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, 1989 - June 30, 1990

R.D. Kern, K. Xie and H. Chen

Department of Chemistry

University of New Orleans

New Orleans, Louisiana 70148

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PROGRESS REPORT

Our work has continued as outlined in our research proposal which covered the period July 1, 1988 - June 30, 1991. There have been no major departures from the proposed plan. Included in this report is a budget for the period July 1, 1990 - June 1991. The funds requested reflect a reduction from the original amount, $ 76,119 instead of $ 77,200. The main focus of our work continues to be the formulation of reaction mechanisms for pyrolytic reaction systems that pertain to the soot formation process.

Several important developments have caused us to re-examine our previous results on the thermal decomposition of acetylene.[1] A shock tube coupled to a time-of-flight (TOF) mass spectrometer was used to obtain the dynamic reaction profiles for C_2H_2, C_4H_2 and C_6H_2 during the course of the available observation period (~ 1 µs). The results were modeled over a wide range of temperatures and initial concentrations of C_2H_2. The total reaction zone pressure was not varied extensively due to the necessity of operating the mass spectrometer within certain specified pressure limits. The mechanism was employed also to model other kinetic studies of C_2H_2 pyrolysis, but there are two troubling features:

1. The initiation step is second order with respect to acetylene and the experimental activation energy associated with the decomposition is ~ 45 kcal/mol. If the initiation reaction[2] is $2\ C_2H_2 \longrightarrow C_2H + C_2H_3$, using the recent thermochemical values for ΔH_f for C_2H[3,4] and C_2H_3[5] leads to a heat of reaction, 85 kcal/mol, which is difficult to reconcile with the measured activation energy.

The initial step that enjoys wide acceptance is $2\ C_2H_2 \longrightarrow C_4H_3 + H$. If the heat of formation for the initiation step is set equal to the activation energy, the heat of formation of C_4H_3 is fixed at 103 kcal/mol. However, there are two isomers of C_4H_3, H-C≡ C- CH = $\overset{\bullet}{C}$H (labeled

n-C_4H_3) and H-C≡ C- $\overset{\bullet}{C}$ = CH_2 (labeled i-C_4H_3), with respective heats of formation of 125 and 115 kcal/mol, respectively.[6] If an activation energy of 45.9 kcal/mol is assigned to the initiation reaction and the products are n-C_4H_3 ($\Delta H_f = 125$ kcal/mol) and H, a **negative** activation energy of 25 kcal/mol must be assigned to the reverse reaction.[6]

2. The second troubling point is the spectroscopic determination of the C-H bond dissociation energy in C_2H_2 and the calculated value for the heat of formation for C_2H. Wodtke and Lee[7] reported a value for ΔH_f (300 K) of 135 ± 2 kcal/mol which has a drastic effect on the decay profiles of C_2H_2 due mainly to the reaction $C_2H + H_2 \longrightarrow C_2H_2 + H$. This reaction is sensitive to ΔH_f (C_2H) and a value of ~ 127 kcal/mol[8] was necessary to model successfully the previous C_2H_2 reaction profiles.[1] Unfortunately, for our argument, several subsequent independent

determinations[9-12] for ΔH_f (C_2H) fall within the error limits of the Wodtke and Lee value.[7] However, the latest published values are significantly lower; ΔH_f = 130.1[3] and 130.4 kcal/mol.[4]

In addition to the troubling features associated with the mechanism, it has been proposed that acetone impurities play a key role in chain radical initiation, that sufficient acetone impurity levels were present in many of the previous studies, and that the effects are significant.[13]

Furthermore, the effect of molecular reactions has been assessed[5,14] and they appear to dominate the pyrolysis mechanism below 1800 K. A comprehensive mechanism which includes molecular and radical reactions has been applied by John Kiefer to experimental results covering a wide range of temperature and pressure.[5]

These recent developments are addressed in the temperature range accessible to our shock tube - TOF apparatus. Mixtures of acetylene were prepared from two sources: tank C_2H_2 that was purified by distillation; and C_2H_2 synthesized from the reaction of CaC_2 and H_2O. Although the tank purified C_2H_2 mixtures contained 30 ppm of acetone, there were no discernible differences in comparing the respective reaction profiles with those obtained from the acetone free reaction mixtures. The temperature range was 1880 - 2620 K at total reflected shock zone pressures of ~ 0.4 atm.

