

**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 and published eight major research projects during the period July 1997-September 2000. The results have been presented at major scientific meetings and have either been published, are in press, or have been accepted. Since the principal investigator retired from the University of New Orleans on May 20, 2000, the equipment for his shock tube laboratory has been dismantled.

From its inception some 21 years ago, our program sponsored by the Department of Energy has focused on the identification and temporal behavior of radical intermediates formed during the combustion and pyrolysis of gaseous fuels. The goals have been the elucidation of the kinetic pathways to soot formation, proposing and testing the pertinent reaction mechanisms, and providing realistic rate constants as functions of temperature and pressure. The basic apparatus employed by us has been a shock tube coupled to a time-of-flight mass spectrometer (TOF) which provided dynamic analysis of reactants, products and intermediates. The TOF data were often combined with the invaluable observations of laser schlieren densitometry (LS) obtained by Professor John Kiefer and his research group at the University of Illinois at Chicago. Their contributions involved precise measurements of the decay rate of the reactant as a function of temperature and pressure, determined whether reaction profile shapes were diagnostic of radical or molecular processes, and identified late-time exothermic excursions associated with recombination reactions. Some other helpful information were furnished from the static analysis of single pulse shock tube work: high-pressure unimolecular dissociation rate constants and quantitation of trace species. Atomic resonance absorption spectroscopy measurements of H-atom profiles assisted in the formulation and testing of mechanisms. A recent addition by Professor Kiefer to the arsenal of shock tube techniques is the

development of the incident-shock-quench-tank experiment which allows GC/MS analysis of the gas sample as studied by LS. Lastly, theoretical calculations by Drs. Branko Jursic at the University of New Orleans and Larry Harding and Al Wagner at Argonne National Laboratory of the energetics and structures of intermediate species have played important roles in the investigations of the pyrolyses of acetylene, allene and propyne, aromatic azines, and cyclopentadiene.

Summary reports of the work accomplished and/or published during the reporting period follows.

#### **1. Unimolecular Dissociation in Allene and Propyne : The Effect of Isomerization on the Low-Pressure Rate**

The unimolecular dissociation of  $C_3H_4$  isomers allene and propyne was examined with two complementary shock-tube techniques: LS and TOF mass spectrometry. The LS experiments covered 1800-2500 K and 70-650 Torr, in 1, 2, and 4% propyne/Kr and 1 and 2% allene/Kr., whereas the TOF results extended from 1770 and 2081 K in 3% allene or propyne in Ne. The possible channels for unimolecular dissociation in the  $C_3H_4$  system of isomers were considered in detail, using new density functional theory calculations of the barriers for insertion of several  $C_3H_2$  isomers into  $H_2$  to evaluate the possibility of  $H_2$  elimination as a dissociation route. The dominant path is C-H fission, from either allene or propyne, although some small amount of  $H_2$  elimination may be possible from allene. Rate constants for C-H fission of both allene and propyne were obtained by the usual model assisted extrapolation of LS profiles to zero time using an extensive mechanism constructed to be consistent with both the time variation of LS gradients and the TOF product profiles. This procedure then provided rate constants effectively independent of both the near-thermoneutral isomerization of the allene/propyne and of secondary chain reactions. Derived rate constants showed a strong, persistent pressure dependence, i.e., a quite unexpected deviation

(falloff) from second order behavior. These rate constants are nearer first than second order even for  $T > 2000$  K. They are also anomalously large; RRKM rates using literature barriers and routine energy-transfer parameters are almost an order of magnitude too slow. The two isomers displayed slightly different rates, and falloff is slightly less in allene. It was suggested that isomerization is probably slow enough for this difference to be real. The anomalously large rates and falloff are both consistent with an unusually large low-pressure-limit rate in this system. Extensive isomerization of these  $C_3H_4$  is possible for energies well below their C-H fission barriers, and this can become hindered internal rotation in the activated molecule. On the  $C_3H_4$  surface three such accessible rotors were identified. State densities for the molecules including these rotors were calculated using a previous general classical formulation. Insertion of these state densities into the RRKM model resulted in rates quite close to the measured magnitudes, and showed much of the observed falloff. The increase in the low-pressure rate is as much as a factor of 8; a necessary but nonetheless remarkable effect of anharmonicity on the unimolecular rate. This work demonstrated the importance of accessible isomerization and consequent hindered internal rotation on the dissociation of unsaturated species and was published in the Journal of Physical Chemistry.

