) \rightarrow C_2H_3(+ C_2H_2) \rightarrow$$
$$n\text{-}C_4H_5(-H) \rightarrow C_4H_4$$

This sequence is identical to the first steps in the ring formation process proposed by Frenklach, et al.[7] The final steps of the proposed process include

$$C_4H_4(-H) \rightarrow n\text{-}C_4H_3(+ C_2H_2) \rightarrow$$
$$\ell\text{-}C_6H_5 \rightarrow \text{phenyl}$$

followed by subsequent formation of benzene or phenylacetylene.

Detailed chemical kinetic modeling of the present experimental data, however, strongly suggests that early (i.e. low temperature) benzene formation arises principally from acetylene addition to the normal-butadienyl radical, not the n-C_4H_3 radical, i.e.,

$$n\text{-}C_4H_5(+ C_2H_2) \rightarrow \ell\text{-}C_6H_7 \rightarrow$$
$$c\text{-}C_6H_7(-H) \rightarrow C_6H_6$$

where ℓ-C_6H_7 is defined to be the 1,3,5-hexatrien-1-yl radical.

Preliminary calculations using this mechanism have also been performed for comparison to the flow reactor data on acetylene pyrolysis obtained by Munson and Anderson.[30] Semiquantitative agreement for the production of benzene and VA was achieved and thus the bimolecular reaction involving intermediate formation of a C_4H_4 diradical is not necessary to describe lower temperature acetylene pyrolysis.

Above 1500°K, cyclic compounds are formed principally by acetylene addition to n-C_4H_3 in agreement with the proposal by Frenklach, et al.[7] Previously it was assumed, however, that n-C_4H_3 was formed through path A, whereas (R-12) was the dominant route under the present conditions

$$n\text{-}C_4H_5(-H) \rightarrow C_4H_4(-H) \rightarrow n\text{-}C_4H_3 \quad A$$
$$C_2H_2 + C_2H \rightarrow n\text{-}C_4H_3 \quad (-12)$$

This conclusion arises from results discussed later in this paper which show that VA decomposition principally involves H-atom addition to C_4H_4, not H-atom abstraction. As temperature increases, the abstraction route will become more significant; however, the concentration of C_2H will also increase so (R-12) still remains competitive. Furthermore (R-12) is a straightforward process for producing the normal radical and, in Fig. 1, assists in adequately describing the production of benzene and phenylacetylene. Demonstration of the relative sources of n-C_4H_3 can be seen in Fig. 2, where reaction sources and sinks are plotted as a function of time for two different temperatures.

Figure 1 shows that the model overpredicts observed benzene and phenylacetylene concentrations above 1600°K. Coincidentally, this is the same temperature at which a significant deficit in recovered mass first appears.[14] Some phenylacetylene and benzene above 1600°K is probably converted to higher molecular weight species which are not observed and not accounted for by the model.

Vinylacetylene

Mixtures of 0.01, 0.115 and 1.0% VA in argon were pyrolyzed over the temperature range 1100 to 2500°K. The data for the lowest and highest concentrations are presented in Figs. 3, 4 and 5. The other species not shown in these figures were observed at concentrations less than 2% of the parent. These species include methane, ethylene, allene/methylacetylene, several unidentified C_5 species, C_6H_4, toluene, and a C_9-hydrocarbon (possibly indene). Data on the series with intermediate concentration have been presented previously.[15] The most significant information is that at low temperatures and

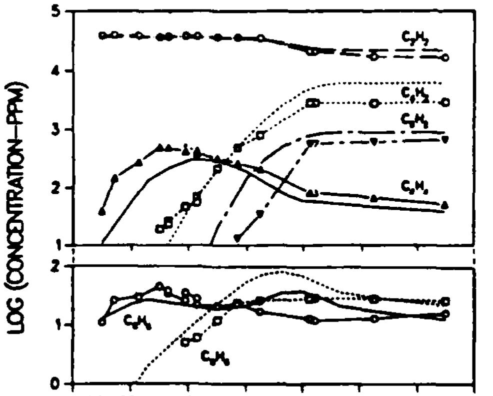

FIG. 1. Experimental and Model Resulus for Pyrolysis of 3.7% Acetylene in Argon. Dwell Time = 700×10⁻⁶ sec. Total pressure = 8 atm.

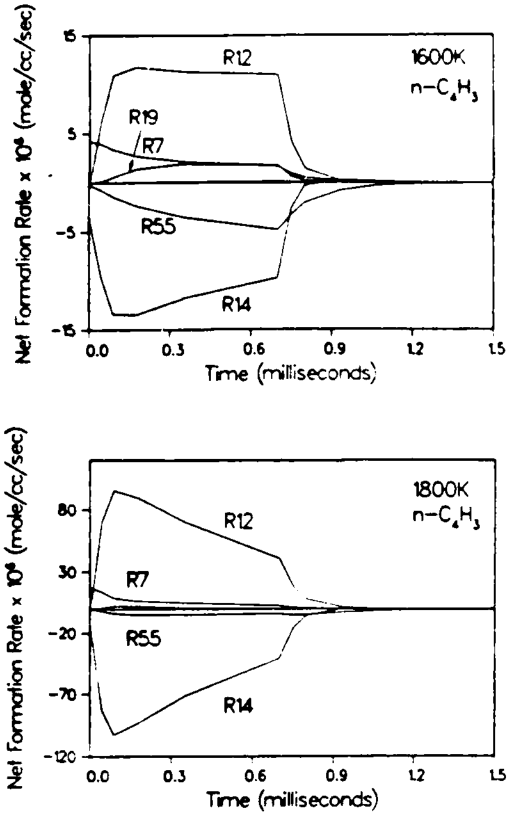

FIG. 2. Net Formation Rate for Production/Destruction of the n-C_4H_3 Radical. 2a) at 1600K, 2b) at 1800K.

Contributing reactions:

R7 $C_2H_2 + C_2H_2 \rightleftharpoons n\text{-}C_4H_3 + H$

R12 $n\text{-}C_4H_3 \rightleftharpoons C_2H_2 + C_2H$

R14 $n\text{-}C_4H_3 \rightleftharpoons C_4H_2 + H$

R19 $C_4H_4 + H \rightleftharpoons n\text{-}C_4H_3 + H_2$

R55 $1\text{-}C_6H_3 \rightleftharpoons n\text{-}C_4H_3 + C_2H_2$

Quenching wave arrives at 700×10^{-6} sec. Total pressure = 8 atm. Pyrolysis of 3.7% acetylene.

low initial concentrations, acetylene is the predominant product, while diacetylene (as well as H_2) is produced at levels approximately ten times less than that of acetylene. Aromatics are produced at higher temperatures and concentrations, but not in quantities sufficient to encourage rapid growth of polycyclics and severe mass imbalance. Relatively little data have been presented previously for comparison to this SPST data. Lundgard's[31] review has identified one previous work which overlaps the present temperature range. Yampol'skii, et al.[32] examined VA pyrolysis between 1023 and

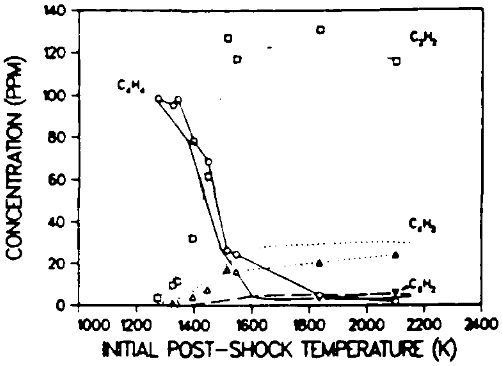

FIG. 3. Experimental and model results for 100 ppm Vinylacetylene in Argon. Dwell time = 700×10^{-6} total pressure = 8 atm.

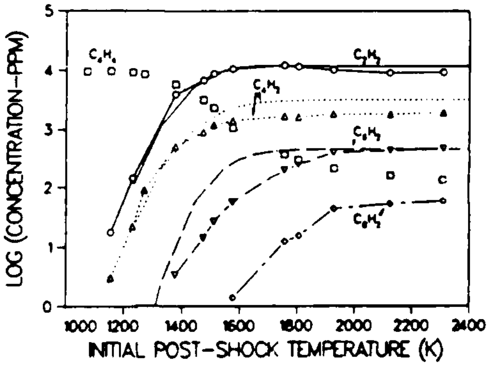

FIG. 4. Experimental and Model Results for Aliphatic Species during Pyrolysis of 1% Vinylacetylene in Argon. Dwell time = 700×10^{-6}sec, total pressure = 8 atm.

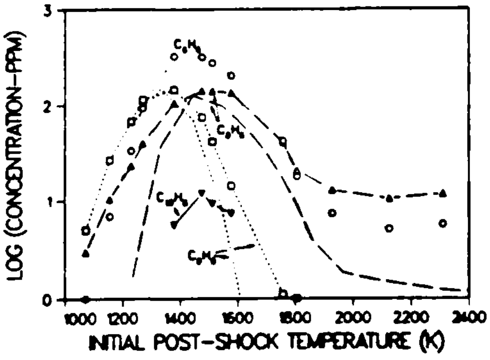

FIG. 5. Experimental and Model Results for Aromatic Products during Pyrolysis of 1% Vinylacetylene in Argon. Dwell time = 700×10^{-6}sec, total pressure = 8 atm.

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1273°K and produced qualitatively similar results to the SPST work. The main low temperature aliphatic found by Yampol'skii was acetylene with traces of methane and ethene, although diacetylene was not detected. Benzene was also observed previously, as well as a polymer whose precursor may be styrene. The overall decomposition of VA observed by Yampol'skii, et al., $k = 1.6 \times 10^{11} \exp(-52{,}800 \mathrm{cal/RT})$ sec^{-1} is approximately five times higher than the SPST results.

Kinetic modeling requires the identification of the initiation step and a chain process which describes the predominant formation of acetylene with minor production of diacetylene, styrene, benzene and phenylacetylene. The three possible initiation processes are

R9 $C_4H_4 \rightarrow i\text{-}C_4H_3 + H$ − 98 kcal mole
R10 $C_4H_4 \rightarrow n\text{-}C_4H_3 + H$ −111 kcal/mole
R51 $C_4H_4 \rightarrow C_2H + C_2H_3$ −122 kcal/mole

where the estimated endothermicities may each be in error by as much as 10 kcal/mole due to uncertainties in heats of formation of the hydrocarbon radicals. In this work, the principal initiation process was assumed to be Reaction 9, which required a rate expression of $10^{15.2} \exp(-42800/T)$ sec^{-1}, although the A-factor seems high and E_{act} low, for the C-H bond scission. It is important to note that the model results were relatively insensitive to the *absolute magnitude of the initiation rate or its* temperature dependence. A factor of three change in the initiation rate resulted in approximately a 20–30% change in the overall rate of decomposition and the formation of products. The explanation for this phenomenon is that the decomposition of VA in the range 1200–1400°K is controlled by a chain mechanism:

		$\log_{10}A$	E_{act}
R9			
initiation	$C_4H_4 \rightleftarrows i\text{-}C_4H_3 + H$	15.2	85000.
R-46			
chain	$H + C_4H_4 \rightleftarrows n\text{-}C_4H_5$	13.0	1370.
R-20			
chain	$n\text{-}C_4H_5 \rightleftarrows C_2H_3 + C_2H_2$	14.0	43360.
R-3			
chain	$C_2H_3 \rightleftarrows H + C_2H_2$	13.0	43710.
		cc.mole.sec	cal/mole

where the last three reactions account for the majority of the decomposition of the parent and the predominance of acetylene in the low-temperature products. This chain is not only important specifically to understanding the pyrolysis of vinylacetylene; but, as discussed earlier in this paper, also to the mechanism of ring formation during acetylene pyrolysis. Explanations for elimination of other mechanisms are presented below.

Alternative chain mechanisms for decomposition of VA would include H-atom abstraction from C_4H_4 resulting in $\dot{C}\text{:CCH:CH}_2$, $\text{HC:C}\dot{C}\text{:CH}_2$, or $\text{HC:CCH:}\dot{C}\text{H}$. Formation of the first of these can be neglected from thermodynamic considerations. In addition, direct formation of two acetylene molecules from this structure seems unlikely. The second isomer, $i\text{-}C_4H_3$, should decompose principally into diacetylene, since breakage of the C-C bond would have a high activation barrier due to the formation of vinylidene as an intermediate. The last isomer, $n\text{-}C_4H_3$, may decompose into $C_4H_2 + H$ or $C_2H + C_2H_2$. Estimated rates

	Log k (1300°K)	$\mathrm{Log}_{10}A$	E
R12			
$n\text{-}C_4H_3 \rightleftarrows C_2H + C_2H_2$	4.72	14.3	57000.
R14			
$n\text{-}C_4H_3 \rightleftarrows C_4H_2 + H$	5.88	12.6	40000.

suggest that Reaction 14, i.e. production of C_4H_2, is faster by a factor of 14 near 1300°K where VA decomposition is observed. At higher temperatures the two rates approach one another. These relative rate estimates are supported by experimental decomposition data of benzene pyrolysis from Kern, et al.[33] Those researchers found that the initial ratio of products C_2H_2/C_4H_2 at 1700°K, is approximately two to one. Assuming the overall decomposition path

$$C_6H_6(-H) \rightleftarrows C_6H_5 \rightleftarrows n\text{-}C_4H_5 + C_2H_2,$$

then the C_2H_2/C_4H_2 product ratio suggests that the branching ratio k_{14}/k_{12} is also approximately two to one. The calculated ratio using the above rates is three (3) at 1700°K. Thus, if $n\text{-}C_4H_5$ is the principal intermediate from VA decomposition, then the initial production rate of C_4H_2 would be similar to or higher than that of C_2H_2 during VA pyrolysis. Such a prediction is not substantiated by the SPST experiments.

