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with increasing tendency to soot, the temperature at which soot occurs increases with the tendency to soot. Ion concentrations will be measured in this set of flames. Calculations of particle electronics and congulation rates have been initiated to determine whether the large molecular ions observed in sooting flames are the cause or effect of soot formation and in preparation for quantitative modeling of soot formation.

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### I. INTRODUCTION AND STATEMENT OF WORK

Understanding the mechanism by which soot is produced in combustion systems is one of the major challenges of combustion science today. In spite of the tremendous amount of effort which has been directed to this problem in the past and the high level of current activity, there is no consensus in the scientific community on the relative importance of a free radical or an ionic mechanism of soot nucleation.

The working hypothesis for the study at AcroChem has been that an ionic mechanism controls the nucleation step: chemi-ions formed in the combustion process initiate a chain of rapid exothermic, ion-molecule growth reactions which lead to larger and larger ions; the nature of the system gradually changes from one controlled by molecular chemical processes to one dominated by aerosol physics. During this growth process ions become neutral molecules or particles by recombination with the electrons produced in the initial chemiionization step. As the particles continue to grow, the work function for electron emission decreases toward that of the bulk substance; some of the particles then become thermally ionized. Subsequent coagulation is influenced by the charge on some of the particles. A schematic summarizing this series of reactions is given in Fig. 1. There are thus two stages in the life of a maturing soot particle in which electric charge plays a role, in nucleation and in coagulation.

In most of our work we have concentrated on the nucleation step (actually a series of reactions), but more recently we have also considered the theoretical aspects of particle charging (there are means other than thermal ionization) and coagulation. This expansion of our activities was initially motivated by the need to determine whether the large molecular ions observed in sooting flames are a cause or a result of soot formation. Some nonadherents to the ionic mechanism have proposed that the large molecular ions are only a product of the formation of soot. It is necessary to test this quantitatively. Another motivation for extending our considerations beyond the nucleation step is the desire to understand and model the total process. We feel we are now in a position to profitably initiate detailed modeling of soot formation in combustion systems.

The dominant motivation for Air Force support of this work is the anticipated need to use off-specification fuels, possibly derived from coal, tar sands,

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and shale oil, or possibly low grade petroleum sources. Such fuel sources all have greater C/H ratios than currently used petroleum crudes, and this is expected to greatly enhance the sooting tendency of any combustion system. Present fuels, in fact, are a problem in many current jet aircraft in terms of the degradation of component lifetimes by flame radiation (from soot particles even when there is no visible smoke emission) and in creating a tactically undesirable smoke trail. Our program thus included some shorter term objectives of a more empirical nature to determine the effect of molecular structure on soot formation and to relate these results to performance in jet aircraft. One objective of this effort was to determine the relevance of work done in the laboratory to performance in real engines. During this reporting period Tyndall Air Force Base initiated a program<sup>1</sup> at AeroChem to permit us to put more effort into this aspect of the problem.

The Statement of Work from the contract reads:

"1. Perform ionic species concentration measurements at high molecular weights (up to approximately 5000 amu) in premixed flames of acetylene, benzene, and hexane to provide experimental data with which to test the ionic mechanism of soot formation.

2. Calibrate the ion concentrations determined with the mass spectrometer by comparing the mass spectral data with electrostatic probe data in flames in which a single ion is dominant.

3. Perform computer simulations of rich and sooting flames to test proposed detailed mechanisms of initial soot nucleation. This study will consider three alternative reactions schemes: an ionic nucleation and growth mechanism, a butadiene intermediate neutral-radical mechanism, and a neutral-radical polyacetylene growth mechanism.

4. Determine the effects of temperatures on soot threshold and ion concentrations in premixed flames of several representative hydrocarbon fuels. Experiments will be performed in flames with constant temperature and variable fuel-air ratio, and with constant fuel-air ratio and variable temperature by heating or cooling the unburned gases and by varying the composition of the inert diluent gas.

5. Determine quantitatively the total ion concentrations (by electrostatic probe) and the temperature at sooting threshold for a series of fuels with different tendencies to soot.

6. Interpret the above data and mechanisms in terms of the potential effects of new fuels on soot formation in air-breathing engines, and possible means of minimizing soot formation in air-breathing engines."

# II. STATUS OF RESEARCH EFFORT

Many of the results of this program have been submitted for publication so they will only be summarized here; the publications and presentations are listed in Sections III and V and copies are included in Appendices A-D.

Some ionic species measurements were made in acetylene-oxygen flames after the AeroChem built quadrupole mass filter (mass range 13-300 amu) was replaced by a commercial high resolution instrument from Extranuclear Labs., Inc. (mass range 30-5000 amu). When the instrument was operated in a high pass mode which permits collection of all ions > 600 amu, large concentrations of ions were observed in sooting but not in nonsooting flames. However, when operated in the normal mode to observe the mass spectra of individual ions, very few detailed ion mass spectra were obtained above mass 300. It appears that the ions grow rapidly from masses of less than 300 amu (corresponding roughly to six ring polycyclic aromatic hydrocarbons) to very large masses. This work is still in progress and any observations at this point must be considered tentative until the experiments can be verified and expanded.

A major difficulty has been the calibration of the mass spectrometer for the high mass range, i.e., the determination of how the relative sensitivity of the instrument varies with mass. For an instrument used with an ionization source this is not a difficult problem; when sampling ions directly from a flame it becomes a serious problem. Several schemes have been devised and will be considered during the next year.

An extensive effort has been directed to developing a suitable Langmuir (electrostatic) probe theory and to performing experiments so that such probes can be used to obtain accurate total ion concentrations in sooting flames. Such data are badly needed and the data in the literature are inconsistent--to the point that this was a major criticism of our hypothesis, see, e.g., Refs. 2 and 3. In performing these experiments, problems were initially encountered with soot coating out onto the probes, altering the electrical characteristics and the size of the small (0.025 cm diam x 0.25 cm long) probes. This problem

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was alleviated by moving the probe in and out of the flame very rapidly and taking measurements rapidly before the probe became coated with soot. The theoretical problems of relating probe currents to ion concentrations were more severe. These were associated with selecting the appropriate theory to convert probe currents to ion concentrations in a system where the flame ions are very heavy, essentially small charged particles. There are numerous probe theories available but none had considered this specific problem. Several potentially applicable theories were thus examined to determine whether their underlying assumptions were applicable to our specific experimental conditions. The applicable theories were then experimentally evaluated to determine whether they correctly predicted the dependence of the results on the experimental parameters (e.g., probe diameter, probe length, and probe voltage). It was found that several theories were applicable for nonsooting flames but very few were suitable for the sooting flames. Thus, for nonsooting flames the theories of Calcote<sup>4</sup> and Clements and Smy<sup>5</sup> were chosen. In sooting flames the Clements and Smy thick sheath convective theory<sup>5</sup> was used.

Another problem in using electrostatic probes in sooting flames is that they require ion mobilities for large ions at high temperatures and these are not readily available. Neither the mass of the ions (particles) nor the mobility as a function of temperature for our conditions were available. A semiempirical mobility relationship as a function of mass and temperature was thus developed by comparing theories for ion mobility with the limited experimental results reported in the literature. For one flame under our conditions Homann and Stroefer<sup>6</sup> had obtained charged particle distribution curves which we used to interpret our probe data. The results of this work will be published next year. It is clear, however, that Langmuir probe and charged particle distribution measurements by mass spectrometry, such as done by Homann and Stroefer, must be made on the same flame in order to obtain reliable total charged particle data. This should be done for several typical flames. Unfortunately, the work required is beyond the scope of the present program.

We have previously' emphasized the importance of determining the effect of temperature on the tendency of flames to soot. One way to study this would be to compare fuel structure effects on the threshold soot point at the same temperature. Our initial efforts in this direction, however, were to use the TSI for premixed flames<sup>6</sup> to obtain the equivalence ratios at which soot forms in premixed flames,  $\phi_c$ , on a specific burner system for a series of fuels. We

then calculated the adiabatic flame temperature at  $\phi_C$  for each flame. These data demonstrated that when the flame temperature is varied by changing the fuel, the tendency to soot increases with increasing flame temperature. This contrasts with the effect of temperature on the tendency to soot for a specific fuel when the temperature is altered, for example, by adding N<sub>2</sub> or O<sub>2</sub>; in this case increasing the temperature decreases the tendency to soot. The difference demonstrates the important role played by molecular structure on the tendency of a fuel to soot. This has been published.

Subsequent to the above publication we measured the flame temperature at the soot point for a series of fuels and confirmed the conclusions. In the next year we plan to determine the total ion concentration in these flames by electrostatic probe measurements.

To support our hypothesis that the large ions observed in incipient sooting flames arise from chemi-ionization and ion-molecule reactions, and are not produced from charged particles we have reviewed the literature on particle electronics. Another motivation for this activity was to further develop the basis for quantitative modeling of soot formation. In reviewing the subject of particle electronics we formulated the quantitative expressions in a uniform manner so that they could be applied consistently, and when an appropriate expression was not available one was developed. This work is continuing and we hope to submit it for publication soon; part of these results was presented as an invited paper at the First Annual Conference of The American Association for Aerosol Research in February 1982.

The processes considered are summarized below (P represents a particle, M a molecule):

Thermal Ionization or Thermionic Emission:

 $P \xrightarrow{\text{energy}} P^+ + e^-$ 

This will be the dominant process in producing charged soot particles.

Diffusive Charging:

 $P + M^+ + PM^+$ 

This process will be important when chemical additives of low ionization potential are used to influence soot formation.

