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**IDENTIFICATION AND TEMPORAL BEHAVIOR OF RADICAL INTERMEDIATES
FORMED DURING THE COMBUSTION AND PYROLYSIS OF GASEOUS FUELS:
KINETIC PATHWAYS TO SOOT FORMATION**

PROGRESS REPORT

July 1, 1991 - June 30, 1994

R. D. Kern and H. Chen

Department of Chemistry
University of New Orleans
New Orleans, Louisiana 70148

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PROGRESS REPORT

We have completed four of the five major areas of research proposed for the period July 1991 - June 1994. The results have been presented at major scientific meetings and have either been published or are in press. We intend to address the fifth area (cyclopentadiene decomposition) during the remainder of the current funding period. In addition, we received supplemental funding to purchase the components for a high speed data acquisition system and have implemented the procedure for processing experimental records for our shock tube: time-of-flight mass spectrometer apparatus.

These advances are presented here in summary form; the reader is referred to the enclosed reprints for details and appropriate references to other work.

1. C_2H_2 and C_4H_4

Three papers and several presentations were made concerning the thermal decompositions of acetylene and diacetylene. Major questions involving the reaction mechanism and the appropriate thermodynamic properties of key species were resolved. Considerable effort was devoted to the rate of the initiation reaction, $2 C_2H_2 \rightarrow C_4H_3 + H$, the rate of a key propagation step, $H + C_2H_2 \rightarrow C_2H + H_2$, and the thermal data for C_4H_2 and the higher molecular weight polyacetylenes, the polyacetylenic radicals, the ethynyl radical, C_2H , and the isomers of C_4H_3 .

The genesis for a new idea on C_2H_2 pyrolysis sprang from a collaborative study with Professor John Kiefer on vinylacetylene decomposition; it was shown using the complementary shock tube techniques of laser schlieren (LS) densitometry and time-of-flight mass spectrometry (TOF) that the major pathways lead to molecular products. The 1,1 elimination scheme including the rapid isomerization of vinylidene to acetylene is shown in the following diagram and accounts for the major products C_2H_2 , C_4H_2 and H_2 .

The production rate of hydrogen atoms measured by atomic resonance absorption spectrometry (ARAS) is much slower via the reaction

as reported by Professor Frank and his co-workers. John Kiefer recognized that the rate of the reverse reaction occurring via an inverse vinylidene insertion mechanism

is sufficient to initiate the high temperature pyrolysis of acetylene according to the following diagram in which the numbers represent the energy levels in kcal mol⁻¹.

This scheme involves the resonance stabilized isomer $i\text{-C}_4\text{H}_3$ with a heat of formation ~ 10 kcal lower than $n\text{-C}_4\text{H}_3$; $n\text{-C}_4\text{H}_3$ is formed via a four-center transition state. The formation of the respective isomers is shown in the following reactions.

Dramatic illustration of the effect of this difference in the thermochemistry of the bimolecular initiation step for acetylene pyrolysis is depicted in the following figure. The rate of production of C_4H_2 in a 6.2% C_2H_2 - Ne mixture at 2178K recorded by the TOF-shock tube system is modeled according to three different assumptions.

The dashed line identified as "0 ppm" represents a modeling calculation by Colket et al. of our TOF data using an initiation step involving $n\text{-C}_4\text{H}_3$. The calculated rate is obviously too slow and is labelled "0 ppm" with respect to an assumed level of acetone impurities in the C_2H_2 mixture. The dashed line "1000 ppm" illustrates the effect of acetone impurities. Colket argued that the observed rates were attributable to the acetone found in acetylene cylinders. We demonstrated that their argument is not valid by synthesizing C_2H_2 in our laboratory (hence, zero ppm acetone) and comparing the TOF data from acetone-free mixtures to those containing 30

ppm acetone as a result of using purified C_2H_2 cylinder gas. There are no differences. Furthermore, modeling of the TOF data using a mechanism involving $i-C_4H_3$ in the initiation step leads to the solid line in the figure which yields a satisfactory fit to the "open circles" data. This work was presented at the 23rd International Combustion Symposium and was published in the Proceedings volume.

