Final Technical Report on

KINETICS AND MECHANISM OF SOOT FORMATION IN HYDROCARBON COMBUSTION

Lewis Grant

IN-25-CR

252537

10P.

submitted to

NASA-Lewis Research Center
Cleveland, Ohio 44135
(Technical Officer: Dr. M. J. Rabinowitz, MS 5-11)

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NASA Grant No. NAG 3-668

October 25, 1985 — February 28, 1989

January 5, 1990

(NASA-CR-186162) KINETICS AND MECHANISM OF SOOT FORMATION IN HYDROCARBON COMBUSTION Final Technical Report, 25 Oct. 1985 - 28 Feb. 1989 (Pennsylvania State Univ.) 10 p
N90-14305
Unclas
CSCL 21B G3/25 0252537

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INTRODUCTION: PROGRAM OBJECTIVES

The goal of this program, supported by NASA-Lewis Research Center from October 25, 1985 to February 28, 1989, was elucidation of the chemical reaction mechanism responsible for soot formation in hydrocarbon flames and development of computer models for practical applications. This program is a continuation of the work, initiated under the previous NASA Grant No. NAG 3-477, which resulted in discovery of the H-abstraction/C_2H_2–addition mechanism responsible for the formation and growth of polycyclic aromatic hydrocarbons (PAHs).

The primary focus of the work reported here was on kinetic modeling. The specific objectives were: detailed modeling of soot formation in premixed flames, elucidation of the effects of fuel structure on the pathway to soot, and development of a numerical technique for accurate modeling of soot particle coagulation and surface growth. We successfully completed all the above tasks, which are briefly summarized below.

DETAILED MODELING OF SOOT FORMATION IN FLAMES

A detailed modeling study of the formation of PAHs in a burner–stabilized low-pressure sooting 23.6 % acetylene – 21.4 % oxygen – argon laminar premixed flame of Bockhorn and co-workers[1] was performed. The model predicted the correct orders of magnitude and relative appearances of the concentration peaks, but overstated the decline of the species concentrations in the post-flame zone. Imprecise knowledge of the thermochemical data and unknown details of the oxidation of hydrocarbon radicals are the reasons identified for the latter. The main reaction pathways for cyclization and growth of PAHs and the results of the sensitivity tests are in close agreement with those of the previous modeling study of acetylene oxidation under shock-tube conditions. It was identified that an additional factor important in the flame environment is the diffusion of hydrogen atoms from the main reaction zone into a cooler preheat region.

ELUCIDATION OF REACTION PATHWAYS TO SOOT

Effect of Fuel Structure

The influence of fuel structure on chemical reaction pathways leading to soot formation was investigated using detailed kinetic models for the conditions of shock-tube pyrolysis of 1,3-butadiene, benzene and ethylene. It was found that reaction pathways to soot relax to the previously identified H-abstraction/C_2H_2-addition mechanism[2,3] in each case. Fuel molecular structure influences the growth process only at its early stages, first, by providing more efficient reaction partners for the formation of aromatic species and, second, by affecting generation of hydrogen atoms. The model explains the relative sooting tendencies of these fuels for the shock-tube pyrolysis conditions[3-5] and agreed with recent observations in laminar diffusion flames.[6-8]

Experimental and Modeling Study of Soot Formation in Mixtures of Hydrocarbons

Soot formation in hydrogen-, allene-, vinylacetylene-acetylene and acetylene-, allene-, vinylacetylene- and 1,3-butadiene-benzene argon-diluted mixtures was studied behind reflected shock waves by monitoring the attenuation of a 632.8 nm He-Ne laser beam. The experiments were performed at temperatures 1500-2490 K, pressures 1.3-3.1 bar, and total carbon atom concentrations $(2.0\text{-}6.8) \times 10^{17}$ atoms/cm^3. The experimental observations were interpreted using detailed chemical kinetic modeling. The reaction mechanism used in the simulations was composed of 520 reversible reactions and 180 species.

The addition of hydrogen to acetylene resulted in the decrease of soot production. Pronounced synergistic effects were observed for soot *amounts* in all binary hydrocarbon mixtures studied. However, the same experimental results expressed in terms of soot *yields* showed much smaller effects and in some cases, like in benzene-acetylene mixtures, the negative effects were obtained. These observations indicate that a) competition between promoting and suppressing factors takes place when individual fuels are mixed together, and b) one must distinguish between various experimental characteristics in the analysis of sooting trends in fuel mixtures.