H-atoms may add to VA at locations other than to the secondary acetylenic carbon. Addition to the other carbons would form $H_2C\text{:}\dot{C}CHCH_2$, $HC_{\wedge}C\dot{C}HCH_3$, or $HC\text{:}CCH_2\dot{C}H_2$. However, each of these radicals would be expected to reform VA, decompose into products other than two acetylenes or involve energetic intermediates. Thus it appears that the decomposition chain involving $n\text{-}C_4H_5$ will dominate. *Detailed chemical kinetic calculations using the*

$\wedge$ ⋮ le

HC⋮ —H

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specific rate constants in Table I are consistent with this analysis.

Production of diacetylene is described by

$$R + C_4H_4 \rightarrow i\text{-}C_4H_3 + RH$$
$$R + C_4H_4 \rightarrow n\text{-}C_4H_3 + RH$$

followed by decomposition of C_4H_3 into diacetylene plus H-atoms. R may be an H-atom or a hydrocarbon radical.

As shown in Fig. 5, reasonable agreement with experimental profiles of aromatic species were obtained using the reaction sequence of Table I. The apparent underprediction of VA at elevated temperatures is presumably an experimental problem due to partial gas sampling of boundary layers which contain the unheated parent hydrocarbon. Above 1600°K, phenyl is formed from the $n\text{-}C_4H_5 + C_2H_2$ recombination and is followed by conversion to benzene or phenylacetylene. At lower temperatures, the predominate formation routes of aromatics are

R45 $C_4H_4 + C_2H_3 \rightarrow C_6H_7$
(1,3,5-hexatrien-3-yl)
$C_6H_7 \rightarrow c\text{-}C_6H_7$
$c\text{-}C_6H_7 \rightarrow C_6H_6 + H$

for benzene formation, and

R52 $C_4H_4 + n\text{-}C_4H_5 \rightarrow C_8H_9$
$C_8H_9 \rightarrow c\text{-}C_8H_9$
$c\text{-}C_8H_9 \rightarrow C_8H_8 + H$

to produce styrene. PA is produced principally by

R53 $C_8H_8 + H \rightarrow C_8H_7 + H_2$
$C_8H_7 \rightarrow C_8H_6 + H$

near 1500°K and below, but at higher temperatures, acetylene addition to phenyl also occurs. Reactions 45, 52, and 53 were assumed to be overall processes and nonreversible. For the conditions (radical concentrations and temperatures) at which these reactions contribute, preliminary calculations confirmed the validity of these assumptions. Despite the good agreement with the experimental data, there are several unsettling features of these proposals. Reaction 45 requires a 1,3 or 1,4 H-atom shift prior to cyclization and Reaction 47, which has been proposed previously[5] should be a preferred route for aromatization. However, $k_{47} \approx 10^{14}$cc/mole-sec would be required to explain the experimental data. This rate is significantly higher than the rate in Table I, 2×10^{11}cc/mole-sec, required by the acetylene modeling, and previous determinations [7.5×10^{10} (Ref. 5) and 2.7×10^{11}(Ref. 6) at 1300°K].

Another concern of the modeling results is that the value of k_{52} required to match the experimental data is approximately 100 times higher than a previous determination using data from a low pressure, premixed butadiene flame. Rate determinations from the SPST data are subject to errors due to boundary-layers, quenching effects, and modeling complexity. However, the flame determination is expected to be a lower limit since, when evaluating the rate constant, Cole, et al.[5] assumed that the $n\text{-}C_4H_5$ radical was the dominant C_4H_5 species. Other isomers, particularly $H_2C{:}CHCCH_2$, which is less reactive and more stable by 3 kcal/mole, can contribute significantly to mass 53.

The assumption of the predominance of $n\text{-}C_4H_5$ in the flame work would only partially explain the difference between the two evaluations. Uncertainties in heats of formation and entropies for $n\text{-}C_4H_5$ and/or vinyl, which may affect the $n\text{-}C_4H_5$ concentration via

$$C_2H_2 + C_2H_3 \rightleftarrows n\text{-}C_4H_5$$

may also help to alleviate the difference; but probably by no more than a factor of five. Alternatively, reactions not considered in the present work may describe production of aromatics or significantly enhance the concentration of $n\text{-}C_4H_5$.

Conclusions

Single-pulse shock tube data have been obtained for the pyrolyses of acetylene and vinylacetylene. The data have been used to support previous proposals for acetylene and benzene pyrolysis with some revisions. A decomposition model for vinylacetylene involving H-atom addition to vinylacetylene has been proposed in order to explain product formation. Severe constraints imposed by simultaneously modeling decomposition of each of the parent hydrocarbons as well as five or more product species have been satisfied with the proposed model. Vinylacetylene, benzene, and phenylacetylene are observed during acetylene pyrolysis. The sequence

$C_2H_2 + H \rightleftarrows C_2H_3$
$C_2H_2 + C_2H_3 \rightleftarrows n\text{-}C_4H_5$
$n\text{-}C_4H_5 \rightleftarrows C_4H_4 + H$
$C_2H_2 + n\text{-}C_4H_5 \rightarrow \ell\text{-}C_6H_7$
(1,3,5-hexatrien-1-yl)
$\ell\text{-}C_6H_7 \rightarrow c\text{-}C_6H_7$
$c\text{-}C_6H_7 \rightarrow C_6H_6 + H$

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describes the low temperature formation of vinylacetylene and benzene (1100–1400°K). Reverse rates calculated from thermodynamics for the first three steps describe the decomposition of vinylacetylene. At temperatures above 1500°K, phenyl is formed by

$$C_2H_2 + H \rightleftarrows C_2H + H_2$$
$$C_2H_2 + C_2H \rightleftarrows n\text{-}C_4H_3$$
$$C_2H_2 + n\text{-}C_4H_3 \rightleftarrows \ell\text{-}C_6H_5$$
(1-hexyne-3,5-dien-6-yl)
$$\ell\text{-}C_6H_5 \rightleftarrows \text{phenyl}$$

and is followed by formation of benzene or phenylacetylene. Reverse rates calculated from thermodynamics are consistent with a previous proposal for decomposition of phenyl during benzene pyrolysis.

Aromatic formation during vinylacetylene pyrolysis at low temperatures is described by

$$C_2H_3 + C_4H_4 \rightarrow C_6H_7$$
(1,3,5-hexatrien-3-yl)
$$C_6H_7 \rightarrow c\text{-}C_6H_7$$
$$c\text{-}C_6H_7 \rightarrow C_6H_6 + H$$
and $n\text{-}C_4H_5 + C_4H_4 \rightarrow \ell\text{-}C_8H_9$
$$\ell\text{-}C_8H_9 \rightarrow c\text{-}C_8H_9$$
$$c\text{-}C_8H_9 \rightarrow C_8H_8 + H$$

The proposed rate constant for the first step is low, but the reaction requires an H-atom shift. The required rate for the addition of the normal butandienyl radical to vinylacetylene is approximately 100 times higher than a previous measurement. Consequently, it is possible that calculated concentrations of $n\text{-}C_4H_5$ are inaccurate or that other mechanisms are significant.

Acknowledgements

This work has been supported in part by the Air Force Office of Scientific Research (AFSC) under Contract No. F49620-85-C-0012. The United States government is authorized to reproduce and distribute reprints for governmental purposes, notwithstanding any copyright notation herein. The author is indebted to Dr. D. J. Seery and Prof. H. Palmer for their constant support and suggestions throughout this research. The author is also grateful to Dr. P. R. Westmoreland for many fertile discussions and his sharing of technical/thermodynamic information. The authors of CHEMKIN and LSODE should be acknowledged, since these computer routines substantially increased the capability for performing the model calculations; particular thanks should go to Dr. R. J. Kee for his suggestions and guidance in modifying the codes. The experimental research has been completed only with the able assistance of D. Kocum. His assistance is greatly appreciated.

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COMMENTS

Replace

F. Temps, MPI F. Stromungsforschung, West Germany. Would the author please comment on the possible role of vinylidene (singlet or triplet) or triplet acetylene on the acetylene pyrolysis?

Author's Reply. Vinylidene appears to be a strong candidate for initiation of acetylene, since it lies only about 44 kcal/mole above the ground state of acetylene and since the intermediate transition state is only two (2) to four (4) kcal/mole above vinylidene[1]. A subsequent step:

$$H_2C-C: + HCCH \rightarrow H_2C\dot{C}CH\dot{C}H \rightarrow i\text{-}C_4H_5 + H$$

is endothermic (overall) by about 15 kcal/mole (or 69 kcal/mole above two acetylene molecules). The overall endothermicity of this sequence is lower than other proposed bimolecular initiators which form $C_2H + C_2H_3$ or n-C_4H_3 + H, which are about 86 and 79 kcal endothermic, respectively. Unfortunately, the endothermicity of the sequence involving vinylidene is still about 13 kcal higher than the activation energy of the bimolecular initiator (Reaction 7) used in the present work.

Vinylidene could also play a role if the above intermediate, $H_2C\dot{C}CH\dot{C}H$, undergoes a 1,4 H-atom shift to produce vinylacetylene. Although this route was considered in the present work, there is no apparent parallel pathway to benzene, which adequately describes experimental profiles. It is, of course, possible that this mechanism contributes to the production of vinylacetylene. A possible role of triplet acetylene was not considered in the above analysis.

REFERENCE

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(C)-11.

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S. E. Stein, Chemical Kinetics Div., National Bureau of Standards, U.S.A. How do you interpret the unusually high rate constant for styrene formation?

Author's Reply. As summarized in the conclusions of the manuscript, the rate expression $k_{45} - 7.9\times10^{15}$ exp(−3000/RT) cc/mole-sec, is about a factor of 100 too high, when compared to rate constants of comparable addition processes. The interpretation is that either other mechanisms dominate styrene formation or that rate coefficients and/or thermodynamics for several of the reactions/species are in error. The most likely alternative mechanism is a dimerization process; the most likely errors associated with rate coefficients and thermodynamics probably involve vinyl and butadienyl radicals.

There is presently insufficient information available to ascertain which of the above (or if all) contribute to the discrepancy. Consequently, the data are presented as is.

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K.H. Homann, Technische Hochschule Darmstadt, West Germany. Did you consider a dimerization step as the first reaction in the pyrolysis of C_2H_2 and C_4H_4? In a recent study of C_4H_2 pyrolysis at 100°C we found that the homogeneous initiation step was $2\ C_4H_2 \rightarrow C_8H_4$. Addition of H atoms to the reaction system had no effect on the products[1].

1. HOMANN K.H. AND PIDOLL U.V.: Ber. Bunsenges. Phys. Chem. 1986, in press.

Author's Reply. In an early analysis of this work, the dimerization of acetylene was considered as the predominant mechanism for vinylacetylene formation. The rate constant ($k = 3.6\times10^{14}$ exp(-44100/RT) cc/mole-sec) reported by Bradley and Kistiakowsky[1] was found to describe nicely the low temperature formation of C_4H_4. Coincidentally, the overall activation energy of this process is similar to the endothermicity for the formation of $H\dot{C}CHCH\dot{C}H$, the diradical intermediate. The endothermicity of this process was estimated to be 35 to 43 kcal/mole by interpreting results from Kollmar, et al.[2]. Despite the good agreement with experiment and reasonable mechanistic explanations (see also the response to Prof. F. Temps regarding the role of vinylidene) several problems arose. First, the Bradley and Kistiakowski data were shown[3] to be misinterpreted, leaving doubt regarding their reported rate constants. Secondly, there appears to be no parallel pathway to the formation of benzene at low temperature which describes the experimental results. In support of the chain mechanism during acetylene pyrolysis is that production of C_4H_4 and C_6H_6 can be explained using the proposed chain which includes rate constants very much consistent with previously proposed rate constants and thermochemistry. Additionally, many other products were not reported due to their relatively low concentrations; but their existence is strongly indicative of radical, chain mechanism. Further support for the chain mechanism is drawn from the fact that the proposed mechanism qualitatively predicts the product distributions observed during low temperature pyrolysis of acetylene[4] (allowing for a small change in the initiation rate and for pressure dependence of addition reactions).

Finally, Callear and Smith[5] have shown convincingly that processes very similar to those described in this work occur at room temperature when H-atoms are added to acetylene. The conclusion of the present work is that a radical, chain mechanism adequately describes the observed dominant products using mechanisms and rates which are reasonable. Dimerization processes cannot as yet be ruled out absolutely (and they may play a contributing role), but it does not seem necessary to invoke their existence to explain the observed results.

As strong a case against dimerization processes cannot be made in the case of vinylacetylene, since it is necessary to add a reaction (#45) which had not been proposed previously and (most disconcerting) to use an unusually high rate for the addition of n-C_4H_5 to C_4H_4 (R52)(see response to question by Dr. S. Stein).[4] However, *with the* lack of evidence of dimerization processes occurring during high temperature acetylene processes, the author favors a chain mechanism for explaining the product distribution. The vinylacetylene data can be fitted reasonably if one assumes dimerization processes dominate aromatic formation. For example, by reducing k_9, k_{45}, k_{52}, *and* k_{55} *by factors of 2, 2, 100, and 2 respectively* and including:

$$2C_4H_4 \rightarrow C_8H_8(a) \text{ and } 2C_4H_4 \rightarrow C_8H_6 + 2H\ (b)$$

(as irreversible steps) with respective rate constants of:

$$k_a - 9\times10^{15}\ \exp(-40000/RT)$$

and

$$k_b - 3\times10^{12}\ \exp(-35000/RT)\ \text{cc/mole-sec}$$

then experimental profiles can be predicted reasonably (although benzene is overpredicted at low temperatures). k_a, in comparison, is approximately two to three times higher than an extrapolation of Lundgard and Heicklen's(6) expression:

$$k - 3\times10^{11}\ \exp(-29200\ \text{cal/mole/RT})\ \text{cc/mole/sec}$$

for the net formation of "dimerized" products, formed via a combination of molecular and radical processes. The radical process at low temperatures was assumed to involve formation of a diradical intermediate, although possible contributions from the chain process as suggested in this paper should not be necessarily ignored.