Another troubling point was the rate of the chain propagation step

The rate constant is determined by measurement of the reverse reaction usually at room temperature, use of the equilibrium constant, and extrapolation of the rate constant to high temperatures. Modeling of the acetylene mechanism at high temperature is very sensitive to this reaction. The equilibrium constant is sensitive to $\Delta H_f(C_2H)$ and the long accepted value of ~ 127 kcal/mol was necessary to model the TOF reaction profiles. However, persuasive spectroscopic determinations and theoretical calculations have built a solid case for a heat of formation (298 K) of 135.5 kcal/mol. This value posed a serious challenge to the modeling of the kinetic data until it was realized that recent revisions in the vibrational frequencies of ethynyl radical produced significant changes in the entropy calculations. The increase in the entropy of C_2H is sufficient to offset the increase in $\Delta H_f(C_2H)$ at 2100K. This happy circumstance resulted in a consensus between spectroscopy, theory and modeling of chemical kinetic data.

The temperature dependence of the rate constant for $C_2H + H_2 \rightarrow H + C_2H_2$ has been addressed by theoretical calculations performed by Harding et al. Interest in this key reaction has resulted in recent and ongoing work by Matsui and co-workers at the University of Tokyo and by Glass and Curl at Rice University to extend the measurements of the rate of ethynyl with hydrogen from room temperature to 855 K. These data provide a test of the non-Arrhenius curvature predicted by calculations and it is hoped that additional work will be stimulated

towards establishing values for this reaction at combustion temperatures.

In a splendid example of collaborative effort between experimental groups (Kiefer and Kern) and high level theoretical calculations (Harding), an extensive mechanism consisting of 86 reactions was employed to model data derived from a variety of shock tube techniques. Values for the thermal properties of the polyacetylenes and their radicals are presented as are pressure dependent expressions for their respective decompositions. The reader is referred to the enclosed reprint from Combustion Science and Technology for details.

We decided to test some of the predictions of the comprehensive 86-step acetylene pyrolysis mechanism by investigating the kinetics of $C_4H_2 - H_2$ mixtures. There were several reasons for this: previous TOF studies of C_4H_2 decomposition were hampered by extensive soot formation; the addition of H_2 suppresses particle formation and enhances the role of molecular reactions such as $H_2 + C_4H_2 \rightarrow 2 C_2H_2$ taking place via an excited $[C_4H_4]^*$ complex; previous modeling required the use of the high pressure limit rate constant of Frank and Just for C_4H_2 decomposition, although the reaction conditions were in the expected fall-off region; lastly, Benson proposed a value for $\Delta H_f(C_4H_2) = 106$ kcal/mol in contrast to our proposed value of 111 kcal/mol. A correct value is needed to establish the bond additivity value for $[C_1 - (C_1)]$ which in turn is used to calculate the thermochemical data C_6H_2 , C_6H , C_8H_2 and C_8H .

Sensitivity analysis was employed to reduce the number of reactions in the mechanism from 86 to 16. This number was shown to model satisfactorily our experimental conditions of 1635-2110K and 0.33-0.51 atm.

The TOF data revealed that the product profiles are very sensitive to the value of $\Delta H_f(C_4H_2)$ and solid evidence is presented in Figures 1-8 of the enclosed reprint to support a value of 111 kcal/mol. The work was presented at the 18th International Shock Tube Symposium held in Sendai, Japan. Fall-off expressions for the decomposition of C_4H_2 , C_6H_2 and C_8H_2 were

employed successfully and in the 1% C_4H_2 - 30% H_2 mixture, particle formation was almost completely suppressed. The molecular reaction, $C_4H_2 + H_2 \rightarrow 2 C_2H_2$, was shown to be dominant for the first 100 μs of reaction time. This finding lends support to the proposal that radical reactions are required to promote the soot formation process.