The computational results, which were found to be in qualitative agreement with experiment, revealed that the main factor affecting PAH (and soot) formation in the hydrocarbon mixtures is the acceleration of acetylene-addition reactions. In mixtures of aliphatic fuels, *e.g.* butadiene-acetylene, most of these reactions are those of the dominant ring formation and growth pathway, while in benzene-additive mixtures they play different, competing roles. The main route to PAH in benzene pyrolysis is the formation of biphenyl by addition of phenyl to benzene followed by sequential addition of acetylene to form pyrene. The increase in the rate of acetylene-addition reactions of this route enhances the production of soot. At the same time, reaction of acetylene with phenyl forming phenylacetylene removes phenyl radicals from a more efficient ring-forming pathway, addition to benzene molecules, which counteracts the promoting factor. In the mixtures of aliphatics the route to soot is that via phenylacetylene and thus no competition for phenyl exists.

The influence of vinylacetylene and butadiene on PAH formation from benzene appeared to be mainly in the production of acetylene. The results obtained in benzene-allene mixtures were interpreted in an analogous way. It was suggested that the first-ring cyclization in allene mixtures proceeds not via a direct formation of benzene, as usually assumed, but by sequential addition of two C_2H_2 molecules to C_3H_3 to form benzyl.

The results of this study, both experimental and computational, provide further evidence for the importance of interaction between aromatic rings and acetylenic species, and that it is acetylene whose reactions appear to be of particular importance.

Soot Formation From Vinylacetylene

Soot formation in vinylacetylene, and vinylacetylene-oxygen argon-diluted mixtures was studied behind reflected shock waves by monitoring the attenuation of a 632.8-nm He-Ne laser beam. The experiments were performed at temperatures of 1600-2500 K, pressures of 2.08-3.09 bar, and total carbon atom concentrations of $(1.99\text{–}2.05)\times10^{17}$ atoms/cm^3. The experimental results obtained in pyrolysis of vinylacetylene are similar to those of acetylene, both in the order of magnitude of the soot yield and the shape of its temperature dependence. It is important that there is a secondary increase in the amount of soot formed from vinylacetylene, after about 2300 K, similarly to the phenomenon observed in the pyrolysis of acetylene. The addition of oxygen to vinylacetylene shifts the "soot bell" to lower temperature and, distinct from all other hydrocarbons studied in our laboratory (acetylene, 1,3-butadiene, allene, benzene and toluene), accelerates the production of soot with reaction time. Thus, it is shown that the soot amounts are smaller in a vinylacetylene-oxygen mixture than in a comparable vinylacetylene mixture at a reaction time of 0.5 ms, but with the increase in reaction time this ratio is reversed.

A detailed chemical kinetic simulation of soot formation was performed for the conditions of vinylacetylene pyrolysis. The reaction model used in this study was the one developed for the analysis of soot formation in binary hydrocarbon mixture. The computational results explain the experimentally observed similarity in soot formation from vinylacetylene and acetylene. Vinylacetylene is hard to decompose. When it does, which takes place at high temperatures, it decomposes quickly to form acetylene, which then explains the noted similarity. Oxygen promotes the decomposition of vinylacetylene, as it does in the case of other fuel molecules. However, in the case of vinylacetylene there is a high concentration of C_4H_3 radicals. Having them and acetylene molecules in high concentrations simultaneously accelerates the production of aromatic species and soot, which explains the effect of oxygen on soot formation observed in this study.

Soot Formation in Benzene-Alcohol Mixtures

Soot formation in benzene-methanol and benzene-ethanol argon-diluted mixtures was studied behind reflected shock waves by monitoring the attenuation of a He-Ne laser beam. The experiments were performed at temperatures 1580-2250 K, pressures 2.0-3.0 bar, and total carbon atom concentrations $(2.0\text{-}2.7) \times 10^{17}$ atoms/cm^3. The results obtained indicate that the addition of alcohol suppresses the formation of soot from benzene at all temperatures and the reduction in soot yields is increased with the amount of alcohol added. The analysis of the results indicates that the suppression effect is probably due to oxidation of soot and soot precursors by OH and removal of hydrogen atoms by alcohol and water molecules.