The rate of the dominant chain initiation, 2 C_2H_2 ----> [C_4H_4] ----> i-C_4H_3 + H, for the conditions herein was calculated from an RRKM analysis of new measurements on the dissociation of vinylacetylene,[15,16] with results in full agreement with the only direct measurements of this process.[17] The mechanism also incorporates the strongly non-Arrhenius theoretical rate constants of Harding et al[18] for the crucial reaction, C_2H + H_2 ----> C_2H_2 + H, along with the recent values for the heat of formation of C_2H.[3,4]

A pM analysis[19] of the reaction profiles reveals the quality of the agreement between the experimental data and a mechanism which incorporates newly determined values for key heats of formation and rate constants. Furthermore, experimental and modeling evidence argues against the proposal that acetone impurities dominate the initiation reation. It is concluded that acetylene pyrolysis in the temperature and pressure range investigated herein is controlled by a fragment chain reaction mechanism.

Additional support for the acetylene mechanism[5] was obtained from mixtures containing C_4H_2, H_2, and C_2H_2: 1% C_4H_2; 1% C_4H_2 - 1% H_2; 1% C_4H_2 - 1% C_2H_2. Since the mechanism contains all of the reaction steps required, profiles for the various observed species were calculated. pM analysis revealed satisfactory agreement between the model and the TOF data. Many of the experiments exhibit well defined concentration plateaus, which the model shows are indeed equilibrium values. Since the plateau levels are sensitive to the thermochemistry employed, the agreement lends supports to the various heats of formation selected for the model calculation.

Establishment of a comprehensive mechansim for C_2H_2 pyrolysis is essential since it is an

integral part of the formulation of mechanisms to describe the decompositions of aromatic fuels, the later stages of hydrocarbon fuel combustion in rich mixtures, and as part of the soot formation reaction sequence.

Future Plans

We have synthesized C_6H_2 and plan to study its reaction kinetics and its role in the complete acetylene mechanism. A re-examination of the toluene mechanism is underway as are new kinetic studies of phenyl radical decomposition. A review paper on the shock tube - TOF technique and its application to pyrolysis and soot formation is being written for the journal Progress in Energy and Combustion Science.

References

1. Wu, C.H., Singh, H.J. and Kern, R.D.: Int. J. Chem. Kinetics 19, 975(1987).

2. Back, M.H.: Can. J. Chem. 49, 2199(1971).

3. Green, P.G., Kinsey, J.L., Field, R.W.: J. Chem. Phys. 91,5160(1989).

4. Segall, J., Lavi, R., Wen, Y., and Wittig, C.: J. Phys. Chem. 93, 7287(1989).

5. Kiefer, J.H. and Von Drasek, W.A.: Int. J. Chem. Kinetics, in press.

6. Colket, M.B.: 21st Symp. (Int.) on Combustion, p. 851, 1986.

7. Wodtke, A.M. and Lee, Y.T.: J. Phys. Chem. 89, 4744(1985).

8. Okabe, H. and Dibeler, V.H.: J. Chem. Phys. 59, 2430(1973).

9. Chen, Y., Jonas, D., Hamilton, C., Green, P.G., Kinsey, J.L., and Field, R.W.: Ber. Bunsenges. Phys. Chem. 92, 329(1988).