## 2. Pyrolyses of Aromatic Azines : Pyrazine, Pyrimidine, and Pyridine

The thermal decompositions of pyrazine, pyrimidine and pyridine in shock waves were investigated using the complementary techniques of LS densitometry and TOF mass spectrometry (1600 - 2300 K, 150 - 350 Torr). A free radical chain reaction with initiation by ring C-H fission in the pyrolyses of all three azines was proposed. The measured C-H fission rates were compared and analyzed by RRKM Theory. Barriers of  $103 \pm 2$  kcal/mol for pyrazine,  $98 \pm 2$  for pyrimidine and  $105 \pm 2$  for pyridine were determined, supporting values lower than the barrier for C-H fission in benzene, 112 kcal/mol. The lower barriers for the azines were explained by the additional

contributions of resonance structures of azyl radicals due to the neighboring N-C interactions, which serve to further stabilize the azyl radicals. Detailed chain mechanisms were constructed to model the LS profiles and the TOF concentration profiles of the major products, hydrogen cyanide, acetylene, cyanoacetylene, and diacetylene. Of particular interest are the TOF observations and the mechanistic explanation of temperature dependent maxima seen in the formation of cyanoacetylene in the presence or absence of excess  $H_2$ . This work was published in the Journal of Physical Chemistry.

### 3. Inhibition of $C_2H_2$ Pyrolysis at High Temperatures by $H_2$ and $HCl$

A new mechanism for acetylene pyrolysis constructed from the results of shock tube experiments employing mass spectrometric detection of reactants and products, laser schlieren measurements, and high level *ab initio* calculations to model inhibitory effects of dihydrogen and of hydrogen chloride when either is present in the initial gas mixture. Three mixtures were investigated over the temperature range 2200 - 2620 K : 2.1%  $C_2H_2$  - 3.5%  $H_2$  ; 2.1%  $C_2H_2$  - 3.5%  $HCl$  ; 2.1%  $C_2H_2$ . The balance of each mixture consisted of diluent containing 3% Ar - 97% Ne.

The reacting gases were analyzed dynamically at 30  $\mu s$  time intervals as the reflected shock zone gas flowed into the TOF ion-source. The data were processed during typical observation times of  $\approx 750 \mu s$  by a high speed transient digitizer. The various  $m/e$  values and their peak heights were measured automatically by an electronically driven cursor. The software, developed in our laboratory, organizes the kinetic data in a format suitable for the subsequent modeling calculations. Three experiments at approximately the same temperatures, 2408 K, 2423 K, and 2467 K clearly demonstrate the inhibiting effects of  $H_2$  and  $HCl$  on the thermal decomposition of  $C_2H_2$ . The major product is  $C_4H_2$  along with lesser amounts of  $C_6H_2$ .  $HCl$  is the only chlorine containing species detected ruling out several possible reactions such as



in the mechanism.

The initial concentration of acetylene in the 2.1%  $C_2H_2$  mixture,  $4.8 \times 10^{-8}$  mol/cm<sup>3</sup>, is decreased to its equilibrium concentration  $2.3 \times 10^{-8}$  mol/cm<sup>3</sup> at 2408 K, a reduction of 52%. By contrast, the reduction of  $C_2H_2$  due to reaction are 48% in the 2.1%  $C_2H_2$  - 3.5% HCl mixture at 2423 K and 16% in the mixture containing 3.5%  $H_2$  at 2467 K. The mixtures without HCl were modeled with a 21 step mechanism. The inhibitory effect of  $H_2$  is due primarily to the reverse of reaction (2)



which effectively decreases the ethynyl radical concentration via reaction (3).