Spheroidal Carbon Clusters in Soot Formation

It has been recently proposed[9] that primary soot particles, being produced rapidly in flame environment and reaching typically an average diameter of 20 to 40 nm, are formed by a spheroidal shell growth of partially closed carbon clusters. The analysis of such a possibility in light of our chemical kinetic model for PAH and soot formation along with the results of electron diffraction analysis obtained by Ebert at Exxon led us to conclude that the importance of the carbon clusters is very unlikely in soot formation.

ANALYSIS OF THE DRIVING FORCE OF PAH FORMATION

A theoretical analysis of the kinetic factors affecting the production rate of polycyclic aromatic hydrocarbons in high-temperature pyrolysis and combustion environments was developed. The analysis is based on a lumped kinetic model, representing polymerization-type growth by one irreversible and two reversible steps, which underlies the H-abstraction/C_2H_2-addition reaction mechanism identified in previous detailed kinetic studies. The analytical solution obtained for the steady-state assumption indicates that PAH production is not determined by a single parameter; several variables influence the process to different degrees depending on experimental conditions. At high temperatures, PAH growth is controlled by the superequilibrium of hydrogen atoms. At low temperatures and low H_2 concentrations, the PAH growth rate is proportional to the rate of the H-abstraction of a hydrogen atom from aromatic molecules; at low temperatures and high H_2 concentrations, it is controlled by the thermodynamics of the H-abstraction and the kinetics of acetylene addition to aromatic radicals. The presence of oxygen mainly affects the small-molecule reactions during the induction period.

AEROSOL DYNAMICS

A new numerical method to the solution of an aerosol dynamics has been developed. It is accurate, extremely economical, applicable to any combination of aerosol processes, and does not require prior knowledge of the particle size distribution function. The method is based on the description of the aerosol evolution by moments of the particle size distribution function. The underlying idea of the method of moments is that the properties one considers in most practical applications are determined by average measures; the history of individual particles can be ignored, and what is lost in resolution can be compensated by a significant increase in computational speed and a dramatic reduction of computer memory requirements. Although the method of moments has been repeatedly explored in the past, it is for the first time an approach has been developed to use it without imposing particle size distribution function.

Also, a method was developed that allows one to combine the formalisms of the detailed description of the chemical nucleation of soot precursors, polycyclic aromatic hydrocarbons, and detailed account of coagulation and surface growth of soot particles; that is, a mathematical formalism which combines the linear and non-linear lumping techniques developed under the present program. This method was applied to analyze particle inception under shock-tube conditions.

PAH FORMATION IN THE INTERSTELLAR MEDIUM

There have been recent reports that previously unidentified the near Infra-Red emission of the Interstellar Medium is due to PAH.[10] It is actually estimated that PAH may be the most abundant organic molecules present in the Interstellar Medium.[11] In collaboration with Professor Eric Feigelson from the Department of Astrophysics at the Pennsylvania State University we have undertaken some computer simulations of PAH formation at the conditions of carbon stars using the mechanisms of PAH formation developed under our NASA-supported program for the conditions of hydrocarbon flames. The significance of such a test is the following. If our model can predict the observations under conditions so different from those of flames, it would further support the mechanism we proposed.

PUBLICATIONS

1. "Dynamics of Discrete Distribution for Smoluchowski Coagulation Model," M. Frenklach, *J. Colloid Interface Sci.* **108**, 237–242 (1985).
2. "Detailed Modeling of PAH Profiles in a Sooting Low–Pressure Acetylene Flame," M. Frenklach and J. Warnatz, *Combust. Sci. Technol.* **51**, 265–283 (1987).