It was hoped that we could synthesize samples of C_6H_2 in order to investigate further the reactions of the polyacetylenes. After rather extensive efforts on our part and after consulting with several synthetic organic chemists, we were able to synthesize reasonable amounts of C_6H_2 . However, C_6H_2 presented severe problems in separation, purification and preparation of suitable gaseous mixtures for shock tube study. We reluctantly abandoned our efforts on the C_6H_2 project.

2. Chlorobenzene

Our results on the thermal decomposition of C_6H_5Cl were presented at the Second International Congress on Toxic Combustion By-products; the paper was published in Combustion Science and Technology. We selected chlorobenzene as a prototype chlorinated aromatic hydrocarbon since it is a matter of interest in detailed studies of toxic and waste material incineration. A 2.1% C_6H_5Cl - Ne mixture was investigated over the temperature range 1580-2000 K and at total pressures of 0.30 - 0.50 atm. TOF analysis revealed that the major products are C_2H_2 , HCl and C_4H_2 ; C_6H_2 , benzene and C_8H_2 are minor products. The only radical detected is phenyl; HCl is the only chlorine containing product recorded. A total carbon atom balance revealed substantial loss of carbon implying the formation of large quantities of soot. The observation is consistent with high values for the soot yield of C_6H_5Cl reported by Frenklach et al. from laser extinction measurements. A 60 step mechanism was employed to model the TOF profiles and also the experimental data from a flow reactor study by Ritter et al.

carried out at lower temperatures. It was concluded that Cl atoms and chlorinated polycyclic aromatic hydrocarbon radicals play an important role in chain reactions which promote the formation of high molecular weight species which in turn form soot.

Another interesting aspect of this study is that since chlorobenzene decomposition is a convenient source of phenyl radicals, the rate constants for phenyl radical disappearance are a significant part of the mechanism. Modeling of the reaction profiles reveals support for the rate constants employed by Kiefer for phenyl radical decomposition in a laser schlieren study of benzene pyrolysis and for the rate constants derived by Skinner in an ARAS study of chlorobenzene pyrolysis.

3. Toluene

Toluene pyrolysis has been the subject of study in shock tube laboratories here and abroad for at least the last ten years. From the early laser extinction experiments which readily identified toluene as a fuel with a high soot yield to reports of detailed kinetic studies, attempts have been made to formulate a satisfactory reaction mechanism. Some of the experimental data are contradictory and have produced several points of disagreement in the literature.

We presented an invited paper at the Sixth Toyota Conference on Turbulence and Molecular Processes in Combustion in which the data was analyzed over a wide range of temperature, initial concentration and total pressure from different research groups employing a

variety of analytical techniques. Our purpose is to construct a comprehensive mechanism and apply it to the various sets of data. The paper has been published by Elsevier in a conference volume.

One of the key points involves the contributions from two channels serving as initiation steps.

	<u>ΔH_r(kcal/mol)</u>	<u>ΔS(e.u.)</u>
$C_7H_8 \rightarrow C_7H_7(Bz) + H$	88.0	27.5
$C_7H_8 \rightarrow C_6H_5(Ph) + CH_3$	102.8	38.9

Although the first reaction is favored at lower temperatures due primarily to a lesser heat of reaction, the second channel will dominate at higher temperature because of the higher value of ΔS . Support for the second channel is derived from the experimental data obtained by TOF, LS and single pulse shock tube (SPST) techniques. Both TOF and SPST confirmed that methane is a major product most likely attributed to subsequent reactions of methyl radical. The observed LS profiles are consistent with an irreversible reactant depletion step. This condition is achieved by the following scheme.

Addition of the second channel to the above reactions results in an essentially irreversible overall reaction.

This argument hinges on the proposition that phenyl radical is more unstable than benzyl at high temperatures.

ARAS experiments reported by Rao and Skinner provide additional support for the arguments. H and D atom production were recorded for the decomposition of $C_6H_5CD_3$; the

observed profiles for H and D are different in shape and the results were modeled with a scheme that favored the second channel at higher temperatures.

