IDENTIFICATION AND TEMPORAL BEHAVIOR OF RADICAL INTERMEDIATES

FORMED DURING THE COMBUSTION AND PYROLYSIS OF GASEOUS FUELS:

KINETIC PATHWAYS TO SOOT FORMATION

FINAL PERFORMANCE REPORT

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FINAL PERFORMANCE REPORT

We have completed eight major research projects during the period July 1994 - June 1997. The results have been presented at major scientific meetings and have either been published, are in press, or have been submitted. In addition, we have developed software in-house to automate the processing of peak heights recorded from our shock tube: time-of-flight mass spectrometer (TOF) experiments in a format suitable for our modeling programs and have performed numerous *ab initio* calculations to provide energy barrier values and thermodynamic data for several key reactions in various reaction mechanisms.

These advances are presented here in summary form; the reader is referred to the enclosed reprints for additional detail.

1.   Propargyl Chloride

In our previous TOF studies of allene and 1,2 butadiene pyrolysis, we proposed that propargyl radical is a key species for benzene production and subsequently for soot formation. This idea has since gained general acceptance via independent experiments performed by other workers using a variety of analytical techniques and substantiated by modeling calculations. In order to test this proposition further, we studied the decomposition of propargyl chloride and presented a paper at the 19th International Symposium on Shock Waves.

We were initially surprised by the near absence of m/e 78 (C_6H_6) in a 3% C_3H_3Cl - Ne mixture in the temperature range 1350 - 1600 K, although C_3H_3Cl readily decomposes yielding C_2H_2, C_4H_2 and HCL.

However, in mixtures of C_3H_3Cl containing H_2, benzene is readily observed in the same temperature range. Experiments on a 3% C_3H_3Cl - 5% D_2 - 92% Ne mixture revealed a constant temporal HCl/DCl product ratio that is approximately equal to 5, as shown in the following figure.

3% C_3H_3Cl- 5% D_2 1350 K, 0.232 atm
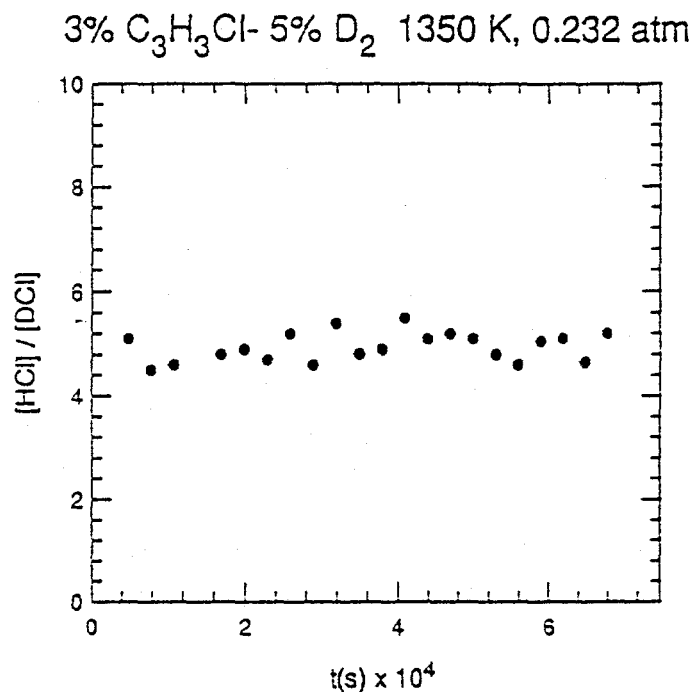
We reasoned that if C - Cl is the major initiating reaction, the HCl/DCl ratio would be < 1 due to the reaction of $Cl + D_2 - DCl + D$. This proposal is clearly contrary to the observed HCl/DCl ratios. Therefore, we proposed that 83% of the C_3H_3Cl dissociation yields HCl and singlet cyclopropenylidene (C_3H_2) and the second channel results in propargyl radical and Cl.

$$C_3H_3Cl \longrightarrow \text{(structure with H, Cl)} \longrightarrow HCl + \text{(structure)} + 54 \text{ kcal/mol, (83\%)}$$

$$C_3H_3Cl \longrightarrow C_3H_3 + Cl \qquad + 72 \text{ kcal/mol, (17\%)}$$
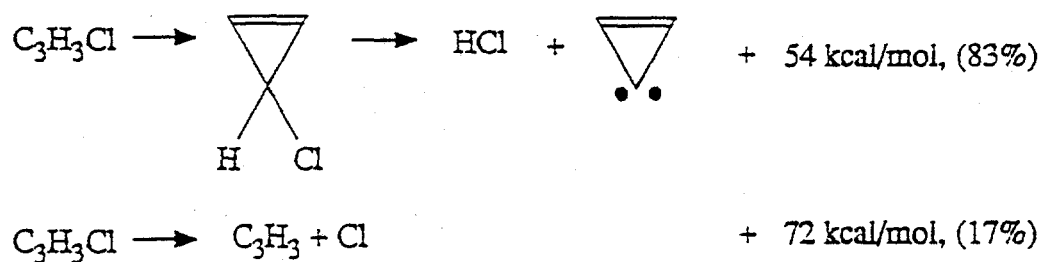
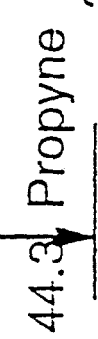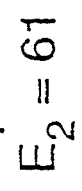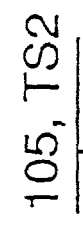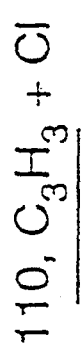In the presence of H_2, C_3H_2 reacts exothermically to form the thermally excited adduct $C_3H_4^{\bullet}$ which readily isomerizes to either allene or propyne as predicted by a bimolecular-QRRK calculation. The calculation at 1450 K and 225 torr reveals that the formation of allene and propyne accounts for 83% of the product distribution. The prefix c represents the cyclic species.