In the presence of HCl, the times required for  $C_2H_2$  to decay to a concentration equal to the average of the initial and equilibrium values are 100  $\mu$ s for the 2.1%  $C_2H_2$  mixture and 200  $\mu$ s with 3.5% HCl present. The concentration of H atoms is reduced via reaction (4).



The confirmation of the observed inhibitory effects by HCl and especially by  $H_2$  on the decomposition of  $C_2H_2$  with established rate constants and thermal data from a variety of literature sources as input to the modeling calculations is indeed pleasing. The work was published in the volume for the 21<sup>st</sup> International Symposium on Shock Waves.

#### 4. Pyrolysis of Furan at Low Pressures: Vibrational Relaxation, Unimolecular Dissociation and Incubation Times

Vibrational relaxation, incubation times, and unimolecular dissociation of furan ( $C_4H_4O$ ) were investigated over the extended temperature range 500-3000 K in 2-5% furan-krypton mixtures, 2% furan-neon mixtures, and in pure furan. The experiments were performed in shock waves using LS and TOF mass spectrometry. At low temperatures and low pressures, only vibrational relaxation



was observed using the LS technique. This relaxation is unexpectedly slow and shows a strong nonexponential time dependence. Unimolecular dissociation was observed in TOF experiments between 1300 and 1700 K in a pressure range of 175 - 250 Torr as well as LS experiments between 1700 and 3000 K for pressures between 100 and 600 Torr. The TOF experiments showed that under the given conditions two molecular dissociation channels leading to  $C_2H_2 + CH_2CO$  or to  $C_3H_4 + CO$  are dominant. The branching ratio between these channels was determined between 1300 and 1700 K. At low temperatures, the molecular channel leading to  $C_3H_4$  and CO is preferred, but a channel switching was observed around 1700 K. The domination of these molecular channels is consistent with the shape of the LS-profiles, and these have been successfully modeled with just these two reactions. The overall unimolecular rate constant is in the falloff regime close to the low-pressure limit. By use of statistical reaction rate theory, the total unimolecular rate constant could be modeled over an extended temperature and pressure range using a value of  $\langle \Delta E \rangle_{all} = 50 \text{ cm}^{-1}$  for the furan dissociation. In a small range of conditions at low pressures and high temperatures, both the vibrational relaxation and dissociation were resolved and incubation times estimated. This work was published in the Journal of Physical Chemistry.

#### **5. Pyrolysis of Cyclopentadiene: Rates for Initial C-H Bond Fission and the Decomposition of the $c\text{-C}_5\text{H}_5$ Radical**

The pyrolysis of cyclopentadiene was investigated in shock waves using the TOF and LS techniques. Experiments encompassed the range 100-450 Torr and 1500-2500 K. The low-temperature LS experiments show brief early maxima indicative of chain reaction initiated by C-H fission. Precise and consistent rate constants were obtained from both experiments for this reaction, and a very good Rice-Ramsperger-Kassel-Marcus fit was possible with standard parameters. The result is a barrier of  $84 \pm 2 \text{ kcal/mol}$  for C-H fission, and a consequent  $\Delta_f H^\circ_{298} = 65.3 \text{ kcal/mol}$  for

c-C<sub>3</sub>H<sub>3</sub> radical. Rate constants were also estimated for the important secondary reaction  $c\text{-C}_3\text{H}_3 \rightarrow \text{C}_3\text{H}_3 + \text{C}_2\text{H}_2$ . These were also successfully RRKM modeled with the aid of high-level density-functional calculations of the transition state for the 1,2 H-atom shift which controls the rate of this reaction. The large rates for this are shown to be a consequence of a newly calculated low barrier of 61.9 kcal/mol and a tenfold reaction path degeneracy which arises from a facile pseudorotation in this Jahn-Teller molecule. The experiments and model provided the first quantitative evidence for the H-atom shift mechanism for this reaction. This work was published in the volume for the 27<sup>th</sup> International Combustion Symposium.