Since the experimental conditions reported in the literature spanned a considerable pressure range, 0.3 - 36.3 atm, RRKM calculations were performed in order to model the various data sets. The RRKM rate constants are fit to the working equation, $k = AT^{\alpha}M^{\psi}\exp(-E/RT)$. M is the total gas density and provides the pressure dependent portion of the rate constant. The fits encompass calculations over the range 1200 - 2200 K and 400 - 5200 Torr. Arrhenius plots for k_{∞} are shown in the following figure: dashed line, channel 1; solid line, channel 2. The solid circles are taken from work by Price which shows the dominance of channel 1 at lower temperatures.

We are able to model the TOF, LS and ARAS profiles (published by Frank et al.). We knew that the ARAS data reported by Rao and Skinner were consistently lower in rate than the ARAS data of Frank et al. Our mechanism appears to favor the Frank group as shown in the

enclosed reprint, Figures 1-14. This finding is quite interesting since Frank and Just argued for the dominance of the first channel and the relative instability of benzyl compared to phenyl radical.

Frank and Just proposed that benzyl isomerization preceded decomposition. Shown below is the most likely intermediate consistent with the rate constant, $k_a = 10^{15.53} \exp(-85.2/RT)$.

However, calculation of $\Delta S^\ddagger$ from their rate expression yields a value of 7.3 e.u. at 1575 K. We would expect a much lower value due to a tightening of the transition state and a value of ~ -1.3 e.u. is more reasonable. This value is similar to that estimated by Benson and O'Neal for a similar isomerization.

We adopted rate constants for benzyl and phenyl radical decomposition that are consistent with the results obtained with our previous studies of toluene, ethylbenzene, benzene and chlorobenzene. Our mechanism applied to ARAS data of Frank and Just provides reasonable fits as shown in the enclosed reprint. However, application of the mechanisms proposed by Frank et al. and by Troe et al. do not fit the TOF, LS and SPST results, particularly with regard to methane production.

We submit that the schemes shown on the next two pages for benzyl and phenyl radical decomposition are more likely at high temperature; namely, that energy requirements are

Benzyl Radical Decomposition

Phenyl Decomposition

overcome by entropic increases as the temperature increases. For instance, in the case of benzyl, formation of $C_7H_6 + H$ is a dead end, while the production of $C_5H_5 + C_2H_2$ and $C_3H_3 + C_2H_2$ yields products that are consistent with experimental results. Likewise, in phenyl decomposition, the route to C_6H_4 results in a dead end; also, C_6H_4 is not detected in the TOF experiments.

Another approach to determine k_{∞} for the first channel is to measure the reverse reaction, k_{-1} , $C_7H_7 + H \rightarrow C_7H_8$. There are two recent reports on the recombination rate: one by Hippler and Troe over the temperature range 900 - 1500 K; and another by Bartels et al. at room temperature. The Hippler-Troe value is temperature independent over the range of measurement and is equal to $2.6 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, somewhat lower than the room temperature value of $3.3 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ of Bartels et al. On the following figure is plotted the Hippler-Troe recombination rate constant (dotted line) and the calculated value of k_{-1} using our values of $k_{1\infty}$ and K_1 (solid line).

One possible explanation for the discrepancy is that the measured recombination rate may consist of two other channels forming the 2,4 and 2,5 isomers of 1-methylene-cyclohexadiene in addition to toluene formation as shown in the following schematic.

Thus, the recombination experiments are measuring an overall rate rather than the specific rate for toluene production.

It is clear that the last word on toluene pyrolysis has not been written, but it is also clear that any complete explanation has to contend with a sizeable collection of experimental results.

Although the Toyota Conference in Nagoya and the kinetics meeting in Tokyo lasted one week, I decided to spend part of my sabbatical semester leave from UNO visiting shock tube laboratories in Japan engaged in combustion research. Seminars were presented to Professors Matsui and Koshi's groups at the University of Tokyo, Dr. Masaaki Oya's group at the National Institute for Resources and Environment at Tsukuba, Professor Ikegami's group at Kyoto

University, Professor Saito's group at Hiroshima University, Professor Hidaka's group at Ehime University, and Professor Fujii's group at Nagaoka University of Technology. It was a very rewarding six week experience. The opportunity to meet with research groups that I knew only from literature, to visit their laboratories and to discuss research problems of mutual interest was truly first-rate.