allene

c-C_3H_3 + H

$B_c k_S$ [M]

$C_3H_4A^*$ $\xrightarrow{k_5}$ C_3H_3 + H

k_2 k_3 k_4

c-C_3H_2 + H_2 $\underset{k_1}{\overset{k_0}{\rightleftharpoons}}$ c-$C_3H_4^*$

k_6 k_7

$C_3H_4P^*$ $\xrightarrow{k_8}$ C_3H_3 + H

$B_c k_S$ [M]

c-C_3H_4

$B_c k_S$ [M]
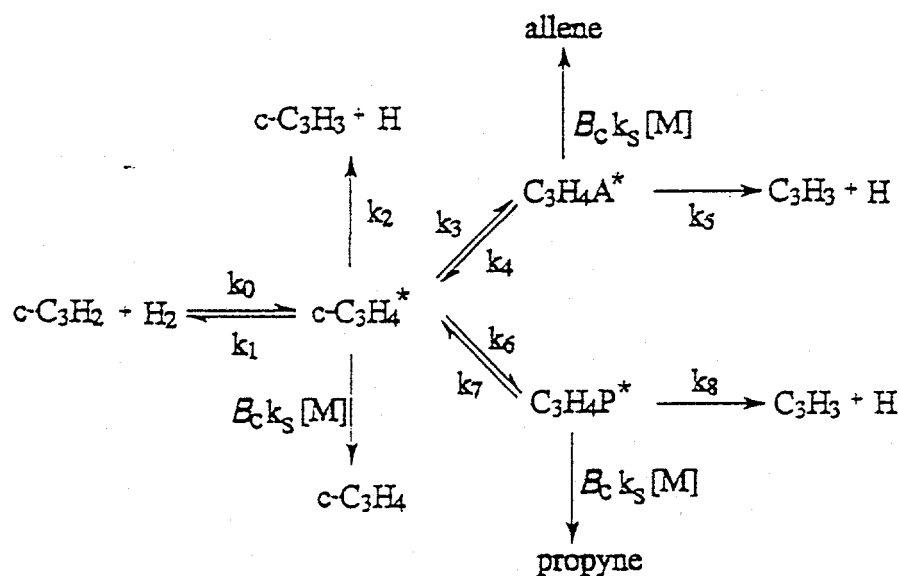
propyne

	k_i/k^0
k_{stable}(c-C_3H_2 + H_2 → C_3H_4P)	0.498
k_{stable}(c-C_3H_2 + H_2 → C_3H_4A)	0.332
k_{rxn}(c-C_3H_2 + H_2 → C_3H_3 + H)	0.087
k_{stable}(c-C_3H_2 + H_2 → c-C_3H_4)	0.011
k_{rxn}(c-C_3H_2 + H_2 → c-C_3H_3 + H)	1×10^{-7}

The energized $[C_3H_4]^{\bullet}$ adduct leads primarily to allene and propyne as shown on the energy diagram shown on the next page; CP, CPCl and PrCl represent cyclopropene, cyclopropenyl chloride and propargyl chloride, respectively.

Furthermore, additional experiments were performed with mixtures of C_3H_3Cl + allene, C_3H_3Cl + propyne, C_3H_3Cl + C_2H_2 and C_3H_3Cl + C_2H_4. All of these mixt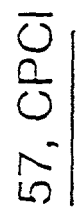ures exhibited benzene production at temperatures 200 - 300 K lower than required for benzene formation in either allene or propyne mixtures. The results may be viewed in Figures 1-6 of the accompanying reprint.

Energy (kcal/mol)

140 — 120 — 100 — 80 — 60 — 40

133, C_3H_3 + H

112, TS1

$E_1 = 66$

45.9 Allene

114, H_2 + C_3H_2, $[C_3H_4]^*$

92, HCl + C_3H_2

66, [CP]

57, CPCl

110, C_3H_3 + Cl

105, TS2

$E_2 = 61$

44.3 Propyne

38.1, PrCl

TS1:

TS2:
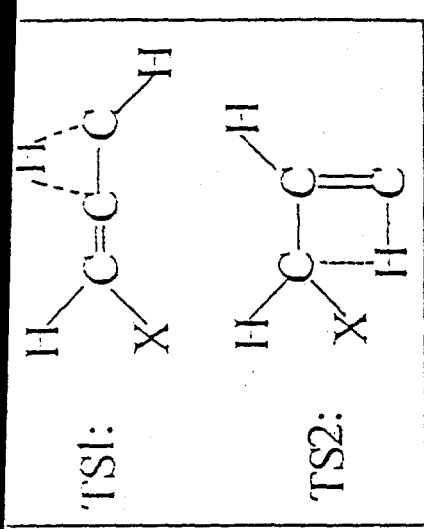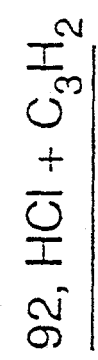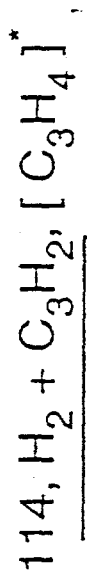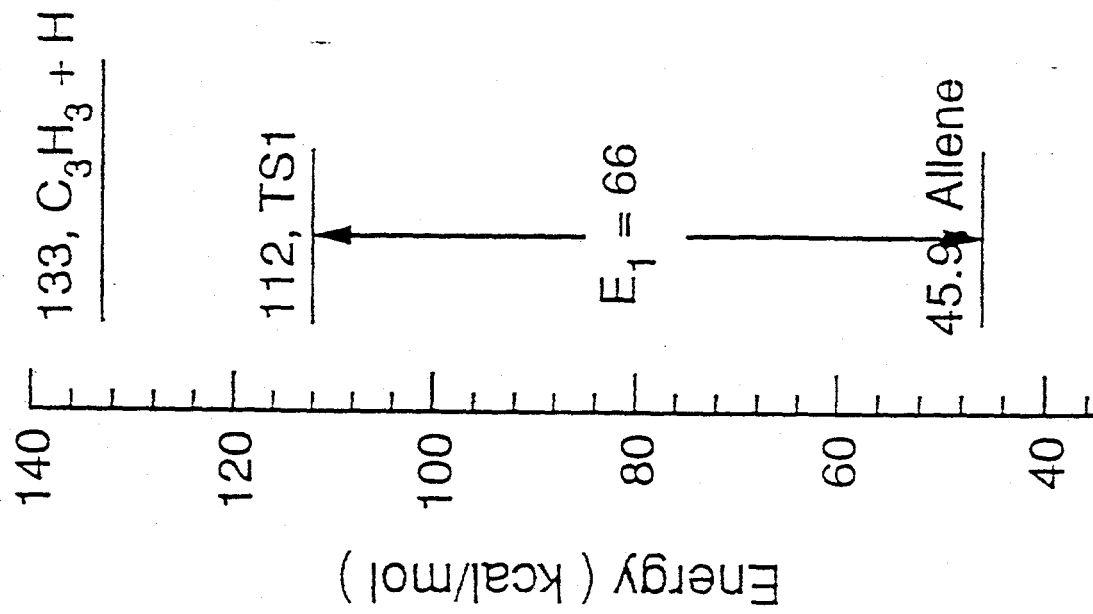
2. Propargyl Bromide

Although a reaction mechanism was proposed to model the six different mixtures in the propargyl chloride study successfully, there are several key rate constants that are not well established, particularly for allene and propyne decomposing in the fall-off region. In order to remedy these uncertainties, we commenced a collaborative effort with Professor John Kiefer using the laser schlieren (LS) technique to measure the dissociation rates of allene and propyne at high temperatures in our pressure regime (~ 0.4 atm) and to measure rates of benzene formation. Part of that effort was presented at the 25th International Combustion Symposium and was published in the Combustion and Flame issue devoted to symposium papers.

To gain additional knowledge of the precursor C_3H_3 and the subsequent formation of benzene, we shocked the following mixtures of propargyl bromide in neon diluent: 3% C_3H_3Br, 3% C_3H_3Br - 5% H_2; 3% C_3H_3Br - 5% D_2. The experiments were performed over the temperature and total pressure range 1310 - 1740 K and 0.20 - 0.34 atm, respectively. Comparisons of the results to those obtained previously with C_3H_3Cl are quite interesting.

In contrast to the observation of only minor amounts (~ 10^{-9} mol/cm^3) of benzene produced in a 3% C_3H_3Cl - Ne mixture in the range 1350-1600 K, m/e 78 appeared readily in the 3% C_3H_3Br - Ne mixture over the range 1310 - 1470 K; e.g., benzene concentrations of 6.4 x 10^{-9} mol/cm^3 were recorded at 1320 K. Addition of 5% H_2 into mixtures of either 3% C_3H_3Cl or 3% C_3H_3Br resulted in ten-fold increases in benzene concentrations; e.g., 7.0 x 10^{-9} mol/cm^3 for the C_3H_3Cl - H_2 mixture at 1380 K and 6.2 x 10^{-8} mol/cm^3 for the C_3H_3Br - H_2 mixture at 1350 K.