3. "Aerosol Dynamics Modeling Using the Method of Moments," M. Frenklach and S. J. Harris, *J. Colloid Interface Sci.* **118**, 252–261 (1987).
4. "Rate Constant for Cyclization/Decyclization of Phenyl Radical," M. J. S. Dewar, W. C. Gardiner, Jr., M. Frenklach and I. Oref, *J. Am. Chem. Soc.* **109**, 4456–4457 (1987).
5. "Chemistry of Soot Nucleation," M. Frenklach, *Proceedings of the XVIIIth Biennial Conference on Carbon*, Worcester Polytechnic Institute, pp. 143–144 (1987).
6. "Shock–Tube and Modeling Study of Soot Formation in Mixtures of Hydrocarbons," M. Frenklach, T. Yuan and M. K. Ramachandra, *Preprints of the 194th ACS National Meeting* **32**(3), 467–473 (1987).
7. "Modeling of Large Reaction Systems," M. Frenklach in *Complex Chemical Reaction Systems, Mathematical Modelling and Simulation* (J. Warnatz and W. Jäger, Eds.), Springer Series in Chemical Physics, Vol. 47, Springer–Verlag, Berlin, pp. 2–16, (1987).
8. "Comment on the Proposed Role of Spheroidal Carbon Clusters in Soot Formation," M. Frenklach and L. B. Ebert, *J. Phys. Chem.* **92**(2), 561–563 (1988).
9. "Effect of Fuel Structure on Pathways to Soot," M. Frenklach, D. W. Clary, W. C. Gardiner, Jr. and S. E. Stein, *Twenty-First Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, pp. 1067–1076 (1988).
10. "Effect of Alcohol Addition on Shock–Initiated Formation of Soot from Benzene," M. Frenklach and T. Yuan, *Proceedings of the 16th International Symposium on Shock Tubes and Waves*, VCH, Weinheim, pp. 487–493 (1988).
11. "Soot Formation in Binary Hydrocarbon Mixtures," M. Frenklach, T. Yuan and M. K. Ramachandra, *Energy & Fuels* **2**, 462–480 (1988).
12. "Formation of Polycyclic Aromatic Hydrocarbons in Circumstellar Envelopes," M. Frenklach and E. D. Feigelson, *Astrophys. J.* **341**, 372–384 (1989).
13. "Soot in Flames and Interstellar Dust," M. Frenklach and E. D. Feigelson, *Earth and Mineral Sciences* **58**(2), 25–30 (1989).
14. "On the Driving Force of PAH Production," M. Frenklach, *Twenty-Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 1989, pp. 1075–1082.

PRESENTATIONS

1. "Soot Formation in Flames," M. Frenklach, DFVLR, Institute für Physicalische Chemie der Verbrennung, Stuttgart, West Germany, April 9, 1986 (invited).
2. "Chemistry of Soot Formation in Flames," M. Frenklach, Technische Hochschule Darmstadt, Institut für Physikalische Chemie, Darmstadt, West German, April 17, 1986 (invited).
3. "Detailed Chemical Kinetic Modeling of Soot Formation," M. Frenklach, Dipartimento di Ingegnena Chimica, Universita di Napoli, Napoli, Italy, May 14, 1986 (invited).
4. "Experimental Aspects of Soot Formation in Shock Tubes," M. Frenklach, Dipartimento di Ingegnena Chimica, Universita di Napoli, Napoli, Italy, May 14, 1986 (invited).
5. "Effect of Fuel Structure on Pathways to Soot," M. Frenklach, D. W. Clary, W. C. Gardiner, Jr. and S. E. Stein, Twenty-First International Symposium on Combustion, Munich, FGR, August 3–8, 1986.