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Electron Attachment:

 $P + e^- \rightarrow P^-$ 

Charged Particle-Electron or Ion Recombination:

 $P^+ + e^- + P$  $P^+ + M^- + PM$ 

Because negative ion concentrations are usually much smaller than electron concentrations and the rate coefficients are smaller, only electron recombination is considered of importance.

Proton or Hydride Ion Removal from Charged Particles:

 $PH^+ \rightarrow P + H^+$  $PH^- \rightarrow P + H^-$ 

For energetic reasons this process would be considered only in a reaction in which the proton or hydride ion becomes attached to a molecular species. The process then becomes equivalent to an ion-molecule reaction:

 $PH^+ + M + P + MH^+$ 

for which the rate coefficient will be very large if the overall process is exothermic. To estimate this rate coefficient the energetics of the proton or hydride ion removal from charged particles was calculated.

### Coagulation:

The rate of coagulation or agglomeration for particles of equal diameter, d, which are small compared to their mean free path, is calculated by the equation:

$$\frac{dN_p}{dt} = k_c N_p^2$$

where:

$$k_{c} = 0.866 d^{1/2} \left(\frac{kt}{\rho_{p}}\right)^{1/2} G \cdot \alpha \cdot S$$

in which  $\rho_p$  is the density of the particle, G is a complicated function which takes into account particle dispersion and electrostatic forces,  $\alpha$  is the collision integral for a self-preserving size distribution, and S is a sticking coefficient. The factor G, has been calculated for soot particles of varying diameter for the processes: P + P + PP  $P^+ + P^- + PP$   $P^+ + P^+ + Pp^{+2}$   $P^- + P^- + Pp^{-2}$ 

The rates of the last two reactions are equivalent.

The above quantitative considerations should be very useful in evaluating the relative importance of various processes in sooting flames and should be especially useful in explaining the role played by chemical additives in affecting soot formation in flames. To demonstrate this usefulness we chose the atmospheric pressure ethylene-air flame studied by Haynes, Jander, and Wagner<sup>10</sup> to which they added alkali metals and alkaline earths. They measured the parti cle number density with and without various additive (seed) concentrations as a function of distance above the burner. The detailed conditions for this flame are given in Table I. We will treat only one point, 2.2 cm above the burner. At this point we calculate the characteristic times for the various processes as indicated on Fig. 2. The significance of being able to make such calculations is that it permits one to choose which processes to consider in a detailed model. It also gives a quantitative understanding of the system. The characteristic flow times vary over five orders of magnitude; those falling far shorter than the characteristic flow time must be considered infinitely fast and those far longer than the characteristic flow time to be infinitely slow. This flame demonstrates that potassium will give different results depending upon whether or not chemi-ions are present; larger concentrations of potassium ions are obtained from chemi-ion transfer than by thermal ionization. When no potassium is present, the ions produced by chemi-ionization, e.g., C.H., will disappear by dissociative recombination with electrons. When potassium is present, charge transfer will occur extremely rapidly producing K<sup>+</sup>, which then disappears very slowly by three body recombination. An additional effect which must be considered is the removal of  $C_3H_3^+$  by the transfer of charge to K thus interfering with the initial ion-molecule steps in soot nucleation, e.g.:

 $C_{3}H_{3}^{+} + C_{2}H_{2} + C_{3}H_{3}^{+} + H_{2}$ 

Calculation of the half life for this process, assuming 0.1% acetylene, gives a value of about  $10^{-7}$  s. Thus at the concentration of potassium present in the Haynes et al. flame the nucleation step is not affected. Further examination

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of Fig. 2 shows that diffusive charging of the soot particles, P, by potassium ions is much faster for smaller particles. Similarly, the effect of particle charge on the coagulation rate is greatest for small particles.

From a consideration of the results presented here, it is clear why the addition of alkali metals to this flame affects the particle size and particle number density. It is also clear that we are in a position to develop detailed quantitative models--in which the important processes are considered simultaneously--of the effect of chemical additives on soot formation.

### TABLE I

PROPERTIES OF ETHYLENE-AIR FLAME OF HAYNES, JANDER, AND WAGNER<sup>10</sup> Distance above burner 2.2 cm

Property	Value
Equivalence ratio	2.28
Temperature	1740 K
Time from flame front	25 ms
Unseeded particle diameter	37 mm
Unseeded particle number density	$3.2 \times 10^9 \text{ cm}^{-3}$
Potassium seed concentration	3.8 × 10 <sup>12</sup> cm <sup>-3</sup>
Seeded particle diameter	13 nm
Seeded particle number density	2.9 x 10 <sup>10</sup> cm <sup>-3</sup>
Equilibrium potassium ion concentration	$4.3 \times 10^{8} \text{ cm}^{-3}$
Potassium ion concentration via chemi-ionization (estimate)	- 5 × 10° cm <sup>-</sup>



FIGURE 2 CHARACTERISTIC TIMES FOR SOME REACTIONS IN AN ETHYLENE-AIR FLAME AT 1 ATM

Measurements from Haynes, Jander, and Wagner.<sup>10</sup> Equivalence ratio, 2.28. At 2.2 cm above burner, 25 ms.

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# III. PUBLICATIONS

 "Importance of Temperature on Soot Formation in Premixed Flames," Calcote, H.F. and Olson, D.B., AeroChem TP-416, Combustion Science and Technology <u>28</u>, 315-317 (1982). 2. "Effect of Molecular Structure on Incipient Soot Formation," Calcote, H.F. and Manos, D.M., June 1982, AeroChem TP-406a. The original manuscript has been considerably modified and submitted to Combustion and Flame. It should be published within the next several months.

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- "Ionic Mechanisms of Soot Formation," Calcote, H.F., Proceedings of NATO Workshop on Soot in Combustion Systems, Le Bischenberg, France, 31 August to 3 September 1981, AeroChem TP-415, to be published by Plenum Press.
- "Langmuir Probe Measurements in Sooty Flames," Gill, R.J., Olson, D.B., and Calcote, H.F., in preparation for submission to Combustion and Flame.
- 5. "Ionic Mechanisms of Soot Formation in Flames," Calcote, H.F., an invited review for Progress in Energy and Combustion Science, in preparation.

## IV. <u>PERSONNEL</u>

The key personnel on this program have been the authors but others have contributed their special talents, especially to the experimental measurements which are unusually tedious because of the fine aerosol nature of soot. The participation of the following technical personnel is thus gratefully acknowledged:

> R.J. Gill, PhD Physical Chemist J.J. Houghton, Research Associate J.C. Pickens, Research Technician R. Taweel, Technician

# V. <u>TECHNICAL INTERACTIONS</u>

Technical interactions with the scientific community have taken many forms, foremost have been technical presentations, and especially presentations and participation at workshops, see below. AeroChem held an informal workshop on soot on 6 May 1981 with 17 people in attendance--no sponsors. This served as an excellent means of information exchange and the comments afterwards were all positive. Technical interactions in another area, that of proposal and manuscript review, seem to have increased on subjects related to ionic effects in soot formation. We like to think the increased activity in this phase of soot work is due, at least partially, to our championing the subject. Our personal contacts with many others in the field have been maintained by contact at technical meetings, correspondence, and phone calls.

### Presentations

- "Kinetics of Ion-Molecule Reactions," Calcote, H.F., "Workshop on Plasma Chemistry in Technology," Ashkelon, Israel, 30 March-1 April 1981.
- 2. "Mechanism of Soot Formation in Flames," Calcote, H.F., Seminar at University of Beer-Shiva, Israel, 3 April 1981.
- "Ionic Mechanisms in Soot Formation," Calcote, H.F., NATO Workshop on Soot in Combustion Systems," Le Bischenberg, France, 31-August-3 September 1981. TA-242.
- 4. "Ionic Mechanisms of Soot Formation in Flames," Calcote, H.F. and Olson,
   D.B., AFOSR Airbreathing Combustion Dynamics Meeting, Clearwater, FL.,
   16-20 November 1981. TA-246.
- 5. "Ion and Charged Particle Contribution to Soot Formation in Flames," Calcote, H.F., Invited presentation at First Annual Conference, American Association for Aerosol Research, Santa Monica, CA, 17-19 February 1982. TA-250.

### VI. INVENTIONS AND PATENT DISCLOSURES

There are no inventions or patent disclosures to report.

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23.2.216

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- 3. Calcote, H.F., "Ionic Mechanisms of Soot Formation," <u>Proceedings of NATO</u> <u>Workshop on Soot in Combustion Systems</u>, Le Bischenberg, France, 31 August to 3 September 1981, Plenum Press, to be published.
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- Haynes, B.S., Jander, H., and Wagner, H.Gg., "The Effect of Metal Additives on the Formation of Soot in Premixed Flames," <u>Seventeenth Symposium</u> (International) on Combustion (The Combustion Institute, Pittsburgh, 1979) p. 1365.

# APPENDIX A

### COMBUSTION AND FLAME

# Effect of Molecular Structure on Incipient Soot Formation

### H. F. CALCOTE AND D. M. MANOS\*

AeroChem Research Laboratories, Inc., P.O. Box 12, Princeton, NJ 08540

A rational threshold sout index (TSI) varying from 0 to 100 is defined for evaluating the onset of sout formation in both premixed and diffusion flames. It is shown that all of the data in the literature on either premixed or diffusion flames, taken by many techniques, are consistent with respect to molecular structure for each of the two types of flames. There is also a closer similarity between the effect of nolecular structure on som formation in premixed and diffusion flames. There is also a closer similarity between the effect of nolecular structure on som formation in premixed and diffusion flames than previously thought. The use of TSI permits one to use all of the literature data to interpret nolecular structure effects and thus arrive at rules for predicting the effect of molecular structure for compounds which have not yet been measured or to correlate the results from one experimental system with another. If a correlation can be demonstrated between the effect of molecular structure on sout formation in laboratory and its effect in practical systems, then TSIs will be useful to the soyfuels program for defining the desired fuel components to be prepared from a given feedstock.