4. Propargyl Chloride

In our previous TOF studies of allene and 1,2 butadiene pyrolyses, we proposed that propargyl radical is a key species for benzene production and subsequently for soot formation. This idea has since gained general acceptance. In order to test this proposition further, we studied the decomposition of propargyl chloride and presented an invited paper at a Fuel Chemistry Symposium on combustion chemistry dealing with aromatic precursors at the 202nd National Meeting of the American Chemical Society.

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 1400 - 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% C₃H₃Cl- 5% D₂ 1350 K, 0.232 atm

We reasoned that if C - Cl bond fission is the major initiating reaction, the HCl/DCI ratio would be < 1 due to the reaction of Cl + D₂ → DCl + D. Therefore, we proposed that 83% of the C₃H₃Cl dissociation yields HCl and singlet cyclopropenylidene (C₃H₂) and the second channel results in propargyl radical and Cl.

In the presence of H₂, C₃H₂ reacts exothermically to form the thermally excited adduct C₃H₄^{*} 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 cyclic species.

	k_i/k^0
$k_{\text{stable}}(\text{c-C}_3\text{H}_2 + \text{H}_2 \rightarrow \text{C}_3\text{H}_4\text{P})$	0.498
$k_{\text{stable}}(\text{c-C}_3\text{H}_2 + \text{H}_2 \rightarrow \text{C}_3\text{H}_4\text{A})$	0.332
$k_{\text{rxn}}(\text{c-C}_3\text{H}_2 + \text{H}_2 \rightarrow \text{C}_3\text{H}_3 + \text{H})$	0.087
$k_{\text{stable}}(\text{c-C}_3\text{H}_2 + \text{H}_2 \rightarrow \text{c-C}_3\text{H}_4)$	0.011
$k_{\text{rxn}}(\text{c-C}_3\text{H}_2 + \text{H}_2 \rightarrow \text{c-C}_3\text{H}_3 + \text{H})$	1×10^{-7}

The energized $[\text{C}_3\text{H}_4]^*$ 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.

Since our initial efforts in 1991, we have collaborated with Professor John Kiefer to obtain the dissociation rates of allene and propyne as a function of pressure in our temperature range. With the LS data obtained in 1992 and with new TOF measurements of propyne dissociation, we constructed a 36 step mechanism to model the TOF data on the propargyl chloride system. Furthermore, additional experiments were performed with mixtures of $\text{C}_3\text{H}_3\text{Cl}$ + allene, $\text{C}_3\text{H}_3\text{Cl}$ + propyne, $\text{C}_3\text{H}_3\text{Cl}$ + C_2H_2 and $\text{C}_3\text{H}_3\text{Cl}$ + C_2H_4 . All of these mixtures 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

Energy (kcal/mol)

accompanying reprint. This more complete effort was presented at the 19th International Shock Tube Symposium in 1993; the paper is currently in press.

5. TOF High Speed Data Acquisition System

Mass spectral data were previously recorded by photographing oscilloscope traces with high speed (at least 10,000 speed) film. The arduous task of measuring peak heights for the various reactant, intermediate and product species was accomplished by reading a reticule scale assisted by a microscope. Since a typical peak half-width is 40 ns, at least 10 points at sampling intervals of 4 ns were required to properly define the peak by electronic digitization. Prior to 1992, such digitizers were either extremely expensive or unavailable.

With the advent of the Tektronix RTD 720A digitizer, the process of digitizing one TOF experiment which might consist of 300 mass peaks occurring at various times during an observation period of one millisecond became a real possibility. With the aid of supplemental funding from DOE, we purchased a digitizer, software, interface, microcomputer and printer. 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 intervals; 2 ms with 2 ns intervals; 4 ms with 4 ns intervals. On the next two pages are shown a previous TOF photographic record and a schematic depicting the new instrumentation which has replaced four oscilloscopes and their cameras.