Mixtures of 3% C_3H_3Cl - 5% D_2 and 3% C_3H_3Br - 5% D_2 yielded quite different values for the ratios HCl/DCl (~ 5) and HBr/[DBr + Br] (~ 1) as shown in the figure on the next page. An analysis of these results revealed that Cl atoms are in very low concentrations (below the TOF

detectability threshold) in the propargyl chloride experiments whilst Br atoms are significantly above the threshold in the propargyl bromide runs. From the value of the HBr/[DBr + Br] ratio, we reasoned the following reactions contribute equally to the initiation process. C-C_3H_2 is singlet cyclopropenylidene.

$$C_3H_3Br + M \rightarrow c\text{-}C_3H_2 + HBr + M$$
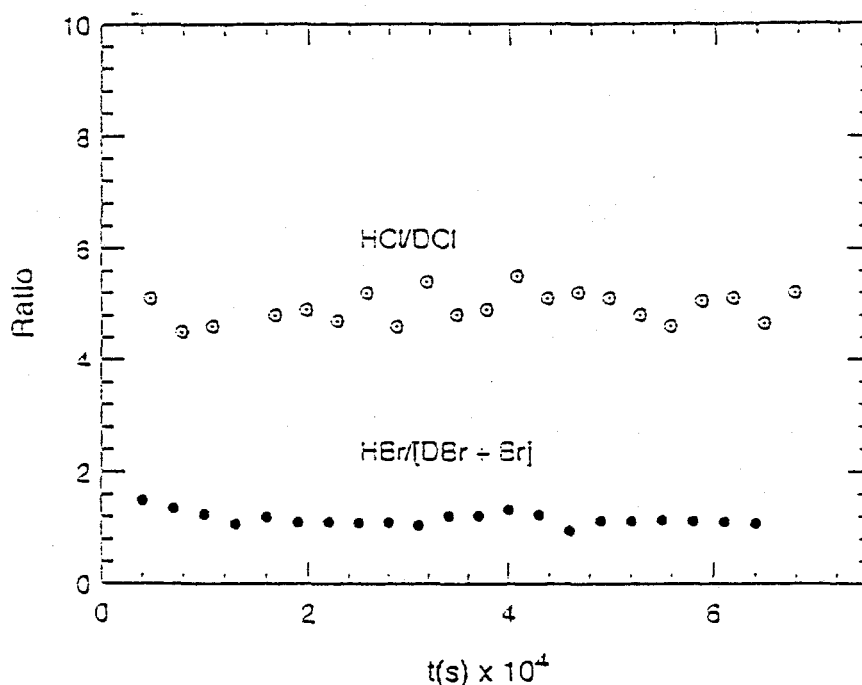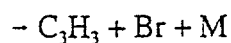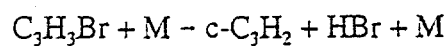
$$\rightarrow C_3H_3 + Br + M$$

An energy diagram shown in Fig. 2 of the enclosed reprint helps us understand the reaction scheme pertinent to benzene production in mixtures of C_3H_3Br (PrBr) with and without H_2. The heat of formation for the intermediate species 3-bromocyclopropene (CPBr) was calculated from group additivity; that for C_3H_3 is derived from high-level computations by Bauschlicher and Langhoff for the C-H bond energy in propyne. The energies for the various transition states were adapted from calculations of the allene $\rightleftharpoons$ propyne isomerization by such authors as Miller, Melius, Oref, Saito and

Yoshimine. The diagram reveals that molecular elimination of HBr and CPBr is endothermic by 38 kcal/mol; production of C_3H_3 + Br from PrBr is endothermic by 62 kcal/mol. Molecular elimination of hydrogen from cyclopropene (CP) to form c-C_3H_2 + H_2 is endothermic by 48 kcal/mol. Reaction of c-C_3H_2 with H_2 to form propyne via a thermally energized adduct $[C_3H_4]^*$ is exothermic by 69.7 kcal/mol; to form the products C_3H_3 + H is endothermic by 22 kcal/mol. A more likely route to C_3H_3 is the following disproportionation reaction.

$$c\text{-}C_3H_2 + C_3H_4 \rightarrow 2\ C_3H_3 \qquad \Delta H_r = 10 \text{ kcal/mol}$$
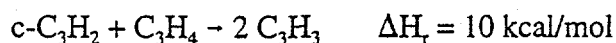
A mechanism consisting of the thermodynamic data for 19 species and 24 reactions was employed to model the major species observed: C_3H_3Br, Br, HBr, C_2H_2, C_4H_2, C_6H_2 and C_6H_6 (benzene).

The channel producing C_3H_3, C-Br fission, requires much less energy than the C-Cl fission in C_3H_3Cl; 62 vs 75 kcal/mol. This effect is apparent in the subsequent formation of benzene recorded for mixtures of C_3H_3Cl (only minor amounts) and C_3H_3Br (readily observed at 1300 K). Adding H_2 to the C_3H_3Br mixture improves the carbon atom balances from 70% to 95% and results in a ten-fold increase in benzene formation at comparable reaction conditions.

It is pleasing to note that the core mechanism utilized to model the C_3H_3Cl results was essentially unchanged for C_3H_3Br pyrolysis except for the inclusion of reactions pertinent to bromine containing species. The results are also in accord with the experiments of Homann involving reactions of either C_3H_3Br or C_3H_3Cl with sodium vapor in which benzene was formed via the dimerization of C_3H_3 radicals and the rate constants for propargyl radical recombination measured by Curl and Glass.