10. Shiromaru, H., Achiba, Y., Kimura, K., and Lee, Y.T.: J. Phys. Chem. 91,17 (1987).

11. Fujii, M., Haijima, A., Ito, M.: Chem. Phys. Lett. 150, 380(1988).

12. Curtiss, L.A. and Pople, J.A.: J. Chem. Phys. 91, 2420(1989).

13. Colket, M.B. and Seery, D.J.: Combust. Flame 75, 343(1989).

14. Duran, R.P., Amorebieta, V.T., and Colussi, A.J.: Int. J. Chem. Kinet. 21, 847(1989).

15. Kiefer, J.H. Mitchell, K.I., Kern, R.D. and Yong, J.N.: J. Phys. Chem. 92, 677(1987).

16. Braum-Unkhoff, M., Kurz, A. and Frank, P.: High Temperature Pyrolysis of Vinylacetylene. Poster paper P99, presented at the 22nd Symp. (Int.) on Combustion, 1988.

17. Frank, P and Just, Th.: Combust. Flame 38, 231(1980).

18. Harding, L.B., Schatz, G.C. and Chiles, R.A.: J. Chem. Phys. 76 5172 (1982).

19. Tanzawa, T. and Gardiner, W.C.: J. Phys. Chem. 84, 236(1980).

Publications During Last Two Years

1. J.H. Kiefer, K.I. Mitchell, R.D. Kern, and J.N. Yong, "The Unimolecular Dissociation of Vinylacetylene: A Molecular Reaction", J. Phys. Chem. 92, (1988) pp. 677 - 685.

2. R.D. Kern, J.N. Yong, J.H. Kiefer, and J.N. Shah, "Shock Tube Studies of Pyridine Pyrolysis and Their Relation to Soot Formation", Proceedings of the 16th Int. Symp. on Shock Tubes and Waves, VCH, Weinheim, W. Germany, 1988, pp. 437 - 442.

3. R.D.Kern, C.H. Wu, J.N. Yong, K.M. Pamidimukkala and H.J. Singh, "Correlation of Benzene Production with Soot Yield Measurements as Determined From Fuel Pyrolyses", Energy & Fuels 2, (1988) pp. 454 -457.

4. R.D. Kern, H.J. Singh, and C.H. Wu, "Thermal Decomposition of 1,2 Butadiene", Int. J. Chem. Kinet. 20, (1988) pp. 731 - 747.

5. R.D. Kern, H.J. Singh and K. Xie, "A Shock Tube Study of the Thermal Decompositions of Acetaldehyde and Ethylene Oxide", 17th Symposium (International) on Shock Tubes and Waves, AIP Conference Proceedings: Current Topics in Shock Waves, 1989, Lehigh, Pennsylvania, in press.

6. R.D. Kern, H.J. Singh and K. Xie, "Identification of Chemi-ions Formed by Reactions of Deuterated Fuels in the Reflected Shock Zone", J. Phys. Chem., in press.

Presentations and Submissions

1. R.D. Kern, H.J. Singh, and K.Xie, "A Shock Tube Study of the Thermal Decompositions of Acetaldehyde and Ethylene Oxide Behind Reflected Shock Waves", 17th International Symposium on Shock Waves, 1989, Lehigh, Pennsylvania.

2. R.D. Kern, H.J.Singh, and K. Xie, "Identification of Chemi-ions Formed by Reactions of Deuterated Fuels in the Reflected Shock Zone", Second International Conference on Chemical Kinetics, 1989, Gaithersburg, Maryland.

3. R.D. Kern, K.XIe, H.Chen, and J.H. Kiefer, "High Temperature Pyrolyses of Acetylene and Diacetylene Behind Reflected Shock Waves", submitted to the Twenty Third Symposium (International) on Combustion, The Combustion Institute, Orleans, France, 1990.

4. R.D. Kern, K. Xie, H. Chen, and J.H. Kiefer, "Re-examination of the Thermal Decomposition of Acetylene at High Temperature: Experiment and Modeling", submitted to the Western States-Canadian Sections Joint Technical Meeting of the Combustion Institute, Banff, Canada, 1990.

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