### INTRODUCTION

As synfuels play a greater role in meeting future energy demands, a better understanding of the factors governing their propensity to form soot is required. Quantitative prediction of the sootforming characteristics of new fuels can probably best be achieved from an understanding of the quantitative behavior of their individual hydrocarbon constituents.

There are two distinct facets to the consideration of the effects of fuel molecular structure on sooting. First, as a given premixed fuel/oxidant combination is made increasingly fuel rich (or as the primary aeration of a diffusion flame is decreased), a rather sharp onset of sooting is observed. This facet of the tendency to soot is important in practical applications where the total absence of sooting is desirable. The second facet is that further increasing the fuel concentration beyond the point of soot onset causes increasingly greater quantities of soot to form at a rate which depends on fuel structure. In this paper, we con-

Copyright (c) 1982 by The Combustion Institute Published by Elsevier Science Publishing Co., Inc., 52 Vanderbilt Avenue, New York, NY 10017 centrate on the specification of the onset of soot formation. Data on this aspect of sooting from a variety of measurements made in both premixed and diffusion flames have been gathered from the literature and correlated. The objective was to determine the degree of consistency, or inconsistency, of the data in the literature on the effect of molecular structure on soot formation in both premixed and diffusion flames, and the relation, if any, between the two types of flames. Assuming a consistency is established for the data, the objective will be to deduce an empirical description of how molecular structure controls the onset of soot. Others have considered the effect of molecular structure on soot formation but have limited themselves to data collected in a single type of apparatus, where they have been limited by the number of compounds studied. These studies usually conclude that certain trends in the effect of molecular structure agree with results of previous work, although significant differences in the actual numerical values occur between different studies. In this study, we have made such comparisons quantitative, so that separately obtained sets of data can be com-

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pared directly and so that all of the available data can be used to deduce molecular structure effects.

We assume that we can define a "threshold soot index" (TSI) that ranks the fuels from 0 to 100 (0 = least sooty) and is independent of the particular experimental apparatus in which the data were obtained. A quantitative value for each molecule is thus obtained so that different molecules studied by different investigators (using different experimental apparatus) can be considered in elucidating the effect of molecular structure on soot formation. One of the first objectives in this paper will be to demonstrate the validity of this assumption.

This kind of information should be of great value in attempts to understand the relation between laboratory data and engine data. Such correlations, if they could be demonstrated, would reduce the number of engine tests required to establish the effect of molecular structure on engine performance. The real impact should be on the synfuels engineer in determining the type of molecules to strive for in the refining processes. The situation is analogous to the empirical understanding of the relation between octane or cetane number and molecular structure and the objectives of petroleum engineers in structuring the products of petroleum refineries.

### SOURCES OF DATA

The data on incipient soot formation are divided into two categories: premixed flames and diffusion flames. Data on premixed flames were taken from Street and Thomas [1], Wright [2], Calcote and Miller [3], Grumer, et al. [4], and Blazowski [5]. Data on diffusion flames came from the work of Minchin [6], Clarke et al. [7], Hunt [8], Schalla and McDonald [9], Van Treuren [10], and Schug, et al. [11]. In addition to measurements on pure hydrocarbons, some of these workers studied fuels consisting of mixtures of hydrocarbons and organic compounds containing heteroatoms (O, N, S, Cl, etc.). Only the reported data on pure hydrocarbons are considered here.

The most extensive data set from premixed flames is that of Street and Thomas [1]. These authors used an apparatus in which a flow of heated fuel was mixed with air to form either a vapor

mixture or fuel mist, according to the compound's vapor pressure. These mixtures were then burned in a shielded Bunsen flame, and the fuel/air ratio was increased until a yellow tip was first observed. This critical composition was reported Grumer et al. [4] burned only premixed fucl vapors. reporting fuelair composition at the yellow tip limit. Similar measurements on completely vaporized fuels were made by Calcote and Miller [3] with a shielded flat flame burner. They demonstrated a sensitivity of their results to the unburned mixture flow velocity, although at higher velocity their results were independent of velocity. Wright [2] used a heavily backmixed, jet-stirred combustor, from which he reported the critical fuel/air ratio which caused the first visible appearance of soot on a probe filter placed in the reactor outlet. This reactor allowed richer mixtures than on a premixed burner to burn without sooting; a number of compounds found to soot in other premixed flame studies reached their rich blowoff limit without sooting in this apparatus. Additional studies from the same apparatus have been reported by Blazowski [5].

For dilfusion flames, Minchin [6] made measurements of the (now standard) smoke point employing a wick-style burner in which the fuel flow was increased until soot was observed to be liberated from the tip of the flame. The flow was decreased just enough to suppress the liberation of soot, and the height of the flame, referred to as the "smoke point," was recorded. Hunt [8] performed the same type of measurement on a very large number of pure compounds, using a burner of different dimensions. Clarke and coworkers [7] also measured flame heights, as described above; however, they burned the liquids as pools in a funnel-shaped burner, rather than on wicks. By clevating the level of the liquid in such a funnel, the area of the pool was increased and more fuel was vaporized into the flame. The physical characteristics of a duplicate of this burner were studied by Van Treuren [10], who reported excellent agreement with the values of Clarke et al. Van Treuren showed that the actual numerical results of such measurements depend strongly on the burner temperature and burner and chimney dimensions. Schalla and McDonald [9] used three different burners, one for gases and two for li-

2

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quids. Liquids were burned either in a wick style lamp or in a burner with prevaporization. Rather than recording the flame height, Schalla and McDonald recorded the volume rate of fuel flow  $[cm^3(STP) s^{-1}]$  at the point where further increases in fuel flow caused the onset of soot. Glassman and associates [11] used an apparatus similar to that described by Schalla and Hubbard [12] consisting of a 1-cm-i.d. central fuel jet and a 10-cm concentric confining tube through which the flow of air was regulated. Both sooting heights and the critical flow velocity were measured.

Because of the various experimental differences between these studies, a direct comparison of the quantitative results is not possible without further data processing. We shall now show how the data were treated to condense all premixed flame data and all diffusion flame data into two internally consistent data sets.

### DEFINITIONS AND METHOD OF TREATING DATA

In this section we define a threshold soot index TSI which is derivable from measured quantities for both premixed and diffusion flames. This allows one to consider all of the data available in these categories and to compare TSI quantitatively for different types of molecules. Qualitative comparisons of this sort, though common [13, 14], can be grossly misleading, as will be demonstrated in the results and discussion section.

It is generally recognized that substances with lower smoke points are in some sence "sootier" than those with higher smoke points. Minchin defined a parameter called "tendency to smoke" as a constant divided by the smoke point. This definition has been accepted since his 1931 paper. Similarly, it has been recognized that in premixed flames, the lower the carbon-to-oxygen ratio C/O, or the lower the critical equivalence ratio  $\phi_{e}$ ,<sup>1</sup> the greater the tendency of the fuel to soot. In defining TSI, it is desirable to define a parameter which reflects the correlation of incipient sooting with molecular structure, i.e., the oxidative chemistry of the fuel, and does not reflect differences in transport properties due to the nature of the measurement apparatus or the quantity of oxygen which must diffuse into the flame front (in the case of diffusion flames).

For premixed flames, consider two hypothetical hydrocarbon fuels of very different molecular weights or C/II ratios both of which liberate soot when burned at identical equivalence ratios. It is clear that a definition of TSI as

$$TSI = a - b\phi_c, \tag{1}$$

with a and b constants for a given set of data, will yield the same value for both of these hypothetical compounds. We therefore adopt the definition of Eq. (1) in this work, recognizing that other definitions are possible, e.g., based on C/O ratios.

Minchin's definition of tendency to soot for diffusion flames as inversely proportional to the height of the flame which would just soot contains an inherent flaw; it does not account for the increased height of the flame which would be required with increasing fuel molecular weights MW. An increase in molecular weight requires more oxygen to diffuse into the flame to consume a unit volume of the fuel. This can be accounted for by defining the threshold soot index for diffusion flames as

$$\Gamma SI = a \left( \frac{MW}{h} \right) + b, \qquad (2)$$

where a and b are constants for any given experimental setup and h is the critical height of the flame for which soot is first observed. A better approximation would be to employ the moles of air required for the combustion of one mole of fuel instead of *MIV*. The accuracy of the data and the arbitrariness of defining the products of combustion are such that the convenience of using the molecular weight is acceptable.

The critical volumetric flow rate V is also used as a measure of the tendency to soot in diffusion

 $<sup>{}^{1}\</sup>phi_{e}$  is defined as the minimum equivalence ratio  $\phi$  for subting, where  $\phi = (fuct flow/oxidizer flow)/(fuct flow/$  $oxidizer flow)_stolehlometrie-$ 

flames. According to the Burke and Schumann theory of diffusion flames [15],

$$h = \frac{V}{4\pi C_1 D},$$
 (3)

where  $C_{i}$  is the fuel mole fraction at the flame tip and D is an average diffusion coefficient of the system. This equation predicts a linear correlation between the height of a diffusion flame and the volumetric flow rate. This has recently been reconfirmed experimentally be Glassman and associates [11]. Thus we can also define for a diffusion flame

$$TSI = a\left(\frac{MW}{V}\right) + b, \qquad (4)$$

where V is the critical volumetric flow rate for production of soot as used by Schalla and Mc-Donald.