#### 6. Thermolysis of Cyclopentadiene in the Presence of Excess Acetylene or Hydrogen

The major products of the thermal decomposition of cyclopentadiene at high temperatures are acetylene and hydrogen. A recent complementary shock tube study of this pyrolysis proposed a mechanism that predicted the formation of these products emanated mainly from two essentially irreversible reactions involving the cyclopentadienyl radical c-C<sub>5</sub>H<sub>5</sub>.



The c-C<sub>5</sub>H<sub>5</sub> radicals and the hydrogen atoms are generated from the initial decomposition of cyclopentadiene which is pressure dependent.



In order to test these propositions more thoroughly, three mixtures consisting of the following compositions were investigated with the TOF shock tube technique :

2% C<sub>5</sub>H<sub>6</sub> ; 2% C<sub>5</sub>H<sub>6</sub> - 5% H<sub>2</sub> ; 2% C<sub>5</sub>H<sub>6</sub> - 5% C<sub>2</sub>H<sub>2</sub>. The balance of each mixture was research grade neon. The temperature range covered was 1328 - 1869 K.

The TOF data were modeled with a 34 step mechanism containing two notable features : a

reaction path degeneracy of 20 was utilized for the rate controlling reaction for the  $c\text{-C}_5\text{H}_5$  dissociation which is a 1,2 H atom shift; a more detailed treatment was presented to support a value of 63.3 e.u. for  $c\text{-C}_5\text{H}_5$ .

## **7. Mass Spectrometric Methods for Chemical Kinetics in Shock Tubes**

An extensive chapter written for the Handbook of Shock Waves with the above title covers the 21 years of work supported by the Department of Energy as well as earlier studies of gas phase isotopic exchange reactions funded by the National Science Foundation for nine years.

## **8. The Pyrolysis of Methylcyclopentadiene: Isomerization and Formation of Aromatics**

The pyrolysis of methylcyclopentadiene (MCP) was investigated in two shock tubes with a variety of techniques. LS experiments were performed over 1000 - 2000 K, and 60 - 600 Torr, in 2% MCP/Kr and 4% MCP/Kr. Incident-shock-quench-tank GC/MS product analyses (a new method) were obtained for 800 - 1900 K in 4.5% MCP/Ar, and TOF mass spectra were recorded in 2% MCP/Ne over 1250 - 1600 K and 145 - 225 Torr. The LS experiments show an initial endothermic reaction from C-C fission and subsequent exothermic reaction from methyl-radical recombination. Rate constants for the dissociation extracted from early gradients form a consistent set with an apparent  $E_a$  of 44 kcal/mol. This highly endothermic dissociation ( $\Delta H_{298}^0 = 75$  kcal/mol) is thus well into falloff, but there is little sign of consequent pressure dependence. A standard Gorin model RRKM calculation, modified for the fact that only the 5-isomer can fission, produces the magnitude and temperature dependence, but not the absence of pressure variation. TOF and quench-tank product analyses show benzene, acetylene, naphthalene and methane as major low-temperature products. The presence of benzene at the lowest temperatures suggests that chain decomposition to fulvene and benzene is indeed efficient in this decomposition, and naphthalene production supports the  $c\text{-C}_5\text{H}_5$  dimerization path, in accord with recent theory. GC/MS analysis of the quench-tank

experiments has provided the first measurements of the distribution of the three MCP isomers at elevated temperatures, showing that 5-MCP is a small but increasing fraction whose enthalpy is about 1.2 kcal/mol above that of the two isomers. This work was presented at the 28<sup>th</sup> International Combustion Symposium and will be published in the symposium volume.