3. Ethylene

It would be ideal to observe simultaneously the concentrations of all species from H-atoms to high molecular weight products that appear during the observation time of the reaction. However, there are difficulties encountered in obtaining comparable TOF mass spectral sensitivities for low and high mass species. In order to explore and hopefully remedy this problem, the thermolysis of a reasonably known system, ethylene, was studied over a range of initial reactant concentrations ($1.5\text{-}4.8 \times 10^{-8}$ mol/cm^3), temperature (2000-2435 K), and total pressure (0.34-0.47 atm). Various mixtures of C_2H_4 in a Ne-1% Ar diluent revealed profiles of C_2H_4 disappearance and C_2H_2 appearance that were successfully modeled using rate constants available from shock tube studies of ethylene and acetylene. The mass spectral sensitivity factor to convert peak heights of acetylene to concentrations was derived from experiments on a 2% C_2H_2 mixture in Ne-Ar diluent at non-reacting temperatures, 1500-1800 K. Attempts to record reliable profiles for H_2 were not successful despite extensive adjustments of the TOF ion source and drift tube magnets. It was possible to obtain profiles for D_2 using C_2D_4 as the initial reactant.

The mass spectral sensitivity factor for deuterium was derived by shocking various mixtures of D_2-Ne in the temperature range 1600-2200 K. The factor is reasonably constant at these elevated temperatures but remarkably different from the value measured at room temperature. The reaction profiles revealed C_2D_2 to be the major product with lesser amounts of C_4D_2 appearing at high temperatures. The thermal data for C_2D_4, C_2D_2 and D_2 are from a 1994 tabulation by Burcat and McBride. The thermal properties of C_4D_2 were calculated using group additivity. The rate constants employed to model the C_2H_4 and C_2H_2 profiles were used to model the C_2D_4 data; evidently the overall isotope effect is minimal. A set of profiles from a 2% C_2D_4-Ne-1%Ar mixture is displayed on the next page. Solid lines represent the results of the modeling calculations.

concentration x 10^8, mol/cm^3

2146 K $\quad$ C_2D_2

C_2D_4

2174 K $\quad$ D_2

$t(s) \times 10^4$
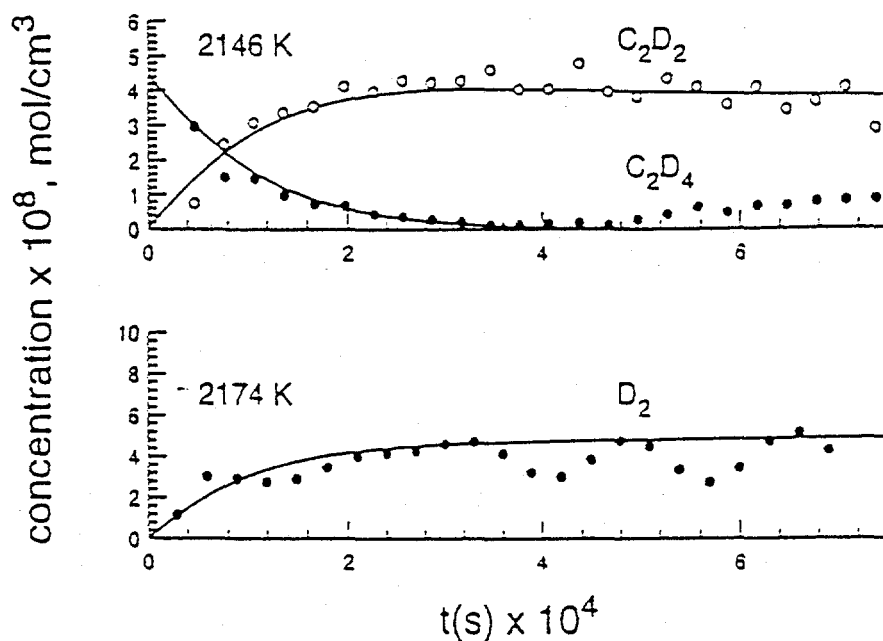
Efforts to obtain useful data for the D_2 profiles at m/e 4 were not generally successful when the TOF was optimized for the mass spectral range m/e 20-52. The peak heights recorded at m/e 4 are of considerably lesser amplitudes resulting in an unacceptable amount of scatter. Significant readjustment of TOF compensating magnets and electronic settings produced a ten-fold increase in the m/e 4 signal. The scatter of the data for the D_2 reaction profiles was also reduced. However, using an optimal TOF setting for m/e 4 resulted in correspondingly reduced m/e 28 signals and unacceptable scatter in the C_2D_2 profiles. The most reasonable compromise was to perform a different set of experiments for the low mass product profiles. The work was presented at the 20th International Symposium on Shock Waves and a reprint is enclosed.