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6. Lundgard, R. and Heicklen, J.: Int. J. Chem. Kin. *16*, 125 (1984)

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S.J. Harris, General Motors Research Labs, U.S.A. Are C_2H_2 and C_4H_2 equilibrated in your system? At what temperatures? If they *are* equilibrated, then you cannot obtain mechanistic information from the contractions. If they are not equilibrated, are they far enough away from equilibrium so that you have confidence that the mechanism is controlling the products?

Author's Reply. For the dwell times (500–800 microseconds) of these pyrolysis experiments, the acetylenes *are equilibrated only* above 1500–1700 K, depending on the concentration and identity of the reactant. Major conclusions of the present work are dependent strongly on the experimental result that products of low temperature (1100–1300 K) pyrolysis of vinylacetylene are principally acetylene, diacetylene, and hydrogen with the product ratios C_2H_2/C_4H_2 and C_2H_2/H_2 approximately ten to one. Perturbations of these product ratios by equilibration reactions would significantly alter the conclusions of this paper. The "non-equilibration" of acetylene at low temperatures and short times can be demonstrated by the following modeling study and by comparison to experiments on benzene pyrolysis.

In an artificial modeling exercise of C_4H_4 pyrolysis, rate coefficients for Reactions 46 and 20 were decreased while coefficients of Reactions 13 and 18 were increased by factors of ten (10) or more. The net result was to convert the overall decomposition pathway from:

$$C_4H_4 \rightarrow 2C_2H_2$$

to

$$C_4H_4 \rightarrow C_4H_2 + H_2$$

The modeling results below 1400 K indicated final C_4H_2/C_2H_2 ratios of approximately one hundred (100) to one which is 2½ orders of magnitude above equilibrium. Consequently, this modeling exercise indicates the relative unimportance of equilibrating reactions under the low temperature conditions at which the decomposition mechanism was deduced.

Experimental evidence for non-equilibration at low temperatures can be inferred from recent data on benzene pyrolysis. At 1500K, several hundred degrees higher than the temperatures at which mechanistic information was obtained in the present work, Colket[1] found an initial C_2H_2/C_4H_2 ratio of approximately three (3) to one (1), a value lower than the equilibrated ratio of about five (5) to one (1) (depending on assumed thermochemistry). The experimental ratio is similar to the value (two to one) obtained by Kern, et al.[2], at yet higher temperatures (1704 K). Consequently, both modeling and experimental data support arguments that early (i.e. initial) formation of acetylenic products are not equilibrated.

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J.H. Kiefer, Univ. of Illinois at Chicago, U.S.A. In answer to Dr. Harris' question, current models of high-temperature acetylene pyrolysis require C_2H *radicals for* C_4H_2 equilibration, and the formation of this radical seems unlikely at these temperatures. I also have questions for the speaker. First, for your chain production of C_2H_2 to proceed sufficiently I suspect you may well need the high rate of vinyl dissociation you assumed. Otherwise the fast process $C_2H_3 + H \rightarrow C_2H_2 + H_2$ would very effectively terminate the chain. Do you think you could stand the low rate of vinyl dissociation of your butadiene work[1]? Finally, if the heat of formation of C_4H_5 were about 130 kcal/mol, as has been suggested to me by Karl Melius, could your model still provide sufficient conversion of C_4H_4?

REFERENCE

1. Kiefer, J.K., Wei, H.C., Kern R.D., and Wu, C.H.: Int. J. Chem.Kin., *17*, 225 (1985).

Author's Reply. The philosophy for selection of reactions and corresponding rate constants presented in Table I was to use well-established mechanisms and rate constants while selecting other mechanisms and rate constants as required by the experimental results, but consistent (in most cases) with thermochemistry. Vinyl decomposition was assumed to be

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pressure independent and its rate constant was not varied in the analysis described by the manuscript. A preliminary examination of the effect of the use of a lower rate for vinyl decomposition was examined by using Kiefer's rate expression which is more than 100 times slower than that used in the present analysis. In the modeling of vinylacetylene, the overall decomposition rate of the parent decreased by only 20%, although the "quasi-steady" concentration of vinyl radicals increased by nearly a factor of 100. The overall route of vinylacetylene decomposition changed only slightly from that described in the manuscript. Main problems that arise are: (1) diacetylene and ethene are overpredicted by about a factor of two and five, respectively; and (2) early formation of both vinylacetylene and benzene from acetylene pyrolysis are underpredicted each by about an order of magnitude. Some features suggest that an intermediate value for vinyl decomposition might be reasonable. The data on vinylacetylene and acetylene from this work, however, do not support the low rate constant as determined in your analysis of my butadiene data.

If C_4H_5 radicals have a heat of formation of 130 kcal/mole, it would tend to support present arguments that H-atoms add to vinylacetylene rather than abstract H-atoms from vinylacetylene. By using this high heat of formation in modeling, however, two major problems will arise. First, the effective activation energy of the initiation process ($C_4H_4 \rightarrow i\text{-}C_4H_5 + H$) was 85 kcal/mole in this work. This low value is questionable as it stands, but would be nearly impossible to reconcile if the overall endothermicity were 113 kcal/mole. A second problem results from the fact that the high heat of formation (vs. 125 kcal/mole assumed in this work) would substantially reduce the "quasi-steady state" concentration of $n\text{-}C_4H_5$. Thus, the formation of phenyl via $n\text{-}C_4H_5$ addition to acetylene would be substantially reduced and benzene and phenylacetylene significantly underpredicted.

●

W.C. Gardiner, University of Texas U.S.A. Inclusion of irreversible steps in polymer formation mechanisms has to be regarded with special care, particularly in the case of soot formation, where the diversity of pathways and unsuspected reversibility of quite exoergic steps make the points of no return first appear at molecular sizes well beyond those considered in this paper[1].

In order to make valid comparisons between computed and measured yields of one-ring and two-ring aromatic compounds, the reaction mechanism must be extended—under provision for reverse reaction—to still larger species, as a minimum to acenapthalene. For this reason it would appear that the rate constants used in this paper to model formation of aromatic rings have to be regarded as artificial

REFERENCE

1. Frenklach, M., Clary, D.W., Gartiner, W.C., and Stein, S.E.: 20th Symp. (Int.) on Combustion, p. 887, The Combustion Institute, Pittsburgh, 1985.

Author's Reply. In general, your comment is very reasonable and should be considered for long reaction times or conditions which allow conversion of significant matter to larger species. However, for the conditions at which the modeling was applied in this work, this effect is relatively unimportant. In the present study, the kinetics analysis was performed for short reaction times (700 microseconds) and low temperatures (<1600 K) for which early formation kinetics (of aromatics) could be observed. Under these conditions, relatively small fractions of the observed aromatics undergo growth processes. For example, in the case of 3.5% acetylene pyrolysis, 10 ppm of benzene was observed at 1100 K, the lowest temperature at which the mixture was pyrolyzed. Concentrations of phenylacetylene at this temperature can be estimated to be 1½ to 2 orders of magnitude lower and do not achieve a comparable concentration until 1500 K (for the same dwell time). Based on data using higher initial concentrations of acetylene (4.9%), naphthalene concentrations are more than an order of magnitude below those of phenylacetylene at these temperatures. An analysis of mass balance indicates good recovery of initial carbon below 1650 K. These results may not be proof, but they indicate strongly that the processes observed in this study are descriptive of the initial formation steps (of aromatics) and perturbation due to lack of inclusion of subsequent growth processes are negligible.

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M. Frenklach, Pennsylvania State Univ., U.S.A. Our mechanism (1,2) to which the author refers, was composed of a very large variety of reaction pathways including all those discussed by the author. No assumptions about the importance of individual elementary reactions in the mechanism were made; our conclusions about dominant reaction pathways leading to polycyclic aromatic hydrocarbons and soot were drawn instead from the results of computer experiments described in the cited references. Thus, contrary to the authors's assertion, the pathway

$$\begin{aligned} n - C_4H_5 &\rightarrow C_4H_4 + H \\ C_4H_4 + H &\rightarrow n - C_4H_5 + H_2 \qquad (1) \end{aligned}$$

was not ***assumed*** but ***deduced*** to be the dominant pathway for the production of $n - C_4H_5$ for the conditions of "soot" formation in shock-tube pyrolysis of acetylene. Although we found the reaction

$$C_2H_2 + C_2H \rightarrow n - C_4H_5 \qquad (2)$$

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to be fast at very short reaction times, it quickly gave way to the sequence (1) that became dominant for soot appearance. The competition between (1) and (2) is sensitive to experimental conditions; e.g., reaction (2) plays a more prominent role in the presence of oxygen (3). Hence, differences in experimental conditions and different assumptions about thermochemical values are the likely sources of the different relative fluxes of (1) and (2) noted in this paper.

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1. **Frenklach, M., Clary, D.W., Gardiner, W.C., Jr., and Stein, S.E.:** *Twentieth Symp. (Int.) on Combustion*, p. 887, The Combustion Institute, Pittsburgh, 1985.
2. **Frenklach, M. Clary, D.W. and Ramachandra, M.K.**, "Shock Tube Study of the Fuel Structure Effects on the Chemical Kinetic Mechanisms Responsible for Soot Formation, Part II", NASA Contractor Report 174880, May 1985.
3. **Frenklach, M., Yuan, T., Clary, D.W., Gardiner, W.C., Jr., and Stein, S.E.:** *Combust. Sci. Technol.*, in press.

Author's Reply. As suggested by Dr. Frenklach, the manuscript should be changed to read: "Previously, it was *deduced* . . . that n-C4H3 was formed through path A, whereas (R-12) was the dominant route under the present conditions." In both the present and previous work, it should be remembered that the authors have been forced to estimate—or assume—values of absolute rate constants for which either no data or little data are available. Oftentimes, substantial uncertainty exists in estimation techniques. Consequently, this procedure, by its very nature, leads to *assumptions* about the importance of individual elementary reactions. Conclusions reached or deduced in any work usually are only as good as the initial assumptions.

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A.M. Dean, Exxon Res. & Eng. Co., U.S.A. Given the fast rate constant for C_2H_3 + C_4H_4 (with no activation energy) that was needed to explain C_6H_6 formation, is it not possible to conclude that the rapid rate of aromatics formation is still a puzzle?

Author's Reply. The rate constant for k_{45} was determined to be 4×10^{11} cc/mole-sec, which is about two orders of magnitude below collision frequency and is similar in magnitude to rate constants determined for other addition reactions. The only unusual feature regarding Reaction 45 is that the linear intermediate, 1,3,5-hexatrien-3-yl, must undergo an H-atom shift and convert to the 1,3,5-hexatrien-1-yl radical prior to cyclization. It is believed, however, that this H-atom shift is not rate controlling. The size of the rate constant, in the opinion of the authors therefore, does not appear to be unreasonably large. The activation energy could not be determined in this experiment; and so none was assigned, although it would not be unreasonable to assume an effective activation energy of at least several kcal/mole.

Certain features of aromatics formation certainly can be considered to be unresolved, or at least under discussion. See, for example, the other questions and responses to this paper. Certainly more experimental and modeling work needs to be performed. One critical area of research is the accurate determination of enthalpies and entropies (and their temperature dependencies) for important radical intermediates.

APPENDIX E

SINGLE-PULSE SHOCK TUBE EXAMINATION OF HYDROCARBON PYROLYSIS AND SOOT FORMATION

by

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East Hartford, CT 06108

A single-pulse shock tube coupled to a capillary gas chromatograph has been used to observe the pyrolysis of a variety of hydrocarbons. Product species, mass balances, and H/C ratios of uncollected material have been determined. Relative "sooting" tendencies have been found to be toluene $\gtrsim$ benzene > allene > vinylacetylene $\gtrsim$ acetylene > 1,3-butadiene $\gtrsim$ cyclohexene for similar carbon-atom densities. A detailed chemical kinetic model has been constructed for the pyrolysis of acetylene and describes profiles of major species as well as the production of vinylacetylene, benzene and phenylacetylene.

Introduction

Shock tubes are frequently used for studying kinetics and mechanisms of both hydrocarbon pyrolysis and soot formation at conditions characteristic of diffusion flames. Single-pulse shock tubes (SPST) have been used perhaps most successfully for measuring rates of primary decomposition processes when fractional decomposition of the parent hydrocarbon is small[1]. Its applications to the study of soot may be limited by wall quenching and finite quenching in the rarefaction wave; but the potential for providing detailed species information with the aid of capillary gas chromatography has motivated the present research.

The ultimate goal of the experimental work is to provide data from which mechanisms of hydrocarbon pyrolysis and soot formation can be obtained. As part of that goal the relative tendency of different hydrocarbons to soot in a SPST is measured in this work. In addition, an objective of this paper is to extend a recent proposal[2] and present some results related to soot formation during the pyrolysis of acetylene. Specifically, experimental and modeling results on the production of vinylacetylene (VA), benzene, and phenylacetylene (PA) are shown.