To compare the sets of data taken in different laboratories or on different burners, for either premixed or diffusion flames, we adjust the arbitrary proportionality constants a and b in Eq. (1) for premixed flames and Eqs. (2) and (4) for diffusion flames for each data set to minimize the error between the TSI values for individual compounds common to more than one set of data. The resulting merged set of TSI values, spanning the range of hydrocarbons measured by all experimenters, is then linearly scaled so that  $0 \le TSI \le$ 100 for the compounds.

The technique can best be demonstrated by an example, for which we shall use diffusion flame data; exactly the same procedure was followed for premixed flames. We chose two compounds from the data set of Hunt which have the highest and near the lowest MW/h, namely, 1-methyl naphtahalene and *n*-hexane. We arbitrarily assign them TSI values of 100 and 2.0 respectively. With the molecular weights and smoke points (*h* in millimeters) from Hunt, Eq. (2) is written for *n*-hexane

$$2 = a_1 \left(\frac{86}{149}\right) + b_1,$$

and for methyl naphthalene

$$100 = a_1 \left(\frac{142}{5}\right) + b_1.$$

Solving for  $a_1$  and  $b_1$  gives

$$a_1 = 3.52, \quad b_1 = -0.0331.$$

With these constants the  $TSI_1$  values were calculated for each of the compounds measured by Hunt, which gives data set 1.

For the second data set, that of Clarke et al., we chose two compounds in common with the first data set, namely, *n*-heptane and decaline, for which we use the TSI value for these substances as calculated using the a and b constants appropriate to Hunt's data and the smoke point value in centimeters as determined by Clarke et al. Thus for *n*-heptane

$$2.36 = a_2^0 \left(\frac{100}{15.9}\right) + b_2^0$$

and for decalin

$$12.8 = a_2^0 \left(\frac{138}{3.5}\right) + b_2^0.$$

Solving for  $a_2^0$  and  $b_2^0$  gives

$$a_2^0 = 0.315, \quad b_2^0 = 0.379.$$

These constants, based on only two fuels, and specific to the data set of Clarke et al., are now used to calculate a preliminary TSI value, written  $TSI_2^0$  for each substance in data set 2.

The next step is to minimize the above differences between the TSIs for the individual compounds of the two data sets. This is done by making a least-squares linear correlation of the two sets of data for  $TSI_1$  and  $TSI_2^0$ , employing only the compounds which are common to both data sets. This procedure yields  $m_2$  and  $C_2$  in the equation correlating the two sets of data:

$$\mathrm{TSI}_1 = m_2 \mathrm{TSI}_2^0 + C_2. \tag{5}$$

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Thus the TSIs for the second set of data can now be put on the same scale as the TSIs for the first set of data (i.e.,  $TSI_1 = TSI_2$ ) by substituting  $TSI_2^0$  in the form of Eq. (2) into Eq. (5), yielding

}

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$$b_1\left(\frac{MW}{h}\right) + b_1 = TSI_1$$
  
= TSI\_2  
=  $m_2 d_2^0 \left(\frac{MW}{h}\right) + m_2 b_2^0 + C_2$   
(6)

(which holds for each individual fuel). Thus for the calculation of TSI by Eq. (2) for data set 2,  $a_2 = m_2 a_2^0$ ,  $b_3 = m_2 b_3^0 + C_3$ . With these values of  $a_2$  and  $b_3$ ; the TSI values for all of the data in the second data set were calculated. The data from the two sources are not in a single quantitatively comparable form.

This process was repeated for each data set, yielding constants for each data set which minimize the differences between the various sets of data. For those compounds which occurred in more than one data set, the TSIs were averages to give a mean value. This gives a TSI for each substance except that the limits are not 0-100. To fix the TSI scale range from 0 to 100, the TSI of the lowest value in the total of all the data sets was set equal to 0 and the highest value equal to 100 [TSI(ethane) = 0, TSI(naphthalene) = 100]. This linear adjustment of the TSI<sub>0-100</sub> was accomplished as follows:

$$TSI_{0.100} = (TSI - X) \left(\frac{100}{Y - X}\right),$$
 (7)

where TSI = TSI value being corrected, X = TSIof ethane on old scale, and Y = TSI of naphthalene on old scale. The constants *a* and *b* reported in Table 1 were thus obtained by combining Eqs. (7) and (2):

$$TSI_{0-100} = \frac{100}{Y-X} \left( a_1 \left( \frac{MW}{h} \right) + b_1 - X \right),$$
 (8)

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$$a = \left(\frac{100}{Y-X}\right) a_1, \quad b = \frac{100}{Y-X} \quad (b_1 - X).$$

This process can clearly be iterated for any new data set (by adjusting the total scale), or the new data set may be fit into the total data base by cal-

Constants for Calculation of TSI from Original Data								
Source	Original Data Form	•	•					
Premixed Flames								
Street and Thomas [1] Grumer et al. [4] Wright [2] Calcote and Miller [3] Blazowski [5]	40 60 60 60 60	219 181 204 303 227	101 81.6 78.1 147 101					
Diffusion Flemes								
Minchen [6] Clarke et al. [7] Hunt [8] Schalla and McDonald [9] Van Treuren [10] Schug et al. [11] /	ት ት ሁ ት ሁ	0.178 0.381 3.10 0.0322 0.594 0.144	15.7 -0.76 1.07 0.85 -1.16 -1.55					

TABLE 1 Constants for Calculation of TSI from Original Date

culation of a and b for the new data through the least-squares linear correlation step above.

The data for premixed flames were treated similarly.

The constants, u and b calculated by Eq. (8) for each data set are given in Table 1. These allow translation of the TSI for any fuel to the conditions of any particular experiment, even though that substance may not have been investigated under those conditions. Suppose, for example, one wishes to know the critical equivalence ratio for soot formation for *n*-cetane in the well-stirred reactor of Wright, where is has not been measured. Rearranging Eq. (1) gives

$$b_c = \frac{a - TSI}{b}$$
.

By substituting a and b for Wright from Table 1 and TSI for *n*-cetane from Table 2, we calculate  $\phi_e$  in the stirred reactor:

$$\phi_c = \frac{204 - 76}{78.1} = 1.64.$$

This can be extremely useful in interpreting data; for example, see Ref. [16].

The consistency of the results shown in Tables 2 (premixed) and 3 (diffusion) may be judged by comparing the deviations in TSI values for those compounds common to two or more data sets. In spite of the very different nature of premixed flame measurements and the uncertainties that are associated with each of them, it is clear from Table 2 that the TSI values are fairly consistent. The reported error is the average deviation from the mean. When the data are averaged for compounds common to more than one data set, the mean scatter introduced is ±8% (excluding acetylene with  $TSI \approx 0$ ). The maximum scatter was ±20% for ethane; only I data point in the total of 63 was excluded for reasons of gross disagreement; that point is indicated in the table in brackets. The above deviation is not more than the absolute error associated with the individual members of the set; some results are reported to only one significant figure. Table 2 includes not only Bunsen burner and flat flame data but also the data by Wright [2] and Blazowski [5] in a back-mixed jet-stirred reactor. The original rationale for taking data in a jet-stirred reactor was that the aerodynamics more closely duplicates that occurring in actual hardware, especially gas turbines. The correlation in Table 2 strongly suggests that chemistry, not aerodynamics, is controlling the critical composition for soot formation.

The mean scatter from averaging the diffusion flame data (Table 3) is ±13%; if propane (±117%) and propylene (±46%) are excluded (and ethane with TSI = 0, the mean scatter is  $\pm 9\%$ . Other substances for which the accuracy of the data is poor are p-cymene ( $\pm 36\%$ ), acetylene ( $\pm 27\%$ ), 2,2 dimethyl propane (18%), tetraline (±18%), 1-pentene (17%), and explene (±16%). Six data points out of 147, or 4% of the data points, were excluded because of gross disagreement with the other points. A data point was excluded only when three or more measurements were available for the same substance and one of them was obviously out of line-see the bracketed numbers in Table 3. Again, the agreement between different investigators using different techniques emphasizes the importance of chemistry in determining the critical composition for soot information.

### **RESULTS AND DISCUSSIONS**

It was demonstrated in the previous section that measurements of the threshold for soot formation for either premixed or diffusion flames made by many different investigators using different methods are consistent when the individual sets of data are appropriately treated using two constants to normalize each data set. This implies that chemistry is the controlling process in soot formation in both premixed and diffusion flames.

Before discussing the question of a correlation between the premixed data and the diffusion data, the effect of molecular structure on premixed and diffusion flames will be discussed separately.