4. Pyrazine

The pyrolyses of nitrogen containing ring compounds are of interest in combustion science particularly with regard to coal and its products. Single pulse studies by Mackie, et al. of the simplest of these compounds, pyrazine, pyrimidine and pyridine, reported the respective product distributions as a function of temperature. However, any non-linear growth of products would not be detected since the technique involves post-reactio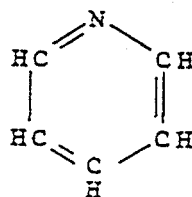n, static analysis of products. We thought that complementary time-dependent investigations of these systems would add to our understanding of these important thermal decompositions. The structural formulas are useful for subsequent discussion.
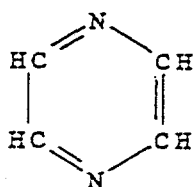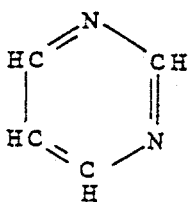
pyrazine   pyrimidine   pyridine

LS experiments (1680-2300 K, 2 and 4% pyrazine in Kr) provided excellent rate data for the initiation reaction, C-H fission, for pyrazine as well as the early rate of chain acceleration. Time-resolved profiles of the major (HCN and C_2H_2) and minor products (C_4H_2 and cyanoacetylene) were obtained by the TOF technique (1460-2267 K, 2% pyrazine in both 2% Ar/Ne and 2% Ar/5% H_2/Ne). Of particular interest are the temperature dependent maxima and subsequent decay rates exhibited by the cyanoacetylene (HC_3N) profiles as shown in the accompanying figure and the extremely low concentrations attributed to cyanogen. No other species of higher mass were recorded.

A tedious process was experienced in constructing the TOF reaction profiles since cracking

pattern contributions from the parent molecule affected the product profiles for C_2H_2 and HC_3N. Appropriate corrections to the raw data were applied that were dependent upon the various reaction temperatures.
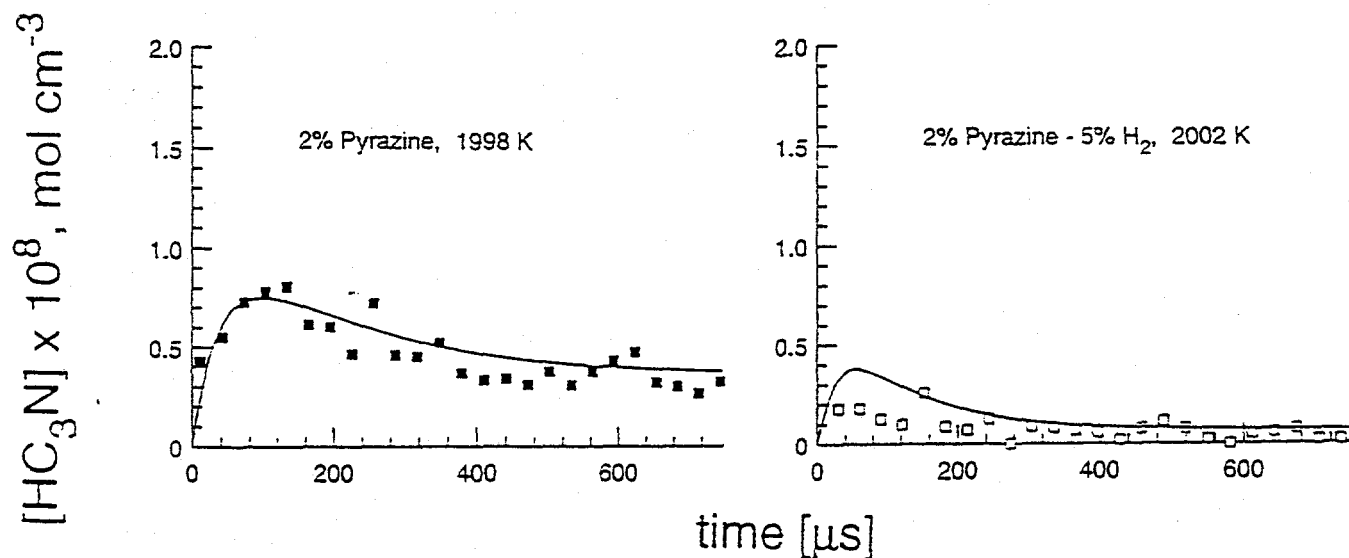
A new chain mechanism for pyrazine decomposition consisting of 35 reactions, many of them pressure dependent, was formulated by Kiefer and Zhang. The LS and TOF profiles were modeled independently over a wide temperature range, 1460-2300 K. The existence of a chain reaction with CN as the major chain carrier was confirmed. Heats of formation for several stable radical and molecular species are proposed; e.g., a value of 96 kcal/mol for HC_3N was selected to match the late time, high temperature TOF profiles which represent partial equilibrium concentrations. The modeling of the HC_3N profiles is extremely sensitive to the value of ΔH^0_f chosen with respect to the profile maximum, its subsequent decay rate, and the level of the late time plateau. In order to estimate heats of formation for radicals derived from imine N-H bond fission, Branko Jursic performed high level *ab initio* calculations using GAUSSIAN 94 implementation of Density Functional Theory with 6-311+G(2d, 2p) and 6-311++G(3df, 3pd) basis sets. A value of 89 kcal/mol for the imine N-H bond energy D_0 was obtained.