6. "Detailed Modeling of PAH Profiles in a Sooting Low–Pressure Acetylene Flame," M. Frenklach and J. Warnatz, Twenty–First International Symposium on Combustion, Munich, FGR, August 3–8, 1986.
7. "Modeling of Large Reaction Systems," M. Frenklach, 2nd International Workshop on Modelling of Chemical Reaction Systems, Heidelberg, FGR, August 11–15, 1986 (invited).
8. "Mechanism of Soot Formation," M. Frenklach, GRI Workshop on *New Flame Radiation Research*, Factory Mutual Research Corporation, Norwood, MA, October 10, 1986 (invited).
9. "Chemistry of Soot Formation," M. Frenklach, The XVIIIth Biennial Conference on Carbon, Worcester Polytechnic Institute, July 19–24, 1987 (invited).
10. "Effect of Alcohol Addition on Shock-Initiated Formation of Soot from Benzene," M. Frenklach and T. Yuan, 16th International Symposium on Shock Tubes and Waves, Aachen, FGR, July 26–30, 1987.
11. "Shock–Tube and Modeling Study of Soot Formation Mixtures of Hydrocarbons," M. Frenklach, T. Yuan and M. K. Ramachandra, Symposium on *Advances in Soot Formation Chemistry*, 194th National ACS Meeting, New Orleans, August 31–September 4, 1987 (invited).
12. "A Unifying Picture of Gas Phase Growth of PAH, Soot, Diamond and Graphite," M. Frenklach, Conference on *Carbon in the Galaxy: Studies from Earth and Space*, NASA–Ames Research Center, November 5–6, 1987 (invited).
13. "Chemistry of Soot Formation and Related Subjects," M. Frenklach, MIT, Department of Chemical Engineering, December 3, 1987 (invited).
14. "PAH Formation in Carbon–Rich Circumstellar Envelopes," M. Frenklach and E. D. Feigelson, American Astronomical Society Meeting, Austin, Texas, January 10–14, 1988 [*Bull. Am. Astron. Soc.* **19**, 2066 (1987)].
15. "Kinetic Modeling of Complex Reaction Systems: PAH, Soot and Diamond," M. Frenklach, The Pennsylvania State University, Department of Chemistry, March 18, 1988 (invited).
16. "Mechanism of PAH and Soot Formation and Growth," M. Frenklach, Conference on *Mechanstic Aspects of PAH and Soot Chemistry*, Roam and Haas, Houston, Texas, March 30, 1988 (invited).
17. "PAH Formation in Carbon–Rich Circumstellar Envelopes," E. D. Feigelson and M. Frenklach, International Astronomical Union Symposium 135 on *Interstellar Dust*, Santa Clara, CA, July 26–30, 1988.
18. "On the Driving Force of PAH Production," M. Frenklach, Twenty-Second International Symposium on Combustion, Seattle, Washington, August 14–19, 1988.
19. "Detailed Modeling of Soot Particles Nucleation and Growth," M. Frenklach, Twenty-Second International Symposium on Combustion, Seattle, Washington, August 14–19, 1988.
20. "Kinetics of Nucleation Processes," M. Frenklach, University of Pennsylvania, Department of Chemical Engineering, September 26, 1988.
21. "Formation of Powders from the Gas Phase," M. Frenklach, The Pennsylvania State University, Department of Materials Science and the Center for Particle Science and Engineering, January 26, 1989 (invited).
22. "Particulate Formation in Hydrocarbon Combustion," M. Frenklach, University of Cincinnati, Department of Chemical and Nuclear Engineering, February 2, 1989 (invited).
23. "Formation of PCA," M. Frenklach, Prepared statement at the workshop on "Current Problems in Soot Formation during Combustion, Especially the Mechanism of Soot

Formation," the Commission on Condensation, Academy of Sciences Göttingen, FRG, March 29–30, 1989 (invited).

24. "Surface Growth," M. Frenklach, Prepared comment at the workshop on "Current Problems in Soot Formation during Combustion, Especially the Mechanism of Soot Formation," the Commission on Condensation, Academy of Sciences Göttingen, FRG, March 29–30, 1989 (invited).

RECEIVED OR GENERATED CLASSIFIED DATA

None.

PATENTS

None.

REFERENCES

1. Bockhorn, H., Fetting, F. and Wenz, H. W., *Ber. Bunsenges. Phys. Chem.* **87**, 1067 (1983).
2. Frenklach, M., Clary, D. W., Gardiner, W. C., Jr., and Stein, S. E., *Twentieth Symposium (International) on Combustion* , The Combustion Institute, Pittsburgh, 1985, p. 887.
3. Frenklach, M., Clary, W. C. and Ramachandra, M. K., NASA CR 174880, NASA–Lewis Research Center, 1985.
4. Frenklach, M., Taki, S., Durgaprasad, M. B. and Matula, R. A., *Combust. Flame* **54**, 81 (1983).
5. Frenklach, M., Ramachandra, M. K. and Matula, R. A., *Twentieth Symposium (International) on Combustion* , The Combustion Institute, Pittsburgh, 1985, p. 871.
6. Kent, J. H. and Wagner, H. Gg., *Combust. Sci. Technol.* **41**, 245 (1984).
7. Kent, J. H. and Wagner, H. Gg., *Twentieth Symposium (International) on Combustion* , The Combustion Institute, Pittsburgh, 1985, p. 1007.
8. Gomez, A., Littman, M. G. and Glassman, I., *Combust. Flame* **70**, 225 (1987).
9. Zhang, Q. L., O'Brien, S. C., Heath, J. R., Liu, Y., Curl, R. F., Kroto, H. W., and Smalley, R. E., *J. Phys. Chems* **90**, 525 (1986).
10. Leger, A., d'Hedecourt, L., and Boccara, N., Eds.: *Polycyclic Aromatic Hydrocarbons and Astrophysics* , Reidel, Dordrecht, Holand, 1987.
11. Leger, A. and d'Hedecourt, L.: p. 223 in Ref. 10.