### Premixed Flames

Most of the TSI data in Table 2 are plotted against the number of carbon atoms in the molecule and

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Threshold Soot Index (TSI) for Compounds Measured in Premixed Flames

					Threshold soot index (TSI)				
		Mole				Reference			
Formula	Name	wi,	C/II	<u>_01</u>	[2]	131	141	151	Mean
CH	Methane	16	0.250				34		
Calle	Ethane	30	0.333	42			28		35 ± 7
Calla	Propane	44	0.375	53		47	49		50 + 2
C <sub>4</sub> H <sub>10</sub>	n-Bulane	58	0.400	61			53		57 ± 4
Calliz	я-Penta <b>ne</b>	72	0.417	• 63					
C <sub>5</sub> ll <sub>12</sub>	Isopentane	72	0.417	61					
Callia	n-Hexanc	86	0.429	65		63			64 ± 1
Callia	2-Methyl pentane	86	0.429	65					
Callin	Cyclohexane	84	0.500	58		53			56 ± 3
Callin	n-Octane	114	0.444	72		52			62 ± 10
Callia	isooctane	114	0,444	65					
Cioline	Decaline	138	(† 5 <b>56</b>	85					
Cipling	Isododeca <b>ne</b>	170	0.462	70					
Ciallan	n-Cetane	226	0.471	76					
Calla	Ethylene	28	0.500	26	41	33	27	24	30 + 6
Cilla	Propylene	42	0.500	42	37		{63}6		40 + 3
Calle	n-Butene	56	0.500	53	46		()		50 ± 4
Calla	Isobutenc	56	0.500		62		67		65 + 3
Cellia	n-Pentene	70	0.500	56			•••		
Calles	w-lleptene	98	0.500	65		55			60 + 5
Calle	1 3-Butadiene	54	0.667	00	77				0010
Calla	Acetylene	26	1.00	-15	•••	16			0.00 + 1.5
Calla	Renzene	78	1.00	68	91	75	85		80 + 9
Calla	Tolucne	92	0.875	78	87	93	72	86	83 + 7
Callin	Xyknes	106	0.800	85	90	91		95	91 + 5
Collic	Cumenc	120	0.750	#1	79	74		85	80 • 4
Ciolica	Dievelopentadie	130	1.00		85			86	86 + 0
Collen	Tetraline	132	0.833	108	92			94	08.7
~ 10"12 C11	1.Methylnanhthalanof	147	1 10	110	86			104	100 + 9
× 11 ··· 10	Lower and much second conce	174	1.14	110	00			104	100 1 9

• { } indicates an entry included in determining fit but excluded from average when plotting.



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### TABLE 3

Threshold Soot Index (TSI) for Compounds Measured in Diffusion Flames

						Threshold soot index (TSI)				
	•	Mol.				Reference				
Formula	Name	wt.	C/H	[6]	[7]	[8]	[9]	[10]	[11]	Mcan
C. II.	Ethane	30	0.333				1.2	-	-1.3	0.0 ± 1.2
Calle	Propage	44	0.375	•			1.3		-0.07	0.6 ± 0.7
C-11-	Cyclopropans	42	0.500				3.2			
Cillia	n-Butane	58	0.400				1.6		1.2	$1.4 \pm 0.2$
Callia	Isobutane	58	0.400				2,2			
Callin	n-Pentane	72	0.417		1.0	1.3	1.7			$1.3 \pm 0.2$
Callin	Isopentane	72	0.417		1.6					
C <sub>6</sub> H <sub>12</sub>	2,2-Dimethyl propane	72	0.417			2.7	3.8			3.3 1 0.0
C <sub>5</sub> H <sub>10</sub>	Cyclopentane	70	0.500		3.0	3.5	3.5			3.3 ± 0.2
C <sub>6</sub> II <sub>14</sub>	n-Hexane	86	0.429			2.7	2.3	• •		2,5 1 0.2
Calla	2-Methyl pentane	86	0.429			2,9	• •	2.9		2.710
Cell14	3-Meth <b>yl pentane</b>	86	0.429			2.9	2.9			2.0 1 0.2
C <sub>6</sub> H <sub>14</sub>	2,2-Dimethyl butane	86	0.429		4.0	3.3				3.7 I U.4
C <sub>6</sub> H <sub>14</sub>	2,3-Dimethyl butane	86	0.429			3.2				49401
C6H12	Methyl cyclopentane	84	0.500		• •	5.0	4,5			32401
C <sub>6</sub> ll <sub>12</sub>	Cyclohexane	84	0.500		3.4	3.2	3.0	26		27.02
C71116	n-lieptane	100	0.438	•		3.0	2,0	<b>4</b> .J		2.7 1 0.6
C7H18	2-Methyl hexane	100	0.438			3.2				
C71116	3-Methyl hexanc	100	0,438			3.2				
C71116	2,3-Dimethyl pentane	100	0.438			3.5				
C7H16	2,4-Dimethyl pentane	100	0.438			3.0				44+02
C71114	Methyl cyclohexane	98	0.500		4.0	9.2		27		32+00
C <sub>6</sub> H <sub>18</sub>	n-Octane	114	0.444			3.3	3.4	3.4		3,5 - 0.0
C81118	2-Methyl heptanc	114	0.444			3.5				
Callia	3-Methyl heptane	114	0.444			3.7				
C81118	4-Methyl heptane	114	0.444			4.0				
Callia	3-Ethyl hexane	114	0.444			4.5				
Callia	2,2-Dimethyl nexane	114	0.444			3.8				
CaH18	2,3-Dimethyl nexane	114	0.444		61	5.0				5.6 ± 0.6
Callia	2,2,4-1 rimethyl pentane	114	0.444		5.7	•10				
C81118	2,3,4-1 rimethy pentane		0.444		5.7					
C#118	2,3,3,-1 functing percand	114	0.444		•	4.4				
Can18	2-Methy 5-Chyl penals	• 112	0.500			5.9				
C.U.S	Ethyl cyclohexae	112	0.500			4.6				
Calles	Nonane	128	0.450				4.1			
Colleo	Isononane	128	0.450				5.0			
Colle	Decane	142	0.485			4.1		4.5		4,3 ± 0.2
Colla	Decalin	138	0.556	{3.7}•	13	12				13 ± 0.5
CasHa	Undecane	156	0.458	•		4.3				
Calle	Dodecane	170	0.466			4.8				
Cialla	Tridecane	184	0.464			5.2				
Cialla	Tetradecane	198	0.467			5.4				
Cella	Ethylene	28	0.500				1.3		1.3	1.3 ± 0
C,11.	Propylene	42	0.500				2.6		6.9	4.8 ± 2.2
Calla	n-Butens	56	0.500				4,4			
CAH	2-Butenc	56	0.500				4.3			•
C <sub>4</sub> H <sub>2</sub>	laobutene	56	0.500				4.8			43.03
Callia	1-Pentene	70	0.500		4.8		3.5			4.2 ± U./
C <sub>5</sub> H <sub>8</sub>	Cyclopentene	68	0.625				15			
Callis	liexc <b>ne</b> <sup>r</sup>	84	0.500		4.9	3.9	4.4	<b>(8.</b> ]	3	4.4 ± 0.5

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			TABL	.1: 3 (Con	tinued)	Thresh	hold soot	index (T	SD	
				÷						
	••	Mol.	<b>6</b> /11				Refere	Ince		M
Formula	Name	wi.	····	[0]		[0]	171	[10]		Mcan
Callio	Cyclohexcae	82	0.600		5.8	6.3	5.0			5.7 ± 0.5
C71114	1-Hepte <b>ne</b>	98	0.500		4.5	4.1	5.1			4.6 1 0.4
C71114	2-lleptenc	98	0.500	•		4.3	5.3			4.8 ± 0.5
Callia	J-Octe <b>ne</b>	112	0.500			4.4				
Callia	2-Octene	112	0.500			4.4				
C10120	Decene	140	0.570		6.2	5.5	7.6			6.4 ± 0.8
C12H24	Dodecene	168	0.500	•		6.4				
C121122	Dicyclohexylð	166	0.545		11	10				11±0.5
C141128	Tetradecene	196	0.500			7.6				
Ciellan	Hexadecene	224	0.500			8.3				
Ciellas	Octadecene	252	0.500			9.2				
Cille	Acetylene	26	1.00				2.7		4.6	3.7 ± 1.0
Calla	Propyne	40	0.750				5.9			
Calle	Pentync .	68	0.625				15			
Cellia	licxync	82	0.600				20			
Calle	1.3-Butadiene	54	0.667				26		24	25 ± 1.0
C81114	2,5-Dimethyl,1,5- hexadiene	110	0.570				34			
Calla	Benzene	78	1.00		30	31	{24}			31 ± 0.5
Cylla	Toluc <b>ae</b>	92	0.875	52	{34}	48	50	48		50 ± 2
Callin	Xylcne	106	0.800		44	63		46		51 ± 8
Callin	Ethyl benzene	106	0,800	61		56	{75}			59 ± 3
Cullin	Mesity lene	120	0.750			47				
Callin	Trimethylbenzenes	120	0.750			47				
Celliz	Cumene	120	0.750			63				
Callin	Propyl benzene	120	0.750			47	-{III}			
C10/114	p-Cymened	134	0.714		39	84				62 ± 22
Ciolia	Butyl benzene	134	0.714			70				
Cioliza	we Butyl henzene	134	0.714			60				
C101114	tert Butyl benzene	134	0.714			84				
C101114	Dicthyl benzene	134	0.714			60				
Cillia	see Pentyl benzene	148	0.688			58				
Cullin	tert Pentyl benzene	148	0.688			58				
Ciellin	m-Diisopropyl benzene	162	0.667		51					
C121116	Phenyl cyclohexane	160	0.750			72				
Cialliz	Tetralin	132	0.833	58	41	69				56 ± 10
Colla	Indenc <sup>e</sup>	116	1.125			52				
Calla	Styrenc/	104	1.000			81				
Ciolina	Pincnet	136	0.625		24					
Ciolia	Naphthalene	128	1.25			100				
Cullio	I-Methyl naphthalene	142	1.10	89		89				89 ± 0
C11H10	2-Methyl naphthalene	142	1.10			89				
C121112	Dimethyl naphthalenes	156	1.00			98				

• { } indicates an entry included in determining fit but excluded from average.