## 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

1. J.H. Kiefer, P.S. Mudipalli, S.S. Sidhu, R.D. Kern, B.S. Jursic, K. Xie and H. Chen, "Unimolecular Dissociation in Allene and Propyne: The Effects of Isomerization on the Low-Pressure Rate", *J. Phys. Chem.*, 101, 4057-4071 (1997).
2. J.H. Kiefer, Q. Zhang, R.D. Kern, B.S. Jursic, H. Chen and J. Yao, "Pyrolyses of Aromatic Azines: Pyrimidine, Pyrazine and Pyridine", *J. Phys. Chem.*, 101, 7061-7073 (1997).
3. R.D. Kern, J. Yao and Z. Zhang, "Inhibition of  $C_2H_2$  Pyrolysis at High Temperatures by  $H_2$  and  $HCl$ ", 21<sup>st</sup> International Symposium on Shock Waves, Volume I, Panther Publishing House and Printing, Canberra, Australia, 1998, pp. 269-272.
4. D. Fulle, J.H. Kiefer, Q. Zhang, J. Yao and R.D. Kern, "Pyrolysis of Furan at Low Pressures: Vibrational Relaxation, Unimolecular Dissociation and Incubation Times", *J. Phys. Chem.*, 102, 7480-7486 (1998).
5. R.D. Kern, Q. Zhang, J. Yao, B.S. Jursic, R.S. Tranter, M.A. Greybill and J.H. Kiefer, "Pyrolysis of Cyclopentadiene: Rates for Initial C-H Bond Fission and the Decomposition of  $c-C_5H_5$  Radical", 27<sup>th</sup> Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1998, pp.143-150.
6. R.D. Kern, H.J. Singh, Q. Zhang, J.H. Kiefer, R.S. Tranter, E. Ikeda and A.F. Wagner, "Thermolysis of Cyclopentadiene in the Presence of Excess Acetylene or Hydrogen", 22<sup>nd</sup> International Symposium on Shock Waves, in press.
7. R.D. Kern, H.J. Singh and Q. Zhang, "Mass Spectrometric Methods for Chemical Kinetics in Shock Tubes", *Handbook of Shock Waves*, Academic Press, in press.
8. E. Ikeda, R.S. Tranter, J.H. Kiefer, R.D. Kern, H.J. Singh and Q. Zhang, "The Pyrolysis of Methylcyclopentadiene: Isomerization and Formation of Aromatics", 28<sup>th</sup> Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, accepted.

## **Presentations**

1. R.D. Kern, J. Yao and Z. Zhang, "Inhibition of  $C_2H_2$  Pyrolysis at High Temperatures by  $H_2$  and  $HCl$ ", 21<sup>st</sup> International Symposium on Shock Waves, Great Keppel Island, Australia, July 22, 1997.
2. D. Fulle, J.H. Kiefer, Q. Zhang, J. Yao and R.D. Kern, "Pyrolysis of Furan at Low Pressures: Vibrational Relaxation, Unimolecular Dissociation and Incubation Delay", 215<sup>th</sup> American Chemical Society National Meeting, Dallas, Texas, April 1, 1998.
3. R.D. Kern, "Thermal Decompositions of Five and Six Member Ring Compounds", U.S. Department of Energy Workshop on Modeling Coal, Char, Soot and Other Carbon Based Materials, Germantown, Maryland, May 28, 1998.
4. R.D. Kern, Q. Zhang, J. Yao, B.S. Jursic, R.S. Tranter, M.A. Greybill and J.H. Kiefer, "Pyrolysis of Cyclopentadiene: Rates for Initial C-H Bond Fission and the Decomposition of  $c-C_5H_5$  Radical", 27<sup>th</sup> Symposium (International) on Combustion, Boulder, Colorado, August 6, 1998.
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