Another significant test of the mechanism involved the recognition of the sensitivity of the HC$_3$N profile to H$_2$. Indeed, the addition of 5% H$_2$ to the reaction mixture resulted in TOF profiles for HC$_3$N that are drastically lower than those recorded in the absence of H$_2$, as shown in the figures on the preceding page. This observation supports a major departure in the mechanism as previously proposed by Mackie, et al.[1]; namely, that HC$_3$N is produced via exothermic CN addition to parent pyrazine followed by ring opening and subsequent decomposition of the radicals NC-CH≡CH-N=CH-CH=N• and NC-CH=CH-N=CH• to yield 2 HCN + HC$_3$N overall instead of reactions involving the pyrazyl radical as according to Mackie. The addition of H$_2$ reduces the concentration of CN radical via the reaction, CN + H$_2$ – HCN + H, thereby reducing the HC$_3$N concentrations. In contrast to the mechanism of HC$_3$N formation which depends on reactions with the parent, C$_4$H$_2$ is produced via reaction with products; namely, C$_2$H + C$_2$H$_2$ – C$_4$H$_2$ + H. As a consequence, the C$_4$H$_2$ profiles exhibit monotonic growth. However, a reduction of C$_4$H$_2$ concentration is also predicted due to removal of ethynyl radical via C$_2$H + H$_2$ – C$_2$H$_2$ + H which competes effectively with the C$_4$H$_2$ production channel. Other departures from Mackie include a higher value for C-H fission of pyrazine to form pyrazyl radical + H (103 vs 96.6 kcal/mol) and a kinetic explanation for low levels of cyanogen produced in both the single pulse experiments and our TOF work.

An oral presentation of the pyrazine results was given at the 26th International Combustion Symposium.

5.   Gas Sampling and Data Acquisition

We were invited to discuss our dynamic analysis of relatively high pressure gas from a shock tube at a Specialists Workshop on Mass Spectrometric Sampling. Most applications involve sampling of flames, supersonic molecular beams, or laser plasmas at low pressures. Several

particular problems pertain to sampling from the reflected shock: maintenance of hydrodynamic flow conditions, minimization of boundary layer gas into the ion source region, controlling the proper operating conditions during the sudden influx of gas, dealing with pressure fluctuations that accompany the gas flow, conversion of mass spectral peak amplitudes to concentrations, and high speed data acquisition of the various mass spectrometric peak heights generated as a function of observation time during the course of the experiment.

A re-entrant nozzle (0.1 mm hole diameter) located at the end plate of the shock tube with the cone height (1 mm) facing the reflected shock zone solves the first two problems. Large ballast volumes adjacent to the ionization region control the total pressure increase due to shock front arrival at the end wall. Pressure fluctuations in the gas flow from the reflected shock zone to the ion source are smoothed by taking the ratios of the respective peak heights of reactive species to the peak height of a chemically inert species present in the gas mixture (usually neon or argon) at the same reaction time. The conversion of peak heights to concentrations is accomplished by shocking the various components of the reacting mixture individually in the presence of inert gas(es) in a series of calibration runs at non-reacting temperatures to determine the respective mass spectral sensitivities.

A high speed digitizer, Tektronix RTD 720A, was purchased with DOE funds to supplant the 10,000 speed Polaroid film used to record the mass spectral traces from a single experiment on successive oscilloscope screens. The subsequent identification of the various m/e values was performed manually with the aid of a microscope. After the purchase we were able to do away with the cameras, the oscilloscopes, and the arduous task of measuring the mass peak heights. The digitizer has the capability of storing one million points, which means we have the following options: 1 ms observation time with 1 ns sampling rate; 2 ms observation time with 2 ns intervals; 4 ms observation time with 4 ns intervals.

However, the lack of efficient software to handle the large amount of mass spectral data (1 MB/shock) slowed down the data processing and eventually also the experiments. The vendor-recommended software proved to be unsatisfactory in transferring the data and was returned for refund. In 1994, we started an in-house development of computer software. Initially, a Quick-BASIC program for data transfer from the digitizer to a 486 PC and subsequent mass peak analysis was written. This program was employed for several months and successfully handled the mass spectral data. Nevertheless, due to the manual movement of the measuring cursor on the screen, this software was not fast enough to offer on-site data analysis. A Turbo-Pascal software package was developed in our group. This mouse-driven and automatically scanning software reduced the time for data processing substantially and allowed us to do a complete m/e and peak height analysis during the waiting period between experiments. The scanned mass peaks and their peak heights are stored in a multi-column data file with the first column standing for reaction time and each of the other columns denoting a particular species. The peak heights are then converted into concentrations for the purpose of comparison with modeling results. A reprint from the workshop proceedings is enclosed.

A further development of the data analysis software involves the application of a modern software technique called Object-Oriented-Programming. A new package for Microsoft Windows (3.1 & 95) with quick graphing and statistics capabilities has integrated the data transferring and mass peak analyzing software. Making use of the Windows feature of running multiple applications simultaneously, this new software package provides a swift and comprehensive treatment of the mass spectral data.