Fig. 1. Effect of molecular structure on soot formation in premixed flames.

displayed in Fig. 1. To simplify the figure, smooth curves have been drawn through the n-alkane and n-alkene data. Isomers have been left off because inspection of Table 2 shows that they generally produce only a slightly higher TSI. The most striking feature of Fig. 1 is that most of the data fall roughly in a band, with TSI increasing with the number of carbon atoms: th slope is about 7 TSI units per carbon atom. Exceptions are acetylene, 1, 3-butadiene, and the higher-molecular-weight alkanes and alkenes. When TSI is plotted against the C/H ratio (Fig. 2), butadiene is no longer out of order. It is also interesting that butadiene, as well as acetylene but unlike other hydrocarbons attains its maximum burning velocity [17] and minimum ignition energy [18] in very rich mixtures. For example, butadiene has a maximum burning velocity of 57 cm s<sup>-1</sup> at  $\phi =$ 1.23, while butche has a maximum burning velocity of 45 cm s<sup>-1</sup> at  $\phi = 1.08$ . Most hydrocarbons reach their maximum burning velocity between  $\phi = 1.0$  and 1.1.

The adiabatic flame temperature of acetylene is considerably greater than that of the other species; this may tend to mask the effect of molecular structure. It is clear, however, that temperature is not the controlling factor in the tendency of a fuel to soot [16]; for Bunsen burner flames, the calculated adiabatic flame temperatures at the incipient soot point for acetylene, benzene, and *n*-hexane are 2380, 2200, and 1850K, respectively, which bears very little relation to their positions in Fig. 1. Blazowski reported measured temperatures in a stirred reactor at the incipient soot limit for ethylene, 1-methyl naphthalene, and toluene of 1550, 1905, and 1951K, respectively, which again bears little relation to their positions in Fig. 1.

It is also clear from Fig. 1 that increasing the aromatic character increases the tendency to soot; compare, e.g., cyclohexane to benzene (TSI = 56 to 80), and decalin to tetralin (TSI = 85 to 98).

Based only on their results, Street and Thomas [1] reported the following (frequently quoted [13, 14] qualitative, relative ordering for the tendency to soot of hydrocarbons in premixed flames:

acetylene < alkenes < isoalkanes < n-alkanes

< monocyclic aromatic hydrocarbons

< naphthalenes.

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Fig. 2. Effect of molecular structure on soot formation in premixed flames. Arrows indicate increasing molecular weight.

As shown in Fig. 1, these are rather poor summaries of the actual situation. Consideration of the quantitative ordering demonstrates that the reported trend is misleading. Further, it is clear that the effect of increasing the number of carbons within a family is sometimes much greater than changing families at fixed carbon number. As an illustration, compare the relatively small differences between *n*-pentane (TSI = 63) and *n*pentene (TSI = 56) with changing from ethylene (TSI = 30) to *n*-heptene (TSI = 60) or ethane (TSI = 35) to *n*-pentane (TSI = 63).

Another frequently reported qualitative trend is the increase in tendency to soot with increasing C/II ratio [19, 20]. The results of Table 2, plotted in Fig. 2 against C/II ratio, show that while there is a general increase in tendency to soot with increasing C/II ration, the trend is weak and thus of limited predictive value. All the the alkenes (C/H = 0.5) should be equal but have TSI values ranging from 30 to 65, and acetylene with one of the highest C/II ratios has (TSI = 0) the lowest value of any compound measured; further, acetylene and benzene have the same C/II but TSI = 0 and 80, respectively.

Street and Thomas suggested that the somewhat higher TSI of aromatics in premixed flames may be caused by the ability of the benzene ring to resist oxidation and survive into the burned gas zone. Fenimore et al. [21] subsequently studied the onset of soot in premixed flames as a function of various species concentrations in the burned gas zone. They found that the correlation between sooting and the survivial of benzene into this zone was quite strong. In a review summarizing the role of aromatics in soot formation, Bittner and Howard [22] confirmed this observation, but suggested that more information on the role of intact aromatics will be required to clarify the reasons for this large apparent enhancement.

Clearly more data are required on the effect of molecular structure on soot formation in premixed flames.

### **Diffusion Flames**

Much of the data in Table 3 has been plotted in Fig. 3 and 4. Smooth curves have been drawn through the *n*-alkanes, *n*-alkenes, and *n*-alkynes. Isomers and cyclic structures for these substances



Fig. 3. Effect of molecular structure on tendency to soot in diffusion flames.

have been deleted because they differ little from the normal compound and the tendency to soot of the alkanes and alkenes is small compared to other structures. The effect of isomeric structure is demonstrated by examining the octanes in Table 3. This table demonstrates what Clarke et al. [7] recognized, that the more compact the molecular structure, the greater the tendency to soot.

The most striking feature of Fig. 3 is that most of the data, with the exception of the alkanes and alkenes, but including the alkynes, fall in a band



Fig. 4. Effect of molecular structure on tendency to soot in diffusion flames. Arrows indicate increasing molecular weight.

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with TSI increasing with the number of carbon atoms, with slope varying from about 6 to 12 per carbon atom. This is better demonstrated when all of the data in Table 3 except that for the alkanes and alkenes are plotted on a single graph. Only typical molecules are plotted in Fig. 3 because the displayed structures would overlap; the molecules with greatest deviation from the rest of the data have been included, however, Butadiene again stands out as having a greater tendency to soot than any other small molecule; unfortunately, there are no other examples of conjugated systems, Glassman [11] interprets this observation as indicating that hutadiene may be a major "precursor element in soot nucleation." Again, however, when TSI is plotted against C/II (Fig. 4), butadiene falls in with all the other fuels. Styrenc, with its conjugated double bond, is also an outstanding sooter in Fig. 3, but falls within the other fuels in Fig. 4 when TSI is plotted against C/H.

The second most notable features of Fig. 3 are the very low tendency of the alkanes and alkenes to soot and the major importance of aromatic character on the tendency to soot.

The failure of C/H to correlate the data is vividly clear in Fig. 4 in the comparison of acetylene and benzene, of which both have C/II = 1.0but TSI of 3.7 and 31, respectively, or the trend from acetylene to hexyne, for both of which C/H goes from 1.0 to 0.6 and TSI from 3.7 to 20, respectively. We note that it has erroneously been reported [23] that the incipient sooting tendency decreases with increasing size for all compounds except paraffins. These conclusions were based on Fig. 6 of Minchin [6], which has been interpreted as summarizing his experimental data. In fact the credit for this data is usually given to Clarke et al. Garner [7], who simply redrew Minchin's curves. Minchin's Fig. 6 is actually the result of a hypothetical calculation based on only a few data points. The relation used in that calculation is not in agreement with the extensive data subsequently collected by other workers.

It is sometimes stated that in diffusion flames soot formation increases in the order [14]

paraffins < monoolefins < diolefins

< acetylenes < benzenes < naphthlenes.

While this statement is qualitatively true, the inequality signs are not related.

### Comparison between Premixed and Diffusion Flames

It is classical mythology that premixed and diffusion flames have different sooting tendencies [13, 14]. Comparison of Figs. 1 and 3 shows some differences and much in common. The most striking difference is the relative positions of the alkenes and alkanes in the two figures; this is determined by the relative position of acetylene with respect to these two groups of compounds. In premixed flames, acetylene has a much lower tendency to sout than the alkanes and alkenes, but in diffusion flames it has a greater tendency to soot. In addition, the tendency to soot for the alkanes and alkenes is reversed in the two flames. Nevertheless, the tendency to soot increases with increasing molecular weight (increasing number of carbon atoms) in both flames for both classes of compounds, and the tendency to soot increases with isomerization (increasing molecular compactness) in both flames-see Tables 2 and 3. Both Figs. 1 and 3 show major overall trends in common when the total range of fuels is considered. At the extremes in both flames are acctylene and the naphthalenes. Further, it is apparent that aromatic character plays a dominant role in both flame types and that 1.3butadiene has a greater tendency to soot in both flames than the corresponding alkane or alkene with TSI is plotted against numbers of carbon atoms but not when plotted against C/H.

The fuels in common to the two flames are compared in Fig. 5. All of the alkanes and alkenes fall in the cross-hatched area. The correlation, although not linear, between the premixed and diffusion flames is surprisingly good. In diffusion flames, differences between the molecular structure of alkanes and that of alkenes cause only a small change in TSI, while in premixed flames the change is more dramatic; on the other hand, for mono- and dicyclic compounds, large changes are noted for diffusion flames and small changes for premixed flames. It is obvious that more data on premixed flames are required; these are being collected in our laboratory.



The choice of definitions for TSI was somewhat arbitrary; a different choice should be possible to force the points in Fig. 5 to fall more nearly on a 45° line. It should also be pointed out that the manner of presentation of the data as TSI for the whole range of fuels appears to suppress the differences, especially in diffusion flames, among the alkanes, alkenes, and alkynes, although on a percentage basis the differences among these may be quite large. Another caveat is in order-the data reported here should not be interpreted as applying to practical systems such as turbojets, diesels, or power plants until a correlation between the laboratory system and the practical system has been demonstrated. The early examination of such correlations is of great importance to the synfuels program.

### SUMMARY

By defining a rational threshold soot index TSI varying from 0 to 100 to measure the onset of soot formation in premixed and diffusion flames, it is shown that all of the data in the literature on premixed and diffusion flames, taken by many techniques, can be successfully correlated with respect to molecular structure. The differences in effect of molecular structure between premixed and diffusion flames are less than previously thought. The major difference between premixed and diffusion flames is the relative order of alkanes, alkenes, and alkynes; the relative importance of aromatic structure, isomerization, or increasing molecular size is the same. The role of C/H ratio (or hydrogen content), often taken as important in determining the effect of molecular structure, is of very little value in correlating data from laboratory systems.

For premixed flames, the effect of molecular structure on the onset of soot formation as measured by the TSI can be tentatively summarized, until more data are available, in a list whose items are, roughly speaking, of decreasing importance:

- 1. TSI is strongly influenced by the number of carbon atoms in the molecule, about 7 TSI per carbon atom. Two exceptions to the rule are acetylene, with a TSI of 0, about 30 TSI below any other molecule, and butadiene, 20 TSI greater than *n* butane.
- Aromatic character increases the jendency to soot. TSI is increased 15-25 units on converting a saturated ring to an aromatic ring.