Description of Facilities

The SPST used in this program is 258 cm long and has a diameter of 3.8 cm (i.d.). The driver is 88 cm in length and can be tuned by shortening its length in 3.8 cm increments; the driven section is 197 cm long. Pre-stressed aluminum diaphragms were used to control the rupture pressure. An 11.7 liter "dump tank" is located in the driver (lower pressure) section 30 cm downstream of the diaphragm. The pumping station is located at this tee. Pressure profiles were determined using Kistler pressure transducers located 15.25 and 2.50 cm from the end wall. Arrival times were determined to within one microsecond using digitized pressure traces. Calculated quench rates are typically 10^5 K/sec in the rarefaction wave. Starting pressures prior to filling are 0.2μ and leak rates are less than 1μ/min. Post-shock temperatures were calculated based on the measured incident shock velocity and normal shock wave equations.

The procedures for performing an experiment are similar to those described by Tsang[1], except for an automated sampling system. The sample is collected at the endwall of the shock tube using 0.045 inch i.d. tubing heated to over 85 C. Approximately 30 milliseconds after the gas has been shock heated and cooled, a solenoid valve opens to the evacuated sample cell and then closes after 300 milliseconds. All valves and lines in this system have been degreased and rinsed in toluene to minimize condensation on the walls. The sample storage vessel is all stainless steel with an internal volume of 25 cc. Total internal volume of the remainder of the sampling system is less than 3 cc.

The sampling volume is directly coupled to a low volume, heated inlet system of a Hewlett Packard 5880 A gas chromatograph. Typical injection pressures are 0.5 atmospheres and are measured to within two percent using a calibrated pressure transducer. One gas sampling valve injects samples onto a 25 m x 0.33 mm i.d. CP Sil 5 CB (1 micron film thickness) fused silica capillary column (from Chrompack Inc.) followed by quantitative hydrocarbon analysis using a flame ionization detector. A second valve leads to a silica gel packed, stainless-steel column and a single-filament, modulated thermal conductivity detector for analysis of hydrogen. Valves, detectors and software integration routines enable this sytem to provide automatic quantitative detection of hydrogen and hydrocarbon species up to C_{10}-hydrocarbons. Based on repeated injections of calibrated samples, overall measurement accuracies are estimated to be approximately three percent. Calibration gases were stored in stainless steel cylinders with degreased valves and were heated to approximately 60C prior to injection.

Argon (99.999% pure) was obtained from Matheson and was the principal diluent. Other chemicals were at least 99.5% pure according to gas chromatographic analysis, except for vinylacetylene, allene, and acetylene. VA contained approximately 8000 ppm of an unidentified C_5-hydrocarbon. Allene was obtained from several different vendors yet was typically 87 to 93% pure with a variety of other C_3-hydrocarbons as impurities. Bulb-to-bulb distillation enhanced the purity level to approximately 97%. Similarly, the initial concentration of acetone in acetylene was reduced from approximately 2% of the initial acetylene to about 1000 ppm.

Results

Toluene, benzene, cyclohexene, 1,3-butadiene, VA, allene, and acetylene have been pyrolyzed in a bath of argon. For each hydrocarbon, a series of shock tube runs were performed. Densities behind the reflected shock wave range were approximately 1.8×10^{18} carbon atoms/cc. Reflected shock temperatures and pressures ranged from approximately 1100 to 2500 K and 5 to 8 atmospheres, respectively. Dwell times were typically 550 to 800 microseconds although for the bulk of runs, dwell times were close to 700 microseconds. Typical results are shown in Figs. 1a and 1b for the pyrolysis of 1.17% benzene in argon. Presented in these figures are the final product distribution (for 18 separate shocks) after the test gas has been shock heated and then quenched by the rarefaction wave. The general features, i.e., production of aromatics over the 1500 to 1900 K temperature range, and the dominance of hydrogen and 'equilibrium' concentrations of the acetylenes above 2200 K is apparent in virtually all fuels. For the non-aromatic fuels, equilibrium concentrations are generally achieved above 1900 to 2000 K. At temperatures below 1500 to 1600 K, the product distribution is controlled by the kinetics of the decomposition of the hydrocarbon parent.

Figure 1 exhibits a relatively large amount of hydrogen produced at low temperatures. Modeling demonstrates that this 'low temperature' hydrogen is principally formed via the sequence:

$$C_6H_6 \dashrightarrow C_6H_5 + H$$
$$C_6H_5 + C_6H_6 \dashrightarrow C_{12}H_{10} + H$$
$$H + C_6H_6 \dashrightarrow C_6H_5 + H_2$$

A comparable amount of biphenyl should be produced, yet is unobserved due to its apparent loss during the sampling process or in the inlet system to the gas chromatograph. The amount of carbon converted to biphenyl at 1400 K would be approximately a few percent of the total and is consistent with the measured mass balance. Total hydrogen and carbon mass balances have been determined for the data in Fig. 1 and are plotted in Fig. 2. Also shown are calculated H/C ratios of the missing material. (Uncertainties in this calculation are obviously large when either hydrogen or carbon are nearly fully recovered.) At low temperatures, the ratio is in reasonable agreement with the assumption that biphenyl ($H/C = 0.825$) or other small multi-ringed compounds are produced. At higher temperatures, the H/C ratio is very low, suggesting the formation of very large polynuclear aromatics (PAH) or even soot. The low ratio of 0.1 observed in these benzene experiments is atypical since for most other hydrocarbons, the H/C ratio of the missing material ranges from 0.2 to 0.3 above 1700 K. This difference between benzene and other hydrocarbons may not be significant in light of the potential errors in calculating the H/C ratios of the missing material.

The fractional mass recovered is a strong function of both the concentration and the density of the parent hydrocarbon. The effect of hydrocarbon type on mass balance is shown in Fig. 3. Assuming that the mass loss is indicative of soot productions, the relative tendency to soot is approximately toluene $\gtrsim$ benzene > allene > VA $\gtrsim$ acetylene > 1,3-butadiene $\gtrsim$ cyclohexene. The single-pulse shock tube data is in excellent agreement with the relative tendencies to soot and with the temperature dependence as determined using optical absorption[3]. The detailed species profiles offer some insight to the relative sooting tendencies. Production of aromatics, particularly PA, appears to be critical. Allene, for example, produces large quantities of benzene and PA. The conversion of allene to benzene is as high as 25% of the initial carbon (and 4% to PA). If some benzene is converted to PAH and possibly soot, then the actual production of benzene may be even larger.

Thus the "sooting" tendency of allene is quite similar to those of the aromatics. In comparison, only 9% of the initial butadiene carbon is converted to benzene and the production of PA is delayed (relative to its production during benzene or allene pyrolysis) by 100 to 150 K. The similarity in mass balance between acetylene and VA at elevated temperatures can be explained by the dominant overall chain process $C_4H_4 + H \dashrightarrow 2C_2H_2 + H$ apparent from the product distribution during VA pyrolysis. Also of interest are significant concentrations of PA, which are presumably formed via C_4H_3 addition to VA, followed by cyclization and H-atom loss. The production of PA near 1400-1700 K may lead to the significant mass deficit observed in this regime. The similarity between cyclohexene and butadiene is explained by the rapid unimolecular decay $c\text{-}C_6H_{10} \dashrightarrow 1,3\text{-}C_4H_6 + C_2H_4$ and the relatively low sooting tendency for C_2H_4 (ref. 3).

Detailed chemical kinetic modeling has been performed using Chemkin and a modified shock tube code originally developed at Sandia National Laboratories. The modified code includes the capability of modeling the quenching effect of the rarefaction wave in an SPST. The basic kinetic mechanism is similar to modifications[2,4] of a proposed mechanism[5] and as shown in Fig. 4 describes well the distribution of mono-, di-, and triacetylene. The production of VA, benzene and PA is indicated below:

	Log A	E(cal/mole)
$H + C_2H_2 \text{--->} C_2H_3$	12.74	2500.
$C_2H_3 + C_2H_2 \text{--->} NC_4H_5$	13.00	8000.
$NC_4H_5 \text{--->} C_4H_4 + H$	13.70	41400.
$NC_4H_5 + C_2H_2 \text{--->} C_6H_6 + H$	12.60	9000.
$NC_4H_3 + C_2H_2 \text{--->} C_6H_5$	12.48	5000.
$C_6H_5 + C_2H_2 \text{--->} C_8H_6 + H$	12.32	5600.

A in units of cc, moles, sec.

The selection of this reaction sequence and rate constants has been based on a combination of the SPST experimental results and pioneering work at other laboratories[2,6-8]. The experimental and modeling results compare well at low temperature, but suggest some revision may be required at temperatures above 1800 K.

Acknowledgments

This work has been supported in part by the Air Force Office of Scientific Research (AFSC) under Contract No. F49620-85-C-0012. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. The author is indebted to Drs. P. M. Westmoreland, D. J. Seery and S. Stein and Professors H. Palmer and I. Glassman for valuable discussions related to this research and to D. Kocum for his assistance in the experimental portion of this work. The author also wishes to thank Professors S. H. Bauer and David K. Lewis for their useful comments on the construction and operation of single-pulse shock tubes.

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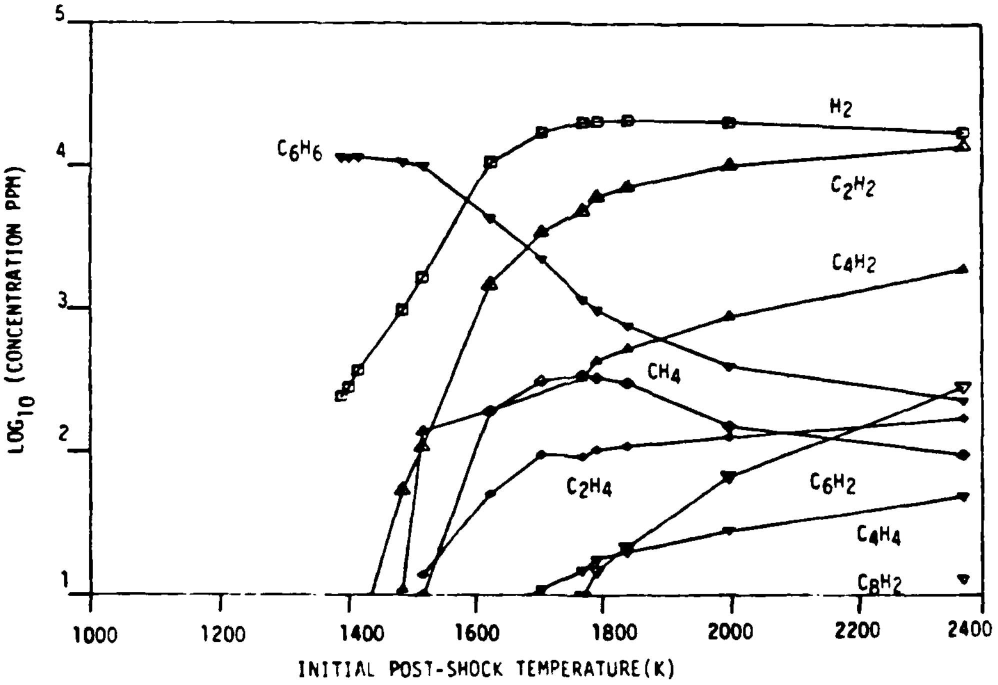

Fig. 1a SPST Pyrolysis of 1.17% Benzene at 6 atmospheres and for 700 microseconds: distribution of aliphatic products.

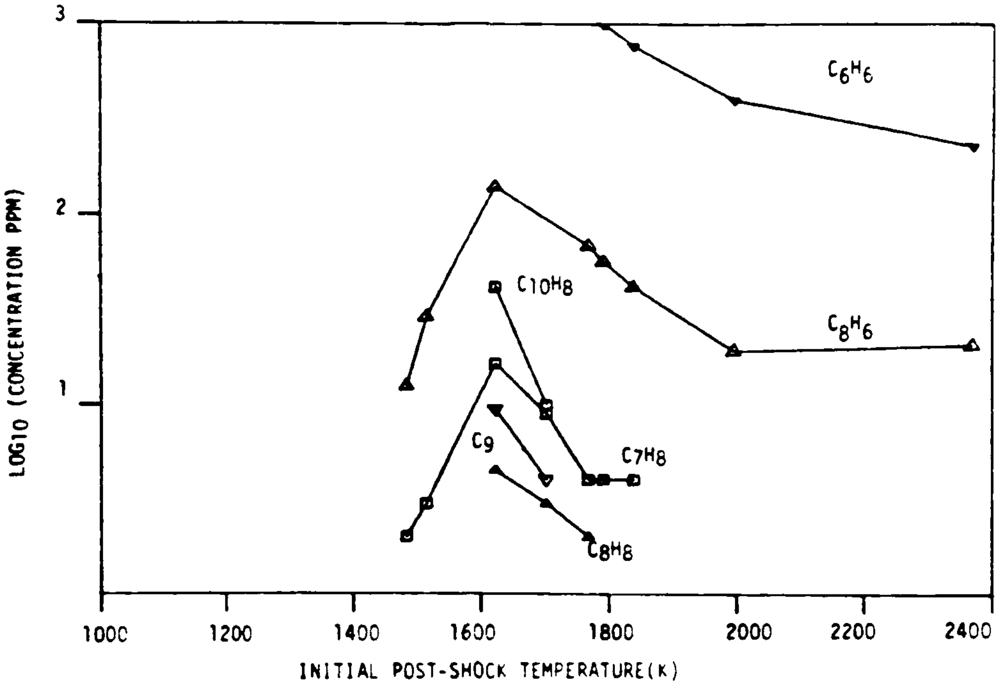

Fig. 1b SPST Pyrolysis of 1.17% Benzene at 6 atmospheres and for 700 microseconds: distribution of aromatic products.