6. Allene and Propyne

Since our initial TOF study of allene pyrolysis in 1987, there has been considerable interest in this system due to the efficiency of propargyl radicals reacting to form benzene and, as a consequence, the subsequent formation of soot. Professor Kiefer's group at UIC has made significant advances in understanding the reaction pathways involved in the isomerization of allene to propyne. More recently, we have collaborated with his group on additional studies of propyne decomposition using the complementary shock tube techniques of LS and TOF to expand the data base for this important reaction system. Dr. Branko Jursic at the University of New Orleans has performed Density Functional Theory calculations using DOE computer time at NERSC. His results have contributed greatly to our understanding of the various reaction pathways for the dissociation steps. These combined efforts have resulted in a paper submitted to the Journal of Physical Chemistry.

7. Inhibition of C_2H_2 Pyrolysis

As a result of a collaborative LS and TOF effort in 1988 on the unimolecular dissociation of vinylacetylene, the idea for a new mechanism for acetylene pyrolysis was conceived. A subsequent joint publication (Kiefer and Kern) appeared in 1992 describing the kinetics and thermodynamics of acetylene pyrolysis reconciling apparently conflicting values for the C-H bond energy in acetylene and also the heats of formation and entropies for ethynyl radical, the polyacetylenes and polyacetylenic radicals. The work was aided greatly by the theoretical calculations of a co-author, Dr. Larry Harding at Argonne National Laboratory.

The mechanism was tested further by probing the effects of added H_2 to initial mixtures of C_2H_2. The inhibitory effects predicted by the new mechanism were confirmed by TOF experiments.

The inhibitory effects of added HCl were also investigated and modeled using the recent kinetic data of Dr. Joe Michael and his group at Argonne to describe the $Cl + H_2 \rightarrow HCl + H$ reaction. These confirmations of predicted behavior strengthen the validity of the new mechanism and also the TOF technique. An abstract of this work has been transmitted to the 21st International Symposium on Shock Waves to be held in July 1997.

8. Pyrolyses of Aromatic Azines

Space limitations of 5500 words for Combustion Symposium papers prevented us from publishing the complete story of pyrazine and pyrimidine decompositions. We have submitted an extensive study of the three simplest azines, pyrazine, pyrimidine, and pyridine, to the Journal of Physical Chemistry (manuscript enclosed).

Included in addition to the previously published mechanism for pyrazine, is the far more complex mechanism for pyrimidine dissociation and a revised mechanism for pyridine pyrolysis. The advantages of the complementary techniques of laser schlieren densitometry and time-of-flight mass spectrometry as sources of dynamic kinetic data are clearly evident in this study.

The LS data provided precise measurements of the initial dissociation rates as a function of temperature and pressure and combined with rigorous application of RRKM theory yielded values for the barriers of C-H fissions for the three azines. All three barriers are lower than the barrier for C-H fission in benzene and their respective decomposition rates are also faster relative to benzene dissociation. The reasons for these differences are fully explained in our submission to the Journal of Physical Chemistry. The TOF experiments furnished the various reaction profiles for the major and minor species over a wide temperature range. The observation of temperature-dependent maxima in the cyanoacetylene profiles required that an acceptable mechanism had to be able to

model this rather complex behavior. In fact, the recording of this behavior provided insight into the formulation of the overall mechanistic scheme. These ideas were further tested by performing a set of experiments containing excess H_2 in the starting mixture in addition to the azine parent. The dramatic reduction of the cyanoacetylene profiles with excess H_2 is a feature predictd by the mechanism and confirmed by experiment.

Summary

Each of the studies described herein has contributed to our understanding of the detailed kinetics of the reactions of acyclic fuels, the thermal decompositions of aromatic ring compounds, the shock tube techniques dedicated to combustion science problems, and the role of theoretical chemistry in providing essential thermodynamic and kinetics information necessary for constructing plausible reaction mechanisms. The knowledge derived from these investigations is applicable not only to the area of pre-particle soot formation chemistry, but also to various incineration and coal pyrolysis problems.

Publications

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2,   R.D. Kern, H. Chen, J.H. Kiefer and P.S. Mudipalli, "Thermal Decomposition of Propargyl Bromide and the Subsequent Formation of Benzene", 25th Symposium (International) on Combustion, Combust. Flame, 100, 177-184 (1995).

3.   R.D. Kern, H. Chen and J. Yao, "High Temperature Thermolysis of Ethylene-d_4", 20th International Symposium on Shock Waves, Volume II, World Scientific, Singapore, 1996, p. 833-838.   -

4.   J.H. Kiefer Q. Zhang, R.D. Kern, H. Chen, J. Yao and B.S. Jursic, "Disociation and Chain Reaction in the Pyrolysis of Pyrazine", 26th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1996, pp. 651-658.

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Presentations

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2. R.D. Kern, H. Chen and H.J. Singh, "Some Interesting Pathways for the Reaction of C_3H_3Cl with H_2 or D_2", 25th International Symposium on Combustion, Irvine, California, August 3, 1994.

3. R.D. Kern, H. Chen, H.J. Singh, E.A. Branley and J. Yao, "Time-of-Flight Mass Spectrometric Analysis of Reflected Shock Zone Gases and High Speed Data Analysis", A Specialist Workshop on Applications of Free-Jet, Molecular Beam, Mass Spectrometric Sampling, Estes Park, Colorado, October 13, 1994.

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