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(The change from tetralin to methyl naphthalene, however, is very small.)

- n-alkanes and iso alkanes have essentially the same TSI (iso alkanes slightly higher), starting at 35, rising to about 65 at pentane, and then rising more slowly for large molecules.
- Alkenes fall below alkanes by about 10 TSI units for small molecules, decreasing to about 5 TSI units for larger molecules.
- 5. Adding a side chain to an aromatic molecule increases the TSI; lengthening the side chain decreases the TSI.

For diffusion flames, the effect of molecular structure on the onset of soot formation can be summarized in a list whose items are, roughly speaking, of decreasing importance:

- TSI, with the exception of alkanes and alkenes, but including the alkynes, is strongly influenced by the number of carbon atoms in the molecule, 6-12 TSI per carbon atom. Two major exceptions to the rule are 1, 3butadiene and styrene, which are about 15 and 20 TSI, respectively, above the average curve.
- 2. Aromatic character greatly increases the tendency to soot; TSI is increased for changing a saturated ring to an aromatic ring by 25-60.
- Alkanes and alkenes have very low tendencies to soot, TSI < 7, with alkenes having TSI from 2 to 6 above alkanes.</li>
- 4. Isomeric or cyclic structures for alkanes or alkenes have a small effect on increasing the tendency to soot when compared with increasing aromatic character; however, making an alkene or alkane more compact can increase the tendency to soot by as much as 80%.
- 5. Multiring structures, including saturated rings, increase the tendency to soot.
- 6. The addition of a side chain to an aromatic molecule has complex effects, generally increasing TSI, but for long side chains decreasing TSI.

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 See e.g., Fig. 4 of Ref. [7]; Fig. 10 of Ref. [14];
 Fig. 8.1 of Ref. [13]; or Fig. 5.1 of Pahner, H. B., and Cullis, C. F., in *Chemistry and Physics of Carbon* (P. L. Walker, Jr., Ed.), Marcel Dekker, Inc., New York, 1965.

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# SHORT COMMUNICATION

# Importance of Temperature on Soot Formation in Premixed Flames

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### INTRODUCTION

The importance of temperature in determining the critical equivalence ratio for soot formation in premixed flames has recently been emphasized by Glassman and coworkers (1979, 1980, 1981). In discussing sooting trends of various fuels they state (1979), "The fuel sooting trends in premixed and diffusion flames follow opposite directions† due to different influences of temperature". After discussing the hypothesis that, in premixed flames, as the temperature rises, oxidative attack on soot precursors increases at a faster rate than precursor formation, they conclude (1979), "The initial fuel structure plays little role in soot formation in premixed flames" and "the dominant factor in determining the tendency to soot is the reaction zone (flame) temperature". They argue that the higher the temperature the less the tendency to soot, and distinguish between aliphatic and aromatic behavior (1980), postulating that aromatics follow the same trends if one allows for a different oxygen demand. Dyer and Flower (1981) have supported this thesis with experiments on propane-air and propylene-air flames in a combustion bomb. They state, "It has been demonstrated that any change that increases the flame zone temperature such as reducing the diluent concentration, decreasing the diluent heat capacity, increasing the initial temperature, or changing the fuel type, reduces the quantity of soot formed."

The fact that the flame temperature has a major effect on the critical equivalence ratio for soot formation for a specific fuel is, of course, not surprising. The mechanism of soot formation involves many chemical reaction steps. some

† For another interpretation of the data on which this statement is made see Calcole and Manos (1982).

probably have activation energies, and the concentration of some reactants may change with temperature. As recognized by both of the above-mentioned groups, Street and Thomas (1955) and Millikan (1962) previously observed a strong effect of temperature on the soot point for individual premixed fuels [see also, Gaydon and Wolfhard (1979)]. The experimental observations which have been made, however, do not support the conclusion that flame temperature *independent of fuel structure* is the dominant factor determining the tendency to soot for various fuels in premixed flames.;

It is the objective of this note to evaluate the relative effect of temperature and of fuel molecular structure on incipient soot formation for a variety of fuels.

### ANALYSIS

For purposes of comparing the relative importance of flame temperature and molecular structure on the tendency to soot, the fuel-air equivalence ratio at which soot just forms in premixed flames will be compared with the adiabatic equilibrium flame temperatures calculated for that specific fuel-air composition for several fuels. By evaluating such data from a large number of fuels one can determine how the soot point varies with fuel structure at a fixed temperature or how the flame temperature varies with structure at the soot point characteristic of each fuel. The calculated adiabatic flame temperature is used because experimental data are not available. Generally, however, the adiabatic flame temperature and maximum experimental

<sup>\*</sup> For diffusion flames Glassman and Yaccarino (1981) conclude that both flame temperature and fuel structure are important.

temperature for flames of the type considered here are in reasonable agreement (Lewis and von Fibe, 1961).

The premixed flame data are taken from a recent summary of the literature (Calcote and Manos, 1982) in which available soot threshold data from several sources were condensed to the same scale by defining a threshold soot index, TSI, as:

$$TSI = a - h\phi_c$$

where *a* and *b* are constants for any given set of data and  $\phi_c$  is the equivalence ratio at the soot point. The a and h are chosen for each self-consistent set of data to minimize the difference between that set of data and other available data on the same fuels. The TSI values vary from 0 to 100 with the greater value indicative of a greater tendency to soot. Using the tabulated TSIs and constants *u* and *b* so derived (Calcote and Manos, 1982), it is possible to reverse the procedure and determine  $\phi_c$  applicable to any given apparatus. A self-consistent set of  $\phi_r$ data was thus derived for the burner of Calcote and Miller (1977) for a series of fuels. These are reported in Table I along with equilibrium adiabatic flame temperature for each fuel at the equivalence ratio listed in Table I, calculated using the Air Force Rocket Propulsion Laboratory ISP computer program (Selph and Hall, 1973). All species in the JANAF Thermochemical Tables (1979) were considered in the calculation, including graphite (although in no case was graphite computed to be formed at these fuel-air ratios).

### **DISCUSSION**

The data from Table I are plotted in Figure 1. Clearly TSI (tendency to soot) does not generally decrease with increasing temperature as postulated by Glassman et al. (1979, 1980, 1981). In fact, the trend is just the opposite. With the exception of ethylene and acetylene, the sooting tendency of fuels increases with increasing flame temperature. In fact, for the alkane series shown in the figure, the trend for TSI to increase with increasing temperature is very linear. Within the aromatics, the TSI varies smoothly from 80 to 100 as the flame temperature varies from 2045 to 2182 K; again the tendency to soot increases with increasing temperature. The alkene data are somewhat different from the other data, and insufficient to allow any firm conclusions to be drawn. Data are not available for alkynes other than acctylene.

TABLE 1 Adiabatic equilibrium flame temperature at TSI in premixed flames

Compound fo	ormula	TSI	ø.	<i>т</i> , к
Acetylene	C <sub>2</sub> H <sub>2</sub>	0	2.06	2405
Ethylene	C <sub>2</sub> H <sub>4</sub>	30	1.86	1980
Methane	CHi	34	1.83	1075
Ethane	C2H6	35	1.82	1740
Propylene	C3H4	40	1.79	1925
Propane	CaHn	50	1.72	1815
n-hutene	C4Ha	50	1.72	1935
n-pentene	CsH10	56	1.68	1940
Cyclohexane	CeHiz	56	1.68	1865
n-butane	C <sub>4</sub> H <sub>10</sub>	57	1.67	1855
n-heptene	C7H14	60	1.65	1940
n-octane	CuHis	62	1.64	1880
n-pentane	C5H12	63	1.63	1885
n-hexane	Call14	64	1.62	1890
iso-octane	CuHin	65	1.62	1890
1,3-butadiene	C4He	77	1.54	2170
Benzene	CeHe	80	1.52	2100
Cumene	CaHia	80	1.52	2045
Toluene	C7Hn	83	1.50	2085
Decalin	CiuHia	85	1.48	2010
Xylenes	CuHio	91	1.44	2110
Tetralin	C10H12	98	1.39	2150
Methy! naphthalene	C11H10	100	1.38	2180



FIGURE 1 Variation of threshold sooting index vs. calculated adiabatic flame temperature at  $\phi_c$ .  $\bigcirc =$  alkanes,  $\triangle$  alkenes,  $\bigcirc$  acetylene,  $\bigcirc \cdot$  aromatics, and  $\diamondsuit =$  1,3-butadiene.

### CONCLUSION

Although increasing the flame temperature of an individual fuel may decrease its tendency to soot, a series of different fuels with increasing flame temperatures at their soot points generally increase

in tendency to soot (ethylene and acetylene are exceptions). Thus one concludes that the initial fuel structure plays a major role in determining soot formation in premixed flames.

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APPENDIX C

1

IONIC MECHANISMS OF SOOT FORMATION

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### I. INTRODUCTION

In a recent review<sup>1</sup> of soot nucleation mechanisms it was demonstrated that mechanisms based upon neutral free radical species are inadequate to explain soot formation in flames. Either rates are too slow to account for the rapid rate of soot formation or there are difficulties in accounting for the large numbers of polycyclic rings observed in soot particles. These problems can be overcome by assuming an ionic mechanism. Ion molecule reactions are extremely fast compared to free radical reactions and ions have a propensity to quickly rearrange to the most stable structure so that there is no difficulty in accounting for the literature indicating the importance of ions in sooting flames and a number of workers have previously suggested ionic mechanisms. For this, the reader is referred to a recent review.<sup>1</sup>

The literature on the soot formation process is, at times, confusing because of the failure to recognize its complexity or to overestimate it, and more specifically, a failure to recognize that charged species or ions may enter into the soot formation process in two completely separate steps. Thus, it seems useful to define the specific steps involved in soot formation:

 Formation of precursors - the generation of those free radicals or ions which are necessary for the initial stages of production of soot nuclei. Soot precursors may grow by reaction with common, high concentration, flame species, often acetylenes. These are called building blocks.