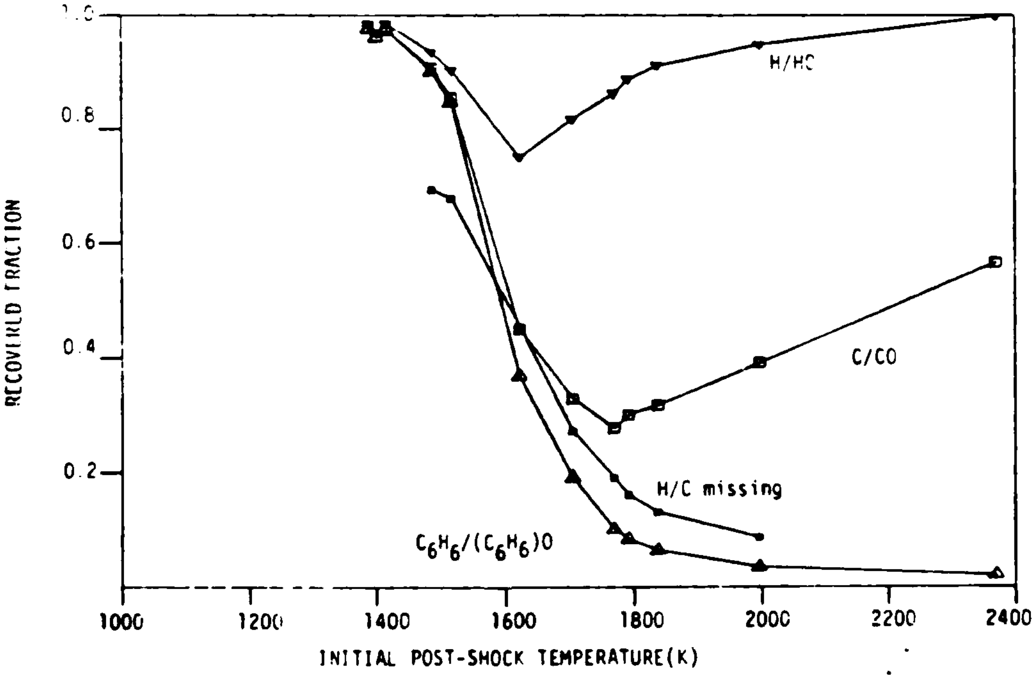

Fig. 2 Fractional recovery of initial hydrogen, carbon, and benzene during pyrolysis of 1.17% Benzene. Also shown is the calculated hydrogen-to-carbon ratio of the uncollected mass.

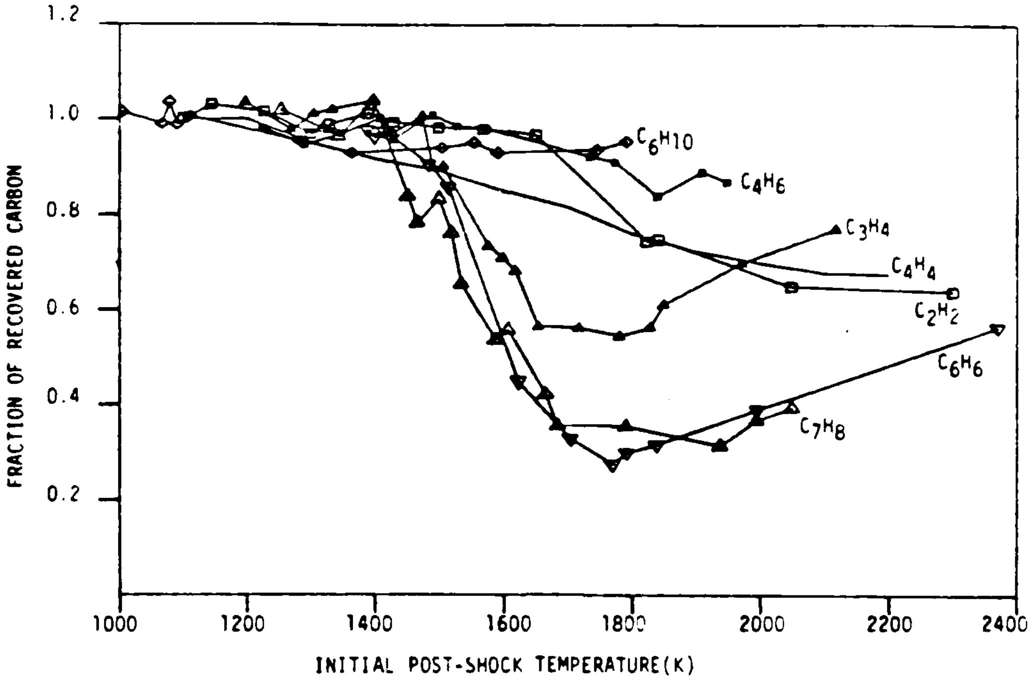

Fig. 3 Fractional carbon recovery for a variety of hydrocarbons at a total pressure and carbon density of approximately 6 atmospheres and 1.8×10^{18} carbon atoms/cc. △-1.0% C_7H_8, ▽-1.2% C_6H_6 ▲-2.3% allene, —-1.75% C_4H_4, □-3.7% C_2H_2, ■-1.75% 1,3-C_4H_6, ◆-1% % C_6H_{10}. (C_4H_4 curve is an estimate based on runs at dissimilar concentrations.)

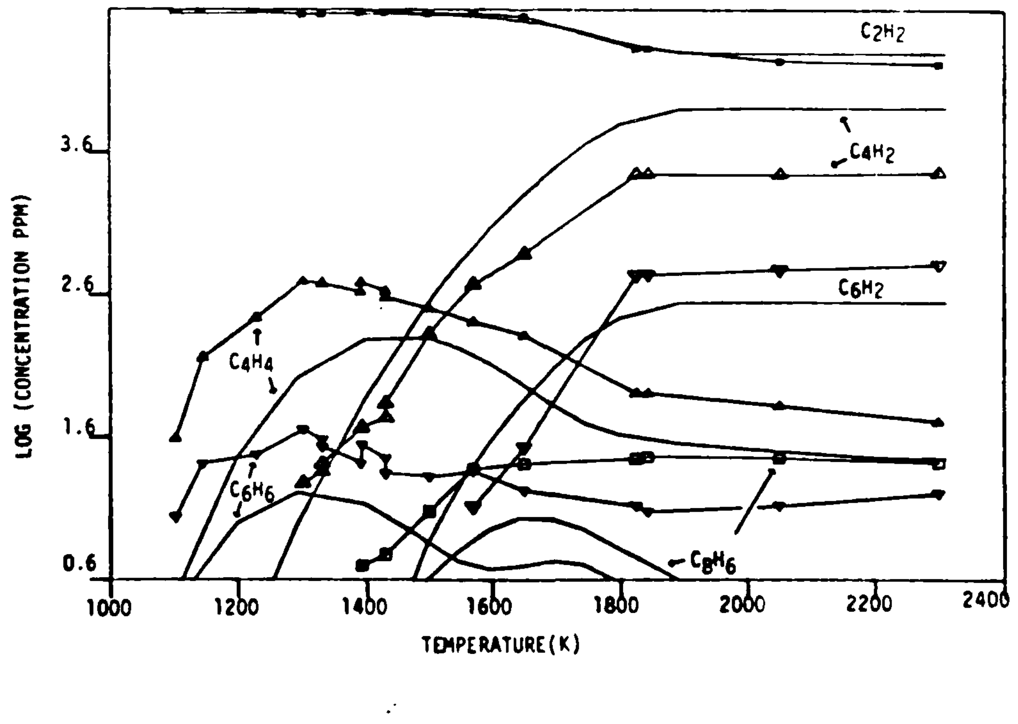

Fig. 4 Experimental and model results for the pyrolysis of 3.7% acetylene.

APPENDIX F

ADDITION OF ALKYL HYDROCARBONS TO AROMATIC RINGS

by

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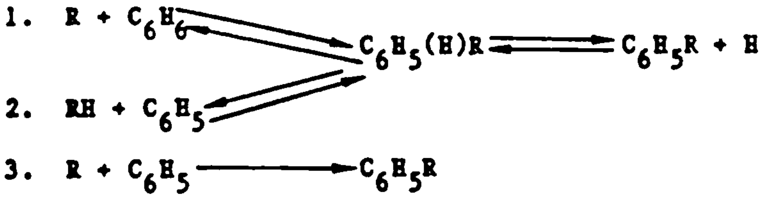
Presentation to ES/CI, December 3-5, 1984
Clearwater Beach, Florida

The addition of alkyl hydrocarbons to aromatic rings is believed to be important in the growth to polyaromatic hydrocarbons in diffusion flames. To examine this problem, we have pyrolyzed 1,3-butadiene in the presence of benzene using a single-pulse shock tube. Butadiene was selected, since the vinyl radical is an important intermediate during its pyrolysis and since 1,3-butadiene is known to pyrolyze at temperatures significantly below those at which benzene pyrolyzes.

Four series of experiments were performed over the temperature range of approximately 1100 to 2000 K, for dwell times of approximately 700 microseconds, and total pressures of approximately five to seven atmospheres. The concentrations in this series of experiments were (1) 0.175% butadiene; (2) 0.175% butadiene, 1.05% benzene; (3) 0.175% butadiene, 4.6% benzene; and (4) 1.1% benzene with the balance argon. The results of the first of these experiments have been described previously (Colket, 1983). In comparison to the pure butadiene pyrolysis, the presence of benzene does little to perturb the overall pyrolysis reactions below about 1450 K except that significant concentrations of toluene, styrene, and phenylacetylene are formed. Above 1450 K, benzene begins to decompose, a significant deficit from the initial mass is observed, and direct comparisons to the pure pyrolysis is questionable. The production of each of the alkylated aromatics in mixtures (2) and (3) can be compared with their production during the pure pyrolyses of butadiene or benzene in Figures 1-3. These figures clearly show significantly enhanced formation of alkylated aromatics due to the presence of benzene. Types of reactions which may be responsible include:



1. $R + C_6H_6 \rightleftharpoons C_6H_5(H)R \rightleftharpoons C_6H_5R + H$
2. $RH + C_6H_5 \rightleftharpoons C_6H_5(H)R$
3. $R + C_6H_5 \longrightarrow C_6H_5R$

When R represents CH_3, C_2H_3, or C_2H, the respective product species are toluene, styrene, and phenylacetylene. It is probable that reactions (1) and (3) can be neglected in the case when $R = C_2H$ since the ratio C_2H/C_2H_2 can be shown to be very low near 1400 K. Alternatively, some of the phenylacetylene may be produced from the decomposition of styrene.

FIG. 2

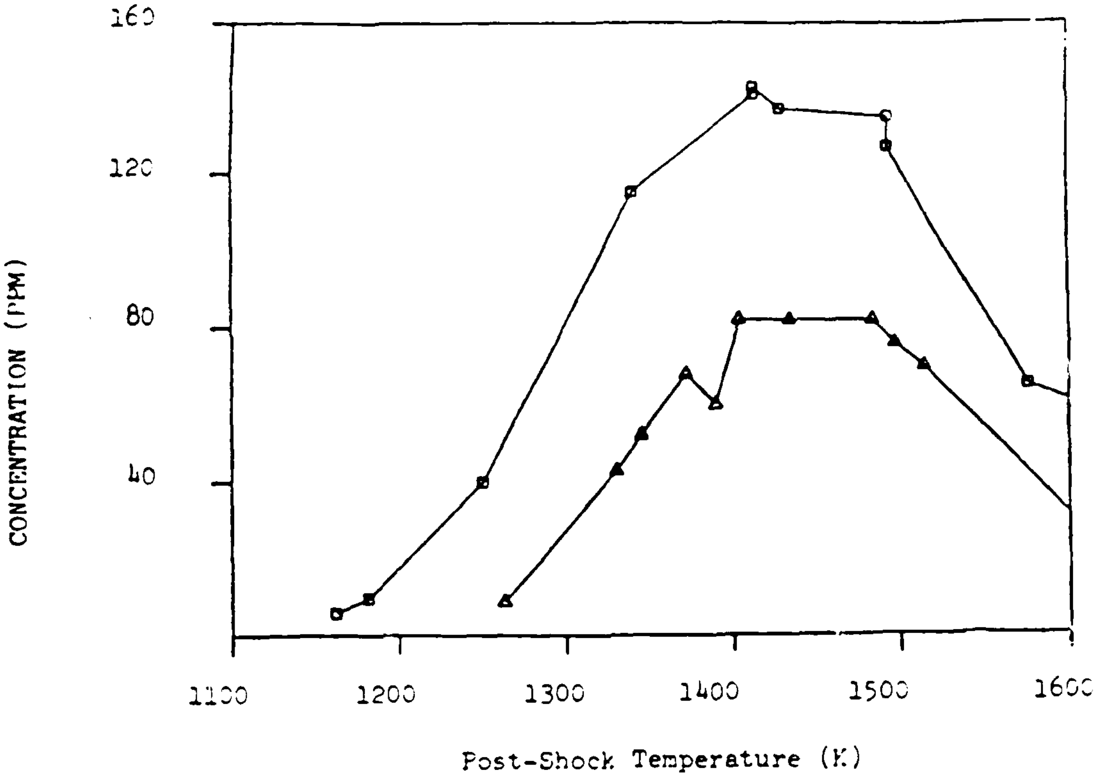


Fig. 2 PRODUCTION OF STYRENE. See Fig. 1 for symbol identification. Negligible styrene was observed at these temperatures during the pyrolysis of the neat fuels.