Although we had tested the digitizer successfully *before* purchase with a TOF-shock wave experiment, we experienced many frustrating times in attempting to transfer the data from the digitizer to the 486 microcomputer *after* the purchase. The vendor-recommended software package proved unsatisfactory in transferring the data and after many telephone calls, the package

**2% HCl - 2% D₂ - 95% Ne - 1% Ar Mixture
Reacting at 2480 K**

TOF SHOCK TUBE

was returned and the software money was refunded. We then set about to develop our own software with the expert help of Ed Branley and Harry Rees of the departmental electronics shop. That effort was complicated by the appearance of intermittent operating problems with the digitizer. After many calls to Tektronix, the digitizer was shipped back to their repair department. They could not fix it, so they sent the unit back to the Tektronix production department who discovered a cold solder joint on one of the boards that was responsible for the intermittent problems. To make a long story short, we have everything working at last and the scopes are in "permanent" storage. The money that we saved on the software was used to purchase a superior high-gain low-noise amplifier for the TOF.

Several sample records are displayed on the next three pages. Plans to exploit our new and powerful data acquisition system are presented in the proposal part of this submission. The system allows us to measure the ion flight time to within 1 ns thus providing more accurate mass identification of the species involved in the reaction. Previously we relied on oscilloscope sweep speeds for this purpose. We are also able to locate time zero for the reaction with greater accuracy.

The capability also exists to easily extend the observation period which permits detection of the cooling wave arrival and of the species formed as a result thereof. The mass range is also extended: at 30 μ s ionization intervals, the mass range is m/e 1 $\rightarrow$ 400; at 40 μ s intervals, m/e is 1 $\rightarrow$ 750. Our previous range with the scopes was m/e 12 $\rightarrow$ 200. The dynamic range of peak height amplitude is rated at 256 to 1; the previous range was about 15 to 1. Specific reaction systems for study taking advantage of these extended limits are described in the accompanying proposal.

rtdspec.010   2% Allene   1736 K   122 us
This waveform # 7 represents 33000 nanoseconds.

One window of $33\mu\text{s}$ duration taken $122\mu\text{s}$ after time zero for a 2% allene - 98% Ne mixture, reaction at 1736 K; m/e range $1 \rightarrow 411$. Triggering signals have amplitudes above and below baseline. Total record length is 1 ms. M/e 1 denoted by dotted line; diluent Ne peak at m/e 20.179.

Expanded portion of preceding window showing mass peaks of interest at higher resolution.

RTDSPEC.010

2% Allene

1736 K

122 us

This waveform # 7 represents 4502 nanoseconds.

Expanded portion of previous window covering m/e 37 to 78 (benzene).

Publications Since Last Three-Year Progress Report

1. R. D. Kern and K. Xie, "Shock Tube Studies of Gas Phase Reactions Preceding the Pre-Particle Soot Formation Process", *Prog. in Energy and Combust. Sci.*, 17, 191-210 (1991).
2. R. D. Kern, K. Xie, H. Chen and J. H. Kiefer, "High Temperature Pyrolyses of Acetylene and Diacetylene Behind Reflected Shock Waves", Twenty Third Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1991, p. 69-75.
3. J. H. Kiefer, S. S. Sidhu, R. D. Kern, K. Xie, H. Chen and L. B. Harding, "The Homogeneous Pyrolysis of Acetylene II: The High Temperature Radical Chain Mechanism", *Combustion Sci. and Tech.*, 82, 101-30 (1992).
4. R. D. Kern, K. Xie, H. Chen, S. S. Sidhu and J. H. Kiefer, "The Reaction of C_4H_2 and H_2 Behind Reflected Shock Waves", 18th Symposium (International) on Shock Waves, Springer-Verlanger, Berlin, Germany, 1992, p. 729-34.
5. R. D. Kern, K. Xie and H. Chen, "A Shock Tube Study of Chlorobenzene Pyrolysis", *Combustion Sci. and Tech.*, 85, 77-86 (1992).
6. R. D. Kern, H. Chen, H. J. Singh, K. Xie, J. H. Kiefer and S. S. Sidhu, "Thermal Dissociation Studies of Toluene at High Temperatures", *Proceedings of the 6th Toyota Conference on Turbulence and Molecular Processes in Combustion*, T. Takeno (Ed.), Elsevier, Amsterdam 1993, p. 117-32.
7. R. D. Kern, H. Chen, Z. Qin and K. Xie, "Reactions of C_3H_3Cl with H_2 , C_3H_4 , C_2H_2 and C_2H_4 Behind Reflected Shock Waves", 19th Symposium (International) on Shock Waves, 1993, in press.