FIG. 3

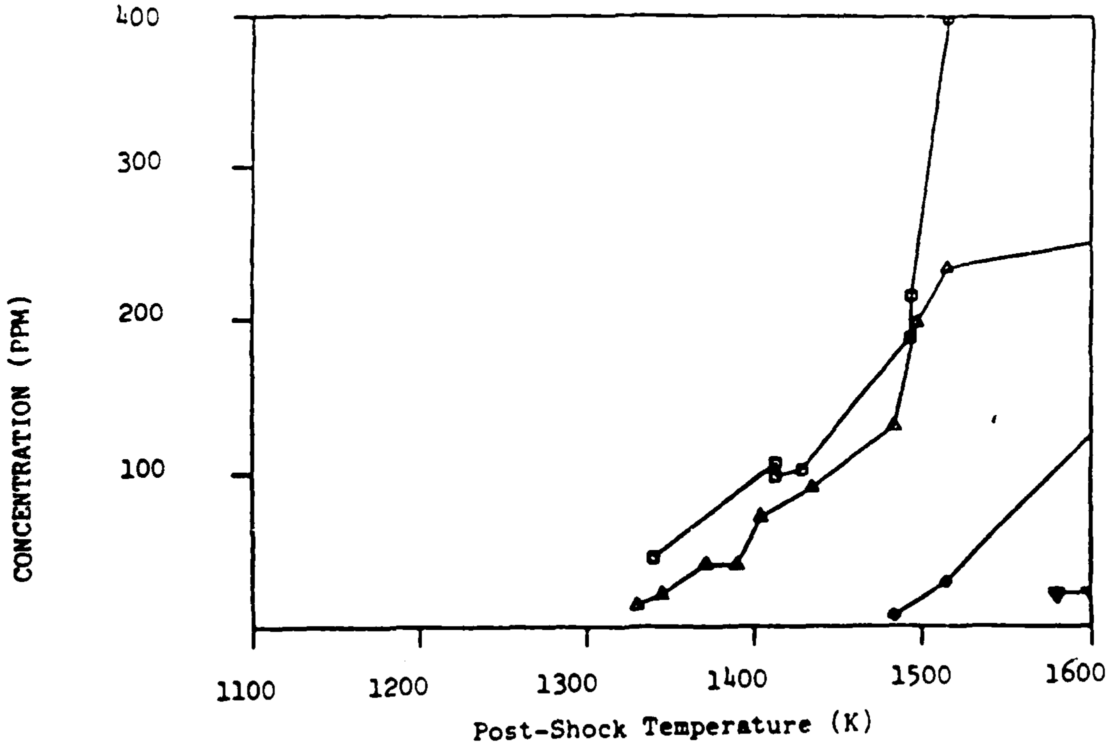


Fig. 3 PRODUCTION OF PHENYLACETYLENE. See Fig. 1 for symbol identification.

AD-A194 744 EXAMINATION OF MECHANISMS AND FUEL-MOLECULAR EFFECTS ON 2/2
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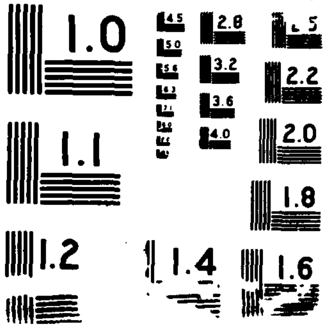
UNCLASSIFIED UTRC/R88-957047 AFOSR-TR-88-0474 F/G 7/4 NL


1.0
1.1
1.2
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6

A surprising experimental result is that an increase in the initial benzene concentration by a factor of about four does not result in a proportional increase in the concentrations of the alkylated aromatics. Very little increase is observed in the case of the toluene or phenylacetylene profiles (below 1450 K) and styrene production is increased only by a factor of 1.5 to 2. The most logical explanation for this result is that the presence of benzene must bring about a significant decrease in concentrations of the alkyl radicals. Furthermore, type 2 reactions are probably not dominant since RH (i.e., CH_4, C_2H_2, and C_2H_4) concentrations are not significantly affected by the presence (or concentration) of benzene, yet an increase in initial benzene concentrations probably results in a corresponding (proportional) increase in phenyl concentrations.

A significant decrease in alkyl radical concentrations can occur if Reactions 1, 3 or $R + C_6H_6 \longrightarrow RH + C_6H_5$ (4) are fast. Since concentrations of alkylated aromatics are about an order of magnitude less than those of C_1- and C_2- hydrocarbons, Reactions 1 and 3 can be neglected relative to Reaction 4. Ignoring thermal decomposition and recombination of radicals, Reaction 4 thus should be compared to $R + C_4H_6 \longrightarrow RH + C_4H_5$ (5).

Reaction 4 should effectively compete with Reaction 5 since the C_6H_6/C_4H_6 ratios for mixture numbers (2) and (3) are about 6 and 25, and since Reaction 4 is only about 2 kcal/mole greater than Reaction 5 (for the prefered route (Cole, 1982) of extraction of a primary hydrogen).

Assuming that Reaction 4 is the dominant loss mechanism for methyl and vinyl radicals, Reaction 1 is the dominant formation route for toluene and styrene, and that phenylacetylene is formed principally from styrene decomposition, then ratios for k_1/k_4 can be estimated to be the ratio of final concentrations of products, i.e., $[C_6H_5R]_f/[RH]_f$. For both methyl and vinyl, k_1/k_4 was found to be approximately .3±.15.

In addition some detailed chemical kinetic modeling has been performed using the shock tube version of the chemkin code (Mitchell and Kee, 1980) but modified to account for the quenching processes in a single-pulse shock tube. The chemical kinetic mechanism proposed by Kiefer, et al, 1984 for butadiene kinetics was used except that the thermal decomposition kinetics of benzene as determined by Fujii and Asaba (1973) were employed. It was found that the profiles for styrene in Figs. 1-3 could be approximately fit regardless of which reaction mechanism was used. The determined rate constants for the vinyl radical when Reactions 1, 2, and 3 were each used individually are $k_1 < 3.5 \times 10^{10}$, $k_2 < 1.2 \times 10^{11}$, and $k_3 < 1.8 \times 10^{13}$ cc/mode-sec and should be considered to be upper limits. These values, however, are critically dependent on the reaction kinetics of the phenyl and vinyl radicals. Additional modeling efforts are in progress to identify which, if any, of the above steps dominate.

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FIG. 1

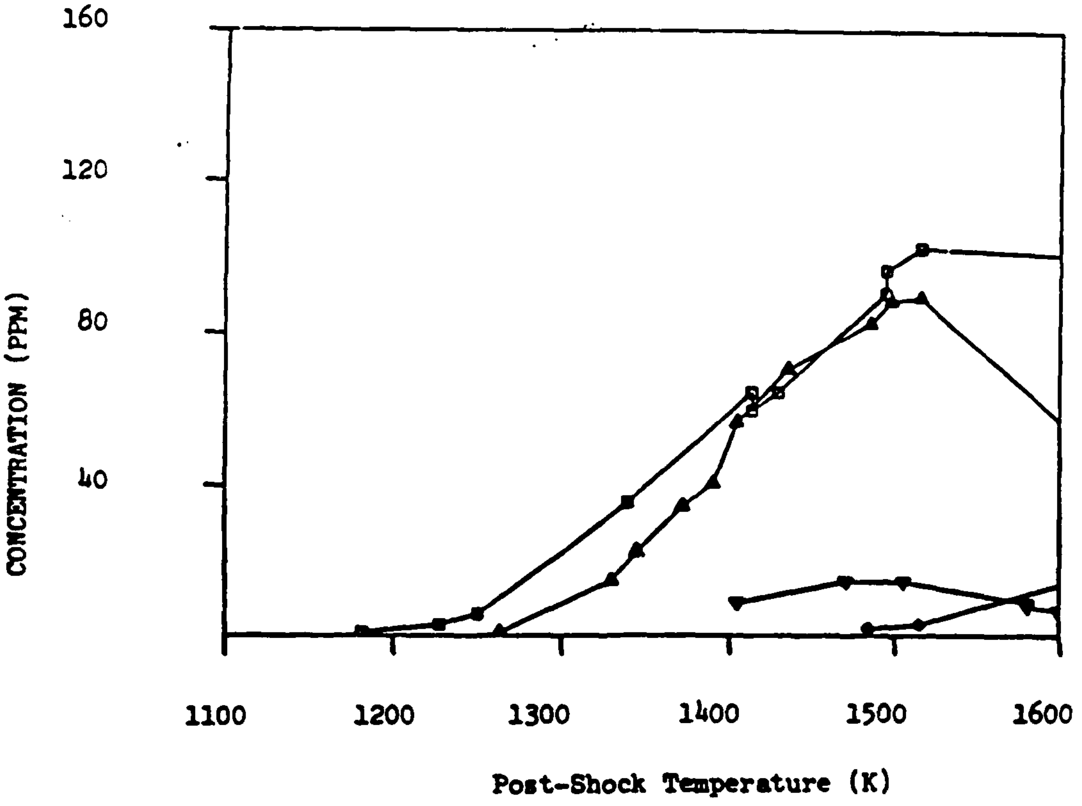

Fig. 1 PRODUCTION OF TOLUENE
□0.17% C_4H_6, 4.6% C_6H_6; △ 0.175% C_4H_6, 1.0% C_6H_6
◇0.17% C_4H_6; ▽ 1.1% C_6H_6. Dwell times are approximately 700 microseconds.

APPENDIX G

PYROLYSIS OF VINYLACETYLENE

by
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Eastern Section of the Combustion Institute
Philadephia, Pa, November 4-6, 1985

Mixtures of 0.01, 0.115, and 1.0% vinylacetylene in argon have been pyrolyzed in a single-pulse shock tube (SPST). Reaction conditions varied from approximately 1100 to 2500 K and 6 to 8 atmospheres and dwell times were about 700 microseconds. Gas samples were collected and analyzed using capillary gas chromatography. Logarithims of the final (quenched) concentrations of stable products are plotted versus initial post-shock temperature in Figs. 1-4. Principal decomposition products at low temperatures and low initial concentrations are acetylene, diacetylene and hydrogen, although acetylene is by far the dominant product. (Hydrogen profiles, although not shown in the figures, are similar to or slightly higher than the profiles for C_4H_2.) With increasing temperature tri- and tetra-acetylenes are produced. At higher concentrations other products are observed including benzene, styrene, phenylacetylene and species not shown in the figures, e.g. methane, ethylene, methylacetylene, a variety of C_5 compounds, C_6H_4, toluene, an unidentified C_9 compound, and naphtalene. The carbon balance was ±5% for the series of 100 and 1150 ppm experiments, although the 1150 ppm series did not extend to elevated temperatures where the largest mass deficits were observed. The mass deficit for the 1% series of experiments was 20-25% at temperatures above 2000 K. The "bell-shape" which has been observed for aromatics was not apparent. Instead, the mass deficit is relatively linear over the temperature range 1400-2000 K and is similar in magnitude and shape to that observed during acetylene pyrolysis at similar concentrations (Ref. 1).

A detailed chemical kinetic model was constructed and model calculations were obtained using a shock tube code (Ref. 2) which has been modified at UTRC to include the effects of the quenching wave in the SPST. The chemical kinetic model principally consists of a model for acetylene pyrolysis which has been based on previous work and has been used to describe recent SPST results (briefly described in Ref. 1). Several reactions specific to the vinylacetylene system were added to this acetylenic mechanism. There are three possible initiation processes:

(1) $C_4H_4 \text{----}\!> i\text{-}C_4H_3 + H$ -98 kcal/mole
(1a) $C_4H_4 \text{----}\!> n\text{-}C_4H_3 + H$ -111 kcal/mole
(1b) $C_4H_4 \text{----}\!> C_2H + C_2H_3$ -122 kcal/mole

where the estimated endothermicities may each be in error by as much as 10 to 15 kcal/mole due to uncertainties in heats of formation of the hydrocarbon radicals. In this work, it was assumed that the principal initiation process was Reaction 1 with a rate expression of $10^{15.2}$ exp(-42800/T) sec^{-1} although the A-factor seems high for the C-H bond scisson. It is important to note that the model results were relatively insensitive to the absolute magnitude of the initiation rate or its temperature dependence. A change of a factor of three in the initiation rate resulted in approximately a 20-30%

change in the overall rate of decomposition and the formation of products. The explanation for this phenomena is that the decomposition of vinylacetylene in the range 1200-1400 K is controlled by a Rice-Herzfeld mechanisms:

		$\log_{10}A$	E
(1) initiation	C_4H_4---->i-C_4H_3 + H	15.2	85000.
(2) chain	H + C_4H_4---->n-C_4H_5	13.13	1379.
(3) chain	n-C_4H_5---->C_2H_3 + C_2H_2	14.82	45060.
(4) chain	C_2H_3---->H + C_2H_2	13.0	46000.
(5)	chain termination		

where Reactions 2-4 account for the majority of the decomposition of the parent and the predominance of acetylene in the low-temperature products. (The Arrhenius factors are given in units of cc, moles, sec and cal/mole.) Termination is rapidly equilibrated with initiation and the overall rate is dependent at most on the square root of the initiation rate. Formation of diacetylene is explained by the chain:

(6)	H + C_4H_4---->i-C_4H_3 + H_2	14.5	14500.
(7)	i-C_4H_3---->C_4H_2 + H	13.0	52500.

although some C_4H_2 is produced via initiation (Reaction 1) followed by Reaction 7.