Presentations Since Last Three-Year Progress Report

1. R. D. Kern, K. Xie and H. Chen, "A Shock Tube Study of Chlorobenzene Pyrolysis", Second International Congress on Toxic Combustion By-Products, 1991, Salt Lake City, Utah.
2. R. D. Kern, K. Xie, H. Chen and J. H. Kiefer, "The Reaction of C_4H_2 and H_2 Behind Reflected Shock Waves", 18th International Symposium on Shock Waves, 1991, Sendai, Japan.
3. R. D. Kern, K. Xie, H. Chen and J. H. Kiefer, "Thermochemistry Pertinent to the Pyrolysis of Acetylene at High Temperatures", International Seminar on High Temperature Chemistry, 1991, The University of Tokyo (Hongo Campus), Tokyo, Japan.
4. R. D. Kern, K. Xie and H. Chen, "The Reactions of Propargyl Chloride and 1,5 Hexadiyne Behind Reflected Shock Waves", Symposium on Combustion Chemistry, Fuel Chemistry Division, 202nd American Chemical Society National Meeting, 1991, New York City, New York. Abstract published in Preprints of Division of Fuel Chemistry 36, No. 4, p. 1423, American Chemical Society, 1991.
5. R. D. Kern, H. J. Singh, K. Xie and J. H. Kiefer, "Shock Tube Studies of Toluene Pyrolysis", Fall Technical Meeting of the Eastern Section of the Combustion Institute, 1991, Ithaca, New York.
6. R. D. Kern, K. Xie and H. Chen, "Shock Tube Studies of Fuel Pyrolyses", Fourteenth Combustion Research Meeting, 1992, Tahoe City, California.
7. R. D. Kern, H. Chen, H. J. Singh, K. Xie, J. H. Kiefer and S. S. Sidhu, "Thermal Dissociation Studies of Toluene at High Temperatures", 6th Toyota Conference on Turbulence and Molecular Processes in Combustion, 1992, Mikkabi Creative Center, Shizuoka, Japan. Invited paper.

8. R. D. Kern, H. Chen, H. J. Singh, K. Xie, J. H. Kiefer and S. S. Sidhu, "Fundamental Reactions Pertaining to the Soot Formation Process", Second International Seminar on High Temperature Chemistry, 1992, The University of Tokyo (Hongo Campus), Tokyo, Japan.
9. Seminars on our work were presented at the National Institute of Resources and Environment (Tsukuba, Japan), University of Tokyo, University of Kyoto, Hiroshima University, Ehime University and Nagaoka University of Technology, October-November, 1992.
10. J. H. Kiefer, P. Mudipalli, R. D. Kern, K. Xie and H. Chen, "Aromatic Formation in the Decomposition of Allene and Propyne", American Institute of Chemical Engineers Annual Meeting, 1992, Miami Beach, Florida. Paper given by Dr. Kiefer.
11. R. D. Kern, "Shock Tube Studies of Fuel Pyrolyses", Department of Energy Program Review Panel, 1992, Gaithersburg, Maryland.
12. R. D. Kern, H. Chen, Z. Qin and K. Xie, "Reactions of C_3H_3Cl with H_2 , C_3H_4 , C_2H_2 and C_2H_4 Behind Reflected Shock Waves", 19th Symposium (International) on Shock Waves, 1993, Marseille, France.
13. R. D. Kern, "High Temperature Gas Reactions Pertinent to the Soot Formation Process", The Lubrizol Corporation, December 2, 1993, Wickliffe, Ohio.

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