Production of benzene and styrene near 1400 K is described by Reactions 2 and 3 followed by:

		$\log_{10}A$	E
(8)	C_4H_4 + C_2H_3---->C_6H_7	11.30	0.
	C_6H_7---->c-C_6H_7		
	c-C_6H_7---->C_6H_6 + H		

and

(9)	C_4H_4 + n-C_4H_5----> C_8H_9	13.6	3000.
	C_8H_9---->c-C_8H_9		
	c-C_8H_9---->C_8H_8 + H		

Phenylacetylene is formed principally by

(10)	C_8H_8 + H---->C_8H_7 + H_2	14.48	7000.
	C_8H_7---->C_8H_6 + H		

at low temperatures, although with increasing temperature acetylene addition to phenyl radicals competes. Reactions 8-10 were assumed to be overall processes and non-reversible to simplify the calculations. The value of k_9 appears to be 1 to 2 orders of magnitude higher than expected for a complex process involving addition and cyclization. This rate, however, as well as many others in this system of reactions is highly dependent on the selected thermodynamics and competitive rate proceses both of which critically affect the quasi-steady state concentrations of the radicals. In regards to thermodynamics, heats of formation at 300 K used in the present modeling effort for certain species are reproduced in Table 1 and are literature values. Of note is that the heats of formation of diacetylene and vinyl-like radicals are in general disagreement with values estimated using group additivity techniques. Of specific interest is the necessity of using a high value for the ΔH_f of diacetylene in order to predict properly equilibrium values of diacetylene. A vaule near 108 kcal/mole, which is consistent with group-additivity techniques, results in a significant over prediction of the equilibrium diacetylene concentrations.

The comparison of the experimental data and the model (including chemistry, thermodynamics and quenching processes) is shown in Figs. 1-4 and exhibits an excellent comparison for a wide range of species inspite of a variation of two orders of magnitude in the initial concentration of vinylacetylene.

TABLE I
Selected Thermodynamics at 300 K

Species	Heat of Formation (kcal/mole)	Entropy (cal/mole/k)
C_2H	127.0	49.6
C_2H_3	63.4	54.5
C_4H_2	111.7	59.9
$i\text{-}C_4H_3$	115.2	71.6
$n\text{-}C_4H_3$	128.1	67.7
C_4H_4	69.4	66.1
$n\text{-}C_4H_5$	82.5	69.1
C_6H_5	78.5	69.4
C_6H_6	19.9	65.2
C_8H_6	78.3	79.6
C_8H_8	35.2	82.4

Acknowledgments

This work has been supported by the Air Force Office of Scientific Research (AFSC) under Contract No. F49620-85-C-0012. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

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2. Mitchell, R.E. and Kee, R.J., "A General-Purpose Computer Code for Predicting Chemical Kinetic Behavior Behind Incident and Reflected Shocks" SAND82-8205, Sandia National Laboratories, March, 1982.

FIGURE 1 100 PPM VINYLACETYLENE PYROLYSIS
data vs. model, 700 microseconds

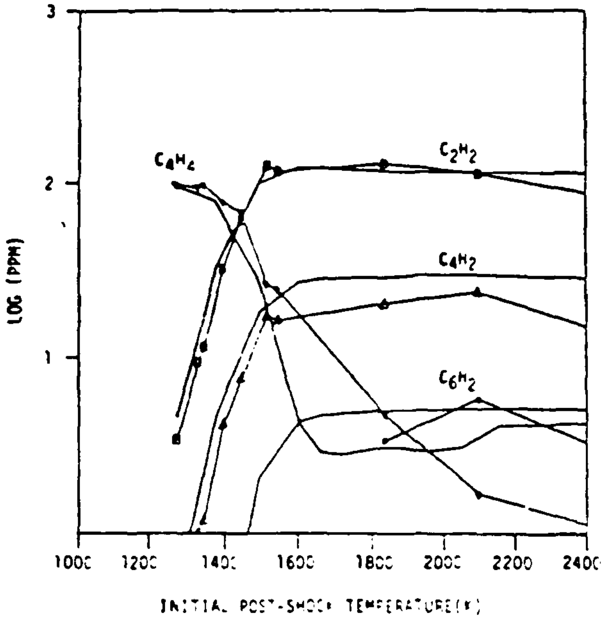


FIGURE 2 0.115% VINYLACETYLENE PYROLYSIS
data vs. model, 700 microseconds

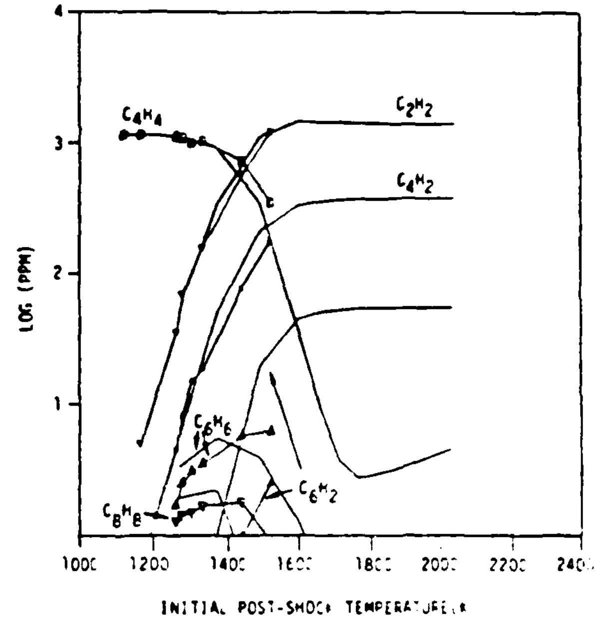


FIGURE 3 1% VINYLACETYLENE PYROLYSIS
data vs. model, 700 microseconds, aliphatics

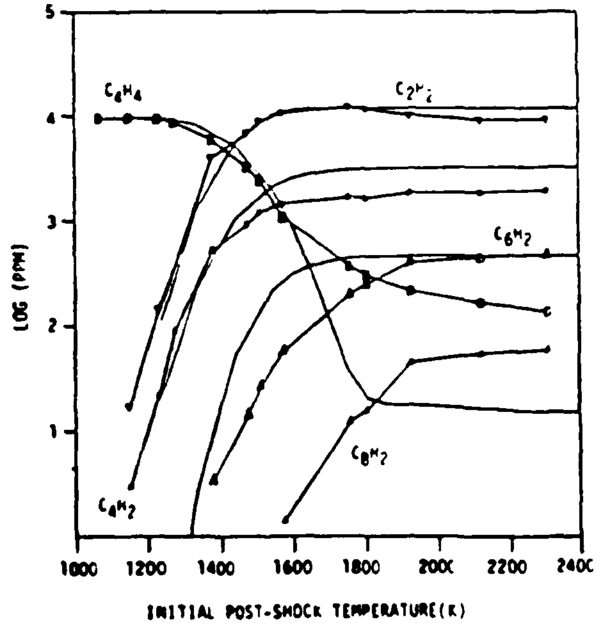
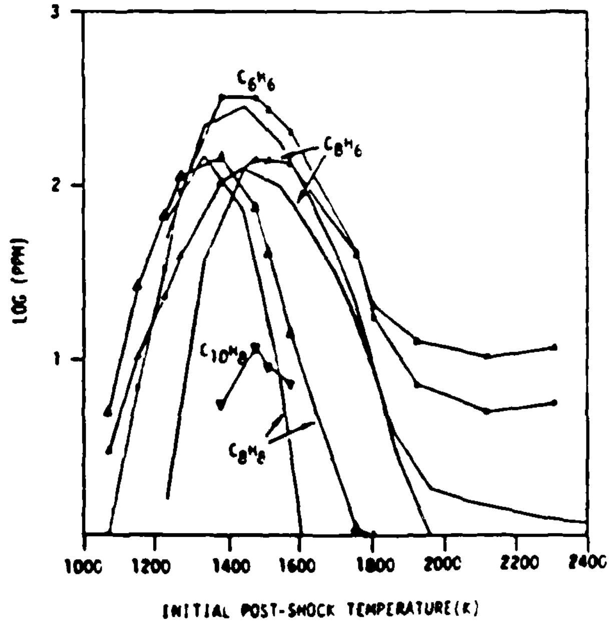


FIGURE 4 1% VINYLACETYLENE PYROLYSIS
data vs. model, 700 microseconds, aromatics



APPENDIX H

Pyrolysis of C_6H_6

by

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Introduction

Several mechanisms for the pyrolysis of benzene at elevated temperatures have been previously proposed. Unfortunately, none of these mechanisms is entirely satisfactory when both experiments and thermodynamics are considered. Yet, knowledge of benzene decomposition will increase the understanding of the breakup and formation of other aromatic compounds. Consequently, a single-pulse shock tube (SPST) investigation of the pyrolysis of benzene has been performed over the temperature range of 1200 to 2400K. In addition, thermochemical estimates and detailed chemical kinetic modeling have been performed to evaluate the previously proposed mechanisms for benzene pyrolysis.

Description of Facilities and Model

The 3.8 cm (i.d.) single-pulse shock tube (SPST) used in this experiment utilizes the "magic hole" technique for quenching pyrolyzed samples at rates above 10^5 K/sec. SPSTs were developed by Glick, Squire, and Hertzberg (1) and the UTRC facility has been described by Colket (2). Gas samples, after dwell times of approximately 700 microseconds, were automatically collected and analyzed for reactant and products using heated gas sampling valves and a Hewlett Packard 5880A gas chromatograph. With a CP Sil 5 CB (from Chrompack, Inc.) capillary column and a silica gel packed column, H_2 and hydrocarbons up to C_{10} were identified and quantitatively analyzed.

Argon (99.999% pure) was obtained from Matheson and LC-grade benzene was obtained from the Burdick and Jackson Laboratory. The initial mixture concentration was 130 ppm benzene in argon and was prepared gravimetrically. Gas chromatographic analysis indicated that impurities included unidentified C_5, C_6 and C_7 hydrocarbons as well as toluene, although the total concentration of impurity was less than 0.2% of the initial benzene.

Detailed chemical kinetics calculations are performed using CHEMKIN(3), LSODE (4), and a version of a shock tube code (5) which has been modified to include the quenching effects in a SPST. Quenching rates varied with shock strength and were calculated using measured pressure traces and assuming isentropic expansion. The modified code also allows monitoring of time-dependent contributions from each reaction to the formation and/or destruction of each species.

Proposed Mechanisms

Mechanisms for the decomposition of benzene are listed in Table I. It is important to note that most are not single-step mechanisms. Radical intermediates equilibrate rapidly and their concentrations are sufficiently low to render them (nearly) undetectable in many systems. Experimental results from the present and previous high temperature works (6,7) suggest that primary stable products are acetylene, diacetylene, and hydrogen and the initial production rate of acetylene is two to three times higher than that of diacetylene. Unfortunately, this information is of minimal use in sorting out the mechanisms since benzene pyrolyzes at high temperatures (relative to pyrolysis temperatures of other hydrocarbons) and all intermediates shown in Table II rapidly pyrolyze to the approximate mixture of acetylene and diacetylene that has been observed.

Mechanism A is the generally accepted reaction sequence; however, only Reaction 1 is understood. The breaking of the C-H bond is believed to be the initiation step in both pyrolytic and some oxidation studies. Its rate has been determined from D-atom production (in pyrolysis of C_6D_6) (8) and from detailed modeling studies of both pyrolysis (9) and oxidation (10). An RRKM fit has been performed by Kiefer, et al (9) using available experimental data and is consistent with thermodynamics. Their k_1^∞, is given by $10^{17.3}$ exp(-118 kcal/RT) sec^{-1}. Knowledge of the mechanism for phenyl decomposition is substantially less than that for Reaction 1. Some information is available on the overall rate, k_3; yet the details of the ring fracturing process have not been defined. The thermochemical estimate by Fujii and Asaba (11) has been until recently the most often quoted rate for this process. More recent modeling (8,9) of benzene pyrolysis has produced similar rates as Ref.11; however, since Reaction 1 is rate limiting over most of the temperatures regimes examined, the modeling results for k_3 are expected to be lower limit estimates with large uncertainties in the temperature dependence. The Fujii and Asaba (11) estimate, $k_3 = 3.16 \times 10^{14}$ exp (-86 kcal/RT) sec^{-1}, was based on an "old" value for the heat of formation for i-C_4H_3 of 102 kcal/mole (12); however, more recent estimates using group additivity (13) and BAC-MP4 (14) techniques fix this value closer to 115 kcal/mole. In addition, n-C_4H_3, which has a ΔH_f of 126 kcal/mole, is the preferred isomer for phenyl decomposition. Consequently, Reaction 3 is over 100 kcal/mole endothermic. If this process involves direct C_2H_2 elimination, then the previous modeling efforts that produced lower limit rates strongly suggest that the high pressure A-factor is at least $10^{17.8}$. This value is orders of magnitude higher than what would be expected for this multibond process. Consequently, it must be assumed that Reaction 3 represents an overall process or that processes involving radicals other than, or in addition to, phenyl are important to benzene decomposition.

One alternative route for benzene decomposition is direct C_2H_2 elimination (Mechanism B) and has received recent support (6,8); however, Kiefer, et al (9) have shown it is not necessary to invoke this step to describe experimental profiles. In addition, it should be noted that the direct elimination is a multibond process which should be unlikely, and presumably involves the intermediate formation of the C_4H_4 diradical. For this intermediate, the effective activation barrier to Reaction 4 may be as high as 180 kcal/mole.

Another possible pyrolysis route involves the production of benzyne, which subsequently decomposes. Unimolecular decomposition of phenyl (Reaction 5) to benzyne is endothermic by 93 kcal/mole, which is nearly as much as Reaction 3. Similar thermochemical arguments can eliminate this decomposition route. The other route, Reaction 6, is a radical termination step and would produce an overall slowing of benzene pyrolysis. Knudsen cell pyrolysis experiments (7) have shown the formation of a C_6H_4 compound. Assuming this compound is benzyne or another product of phenyl decomposition, Smith and Johnson (7) argued that C_6H_4 is an important intermediate during benzene decomposition, especially at elevated temperatures. At least some of the product, however, may be composed of the chained isomers of C_6H_4. These isomers may be produced via hydrogenation of triacetylene, which was also observed in significant concentrations. Consequently, no clear evidence of the importance of Mechanism C is apparent.

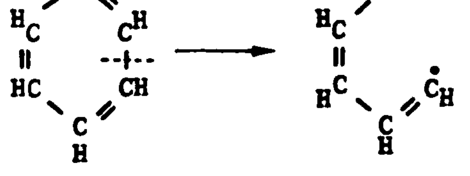
Mechanism D appears to be very attractive, since an extrapolation of the rate coefficient (15) for H-atom addition to benzene (Reaction 8) is approximately an order of magnitude higher (Ref. 9) than H-atom abstraction (Reaction 2) at 1600 K. The addition reaction, however, competes with its reverse reaction. Using thermodynamics for $c\text{-}C_6H_7$ derived from measurement of the forward and reverse rates of Reaction 8 (15), Mechanism D can be shown to have a negligible impact on benzene pyrolysis. However, a different set of thermodynamics for $c\text{-}C_6H_7$ reported in Ref. 15 suggests that Mechanism D may play an important role at low temperatures. Detailed modeling calculations using Mechanism D were limited, due to what appears to be rather large uncertainties in both the heat of formation and entropy. Nevertheless, there are attractive features of this decomposition mechanism, especially at low temperatures, and it should be explored further. It is worth noting that Reaction 8 is not sufficiently energetic (only 16 to 26 kcal), that it can be followed immediately by Reaction 9 (71-81 kcal required). Instead, $c\text{-}C_6H_7$ will collisionally thermalize prior to its decomposition to products. Only a minimal acceleration in rate due to the formation of an excited complex can be expected. Further exploration of this route (Mechanism C) should be performed.

With no fully satisfactory alternatives, and the expectation that phenyl must decompose to aliphatics at sufficiently elevated temperatures (when production of phenyl via Reaction 1 is fast), it is prudent to re-examine Mechanism A. One can separate Reaction 3 into the following sequence:

$C_6H_5 \leftrightarrow 1\text{-}C_6H_5$ 3a

$1\text{-}C_6H_5 \rightarrow n\text{-}C_4H_3 + C_2H_2$ 3b

This sequence is the reverse of the processes suggested for the formation of phenyl during acetylene pyrolysis (17) and has been shown to compare favorably with recent experimental data (2). If one assumes that the ring breaks at the single bond as shown



then this is a relatively straightforward process analogous to the decomposition of nC_4H_5; i.e. $CH{:}CH.CH{:}CH_2 \rightarrow C_2H_2+C_2H_3$. Breakage of either of the other two single-bonds would require a more complex process involving H-atom shifting or the formation of energetic intermediates. The resultant linear compound would be expected to decompose to acetylene and $n\text{-}C_4H_3$ or re-cyclize to phenyl. Detailed chemical modeling was performed using the reaction sequence in Table II coupled with an acetylenic mechanism similar to that reported (17, 18). A comparison of the model and single-pulse shock tube data is presented in Figure 1 for a series of shocks at an initial concentration of 130 ppm benzene in argon. In this figure, final concentrations produced after a dwell time of 700 microseconds followed by quenching are plotted as a function of initial post-shock temperature. Total pressure for these experiments is approximately seven atmospheres.

The comparison is quite reasonable. The higher fractional decomposition at low temperatures observed in the experiment may be due to impurities from the wall initiating the reaction at low temperature. The residual benzene observed experimentally at elevated temperatures may be caused by sampling a portion of the boundary-layer near the walls of the shock tube. The mechanism proposed in Table II is essentially consistent with Kiefer et al's except that Reaction 3 has been separated to 3a and b. An effective rate constant for Reaction 3 can be estimated by assuming a steady-state concentration for $l\text{-}C_6H_5$, i.e.

$$[l\text{-}\ C_6H_5]_{s.s.} = \frac{k_{3a}[C_6H_5]}{(k_{-3a}+k_{3b})}$$

therefore $k_3^{\text{effective}} = \dfrac{k_{3a}\ k_{3b}}{k_{-3a}+k_{3b}}$

This curved evalution is depicted as a solid line in Fig. 2 over the temperature regime where sensitivity to this rate was observed. The curve is extrapolated to both low and high temperatures to facilitate comparisons to other evaluations. The relatively high values obtained in this work for k_1 and $k_3^{\text{effective}}$ are not surprising since the rate constant determined in these experiments are expected to be close to the high pressure limiting value.

Conclusions

Previously proposed mechanisms for the pyrolysis of benzene at high temperatures have been reviewed using detailed chemical modeling and a brief thermochemical examination. The most widely accepted sequence, $C_6H_6 \rightarrow C_6H_5(+H) \rightarrow C_4H_3+C_2H_2$, is slightly modified to $C_6H_6 \rightarrow C_6H_5(+H) \rightarrow l\text{-}C_6H_5 \rightarrow n\text{-}C_4H_3+C_2H_2$ and the structure of the linear C_6H_5 intermediate is proposed. Forward and reverse rates are consistent with thermochemistry and experimental data. A benzene decomposition route involving $c\text{-}C_6H_7$ and $l\text{-}C_6H_7$ was examined, yet sufficiently accurate thermochemistry was not available to reach final conclusions.

Acknowledgements

This work has been supported by the Air Force Office of Scientific Research (AFSC) under Contract No. F49620-85-C-0012. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

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TABLE I
Previous Mechanisms for Benzene Pyrolysis

A	$C_6H_6 \rightarrow C_6H_5+H$	(1)
	$H+ C_6H_6 \rightarrow C_6H_5+H_2$	(2)
	$C_6H_5 \rightarrow C_4H_3+C_2H_2$	(3)
B	$C_6H_6 \rightarrow C_4H_4+C_2H_2$	(4)
C	$C_6H_5 \rightarrow C_6H_4+H$	(5)
	$H+ C_6H_5 \rightarrow C_6H_4+H_2$	(6)
	$C_6H_4 \rightarrow C_4H_2+C_2H_2$	(7)
D	$H+ C_6H_6 \rightarrow c\text{-}C_6H_7$	(8)
	$c\text{-}C_6H_7 \rightarrow 1\text{-}C_6H_7$	(9)
	$1\text{-}C_6H_7 \rightarrow n\text{-}C_4H_5+C_2H_2$	(10)

TABLE II
Proposed Reaction Sequence for Benzene Pyrolysis

		Forward rate		Reverse Rate		
		$\log_{10}A$	E cal/mole	$\log_{10}A$	n	E cal/mole
1.	$C_6H_6 \rightleftarrows C_6H_5+ H$	16.18	107,900.	10.05	0.98	-5690.
2.	$H+C_6H_6 \rightleftarrows C_6H_5+ H_2$	14.40	16,000.	8.35	1.12	6420.
3a.	$C_6H_5 \rightleftarrows l\text{-}C_6H_5$	14.00	65,000.	13.11	-0.68	3300.
3b.	$l\text{-}C_6H_5 \rightleftarrows n\text{-}C_4H_3+C_2H_2$	15.34	38,000.	5.97	1.97	-3610.
11.	$n\text{-}C_4H_3 \rightleftarrows H+C_4H_2$	12.43	37,000.	11.29	0.44	-2790.
12.	$n\text{-}C_4H_3 \rightarrow C_2H+C_2H_2$	14.60	54,000.	7.89	1.66	-3120.
13.	$C_2H+C_6H_6 \rightarrow C_2H_2+C_6H_5$	13.30	0	12.00	0	12520.

FIGURE 1. 130PPM BENZENE PYROLYSIS
COMPARISON OF MODEL AND EXPERIMENT

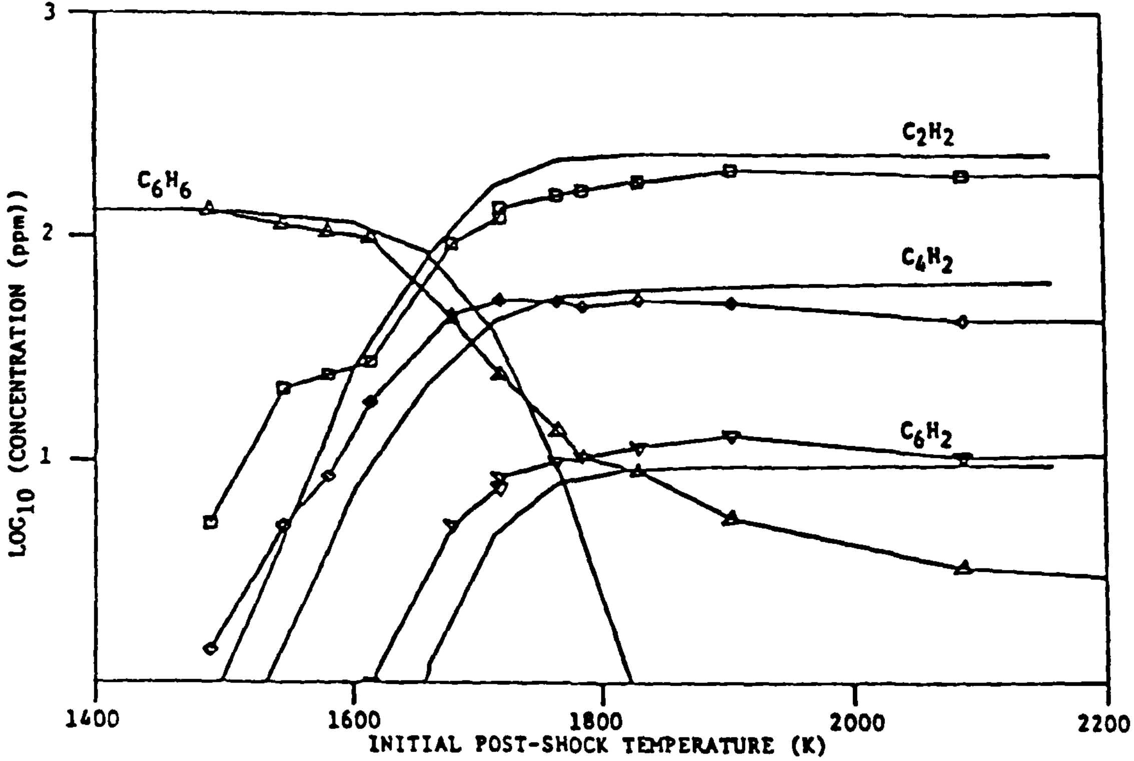
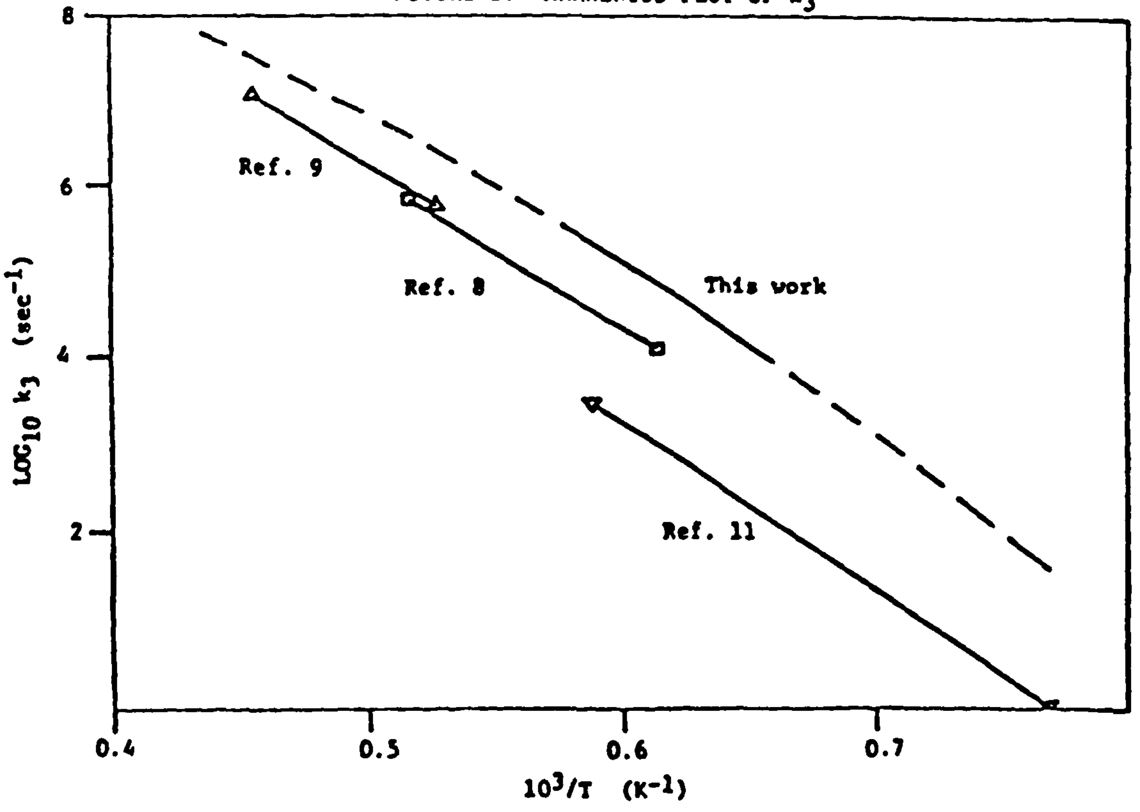


FIGURE 2. ARRHENIUS PLOT OF k_3



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