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- 2. Nucleation the transformation from a molecular system to a particulate system, i.e., incipient soot particles in which the growing species take on the properties of particles as opposed to large molecules. In soot formation this transformation occurs over a range of molecule/particle diameters unlike usual nucleation phenomena in which an abrupt transformation occurs because of the crossing of two rate-controlling steps.
- 3. Growth the increase in size of the incipient soot particles by the further addition of molecular species.
- 4. Congulation the collision and conlescence of two particles of the same or different size into a single particle in which the identities of the two original particles are completely lost.
- 5. Agglomeration a process where a series of particles collide one at a time and adhere to each other to form a chain of individual particles which are still distinguishable from one another.
- 6. Aggregation a process where a series of particles collide one at a time to form a cluster of individual particles in which the particles are still distinguishable.
- 7. Oxidation oxidative reactions of the growing nuclei or particles in any of the abovementioned forms to reduce the particle size and to reduce the N/C ratio.

We believe that charged species are important in steps 1, 2, and 5. Much of the confusion in the literature arises from not identifying observed effects of charged species with either step 2 or step 5. Since step 5 is much better understood than step 2 and since there is considerable controversy as to the validity of an ionic mechanism for step 2, we will concentrate this discussion on soot nucleation, step 2.

After a brief review of the basic premise of ion molecule nucleation and some comments on the source of charged particles which are important in step 5, the relationship between flame ion concentration and concentration of soot particles will be discussed in some detail. This will be collowed by a consideration of possible alternative sources of the large molecular ions observed in flames, i.e., alternative to the ion molecule nucleation hypothesis.

### **II. BASIC PREMISE**

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Recent measurements using mass spectrometers to observe individual ion concentrations in flames at AeroChem<sup>2</sup> and by Michaud et al.<sup>3</sup> have demonstrated a dramatic change in the ions observed in nonsooting and sooting flames. This is demonstrated in Figs. 1 and 2 which are for a nonsooting and a sooting acetylene-oxygen flame at 2.0 kPa. The equivalence ratio at which acetylene soots in this flame is 2.6. It is interesting to note that even in the nonsooting flame, Fig. 1, very large fons, greater than 300 amu, appear very early in the flame and then disappear. In the sooting flame, Fig. 2, these large ions dominate and then disappear. Ions > 300 certainly do not include ions over 1000 amu because of the reduced sensitivity



Fig. 1 Ion profiles in a nonsooting flame. Acetylene-oxygen, \$ =
2.0, P = 2.0 kPa, T = 2300 K (Ref. 4).



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Fig. 2 Ion profiles in a sooting flame. Acetylene-oxygen,  $\phi = 2.7$ , P = 2.0 kPa, T = 2170 K (Ref. 4).

of the mass spectrometer above 1000 amu. Thus it is assumed that as the > 300 amu ions disappear, larger ions are produced. Figure 3 shows the effect of equivalence ratio on the peak mass spectrometer ion current for selected ions. The interesting feature here is that as the equivalence ratio for the production of soot, indicated by the shaded area, is approached the ions which are dominant just before sooting decrease very rapidly and large ions, > 300, increase dramatically. It is also interesting to note that the largest ion recorded in this set of data  $C_{1,H_{11}}^+$  begins to increase in concentration as the sooting equivalence ratio is approached and then disappears rapidly presumably becoming a larger ion.

The basic premise by which we view the effect of ions and charged particles on soot growth is summarized in Fig. 4. Primary flame ions produced by chemi-ionization react by rapid ion molecule



Fig. 3 Effect of equivalence ratio on ion profiles. Acetyleneoxygen, P = 2.0 kPa (Ref. 4).

reactions with neutral flame species, such as acetylene, polyacetylenes, and free radicals, to produce larger ions which rapidly rearrange to produce even larger polycyclic aromatic ions. Some of these ions are neutralized by recombination with electrons produced in the primary flame ion reaction and become neutral incipient soot particles; others grow to produce charged soot particles. These particles then grow by surface addition as well as by congulation to form larger soot particles. As these particles reach a critical size at a high enough temperature, their ionization potential becomes sufficiently low that the particles are thermally ionized. The charge on these particles determines their rate of agglomeration and produces chains of individual particles distinct from aggregates. It is also at this point that many of the effects of chemical additives or of electric fields are observed to affect the formation of



Fig. 4 Mechanism of soot formation.

soot in flames. Of course several of these steps are going on simultaneously; they are not necessarily sequential as indicated.

The formation of precursor ions in the proposed scheme is basically the same step observe in all hydrocarbon flames in which highly nonequilibrium concentrations of ions are produced by chemiionization. The basic reaction is

$$CH + O \rightarrow CHO^+ + e^-$$
 (1)

The CHO<sup>+</sup> so produced rapidly transfers a proton to water

$$CHO^{+} + H_2O + H_3O^{+} + CO \qquad (2)$$

or by a series of ion molecule reactions produces the large numbers of ions that are observed normally in flames. In particular  $C_3H_3^+$  can be produced by a set of reactions such as

$$CHO^{+} + CH_2O \rightarrow CO + CH_2O^{+}$$
(3)

$$CH_{3}O^{+} + C_{2}H_{2} \rightarrow C_{3}H_{3}^{+} + H_{2}O$$
 (4)

There are, in fact, a large number of routes from  $CHO^+$  through other ion nuclecule reactions to  $C_{3}H_{3}^+$ . In rich hydrocarbon flames,  $C_{3}H_{3}^+$ 

is the dominant ion while in leaner flames, i.e., equivalence ratios slightly greater than 1 to much less than 1.  $H_2O^+$  is the dominant ion. Another proposed mechanism for the production of  $C_3H_3^+$  is:

 $CH^{+} + C_{3}H_{3} + C_{5}H_{3}^{+}$ (5)

Evidence for Reaction (5) is fragile. It is also difficult to imagine that Reactions (1) through (4), leading to  $C_3H_3^+$ , might occur in very rich flames where the oxygen atom concentration can be safely assumed to be fairly low. Nevertheless, very large concentrations of  $C_3H_3^+$  are observed in rich flames approaching sooting; therefore in our argument for an ionic mechanism of soot formation, at this stage, we accept an initial large concentration of  $C_3H_3^+$  and assume that it is the initial precursor ion upon which ion molecule reactions build larger and larger ions. Further work is clearly needed to determine the mechanism by which  $C_3H_3^+$  is produced in very rich flames.

Given  $C_3H_3^+$  as the initial ion it is easy to write a series of ion molecule reactions in which the preduct ions continue to grow employing only those ions and neutral species which have been observed in sooting flames. Where thermodynamic data are available, all of the reactions employed are exothermic so that fast reaction rate coefficients are a good assumption. In fact, there is evidence that the rate coefficients of ion molecule reactions for a given homologous series are proportional to the exothermicity of the reaction.<sup>5</sup> Such a reasonable set of reactions, by no means inclusive, is summarized in Table 1. It is easy to envision the set of reactions in Table 1 continuing to produce larger and larger ions. Of course, while this growth process is proceeding, ion recombination with the electrons produced in the initial chemi-ionization reactions will neutralize some of the ions and thus reduce their concentrations. The rate coefficients for these recombination processes would be expected to increase with increasing molecular size. Thus the proposed ion molecule reactions naturally can be expected to rapidly produce large ions and incipient charged soot particles and, through ion/charged particle-electron recombination, incipient neutral soot particles. These incipient soot particles grow by surface addition of molecular species and by congulation. At some point their work function or ionization potential decreases (Fig. 5) so that eventually they become thermally ionized. In fact it has been demonstrated that in the well-studied acetylene-oxygen 2.7 kPa flame the concentration of charged particles can be calculated by assuming thermal ionization and using the measured temperature and concentration of neutral soot particles."

# $C_{3}H_{3}^{+}$ + $\begin{pmatrix} C_{2}H_{2} = C_{3}H_{3}^{+} \\ C_{4}H_{2} = C_{5}H_{3}^{+} + C_{2}H_{3} \\ C_{4}H_{2} = C_{7}H_{5}^{+} \end{pmatrix}$ $C_{3}\dot{H}_{3}^{+} + \begin{pmatrix} C_{2}H_{2} = C_{7}H_{3}^{+} \\ C_{4}H_{2} = C_{7}H_{3}^{+} + C_{2}H_{2} \\ C_{4}H_{2} = C_{9}H_{3}^{+} \end{pmatrix}$ $C_{3}H_{3}^{+}$ + $\begin{pmatrix} C_{2}H_{2} = C_{7}H_{7}^{+} \\ C_{4}H_{2} = C_{7}H_{5}^{+} + C_{2}H_{2} \\ C_{4}H_{2} = C_{9}H_{7}^{+} \end{pmatrix}$ $C_7 H_5^+ + \begin{cases} C_2 H_2 = C_9 H_7^+ \\ C_4 H_2 = C_9 H_5^+ + C_2 H_2 \\ C_4 H_2 = C_{11} H_7^+ \end{cases}$ $C_{7}H_{7}^{+} + \begin{cases} C_{2}H_{2} = C_{9}H_{9}^{+} \\ C_{4}H_{2} = C_{9}H_{7}^{+} + C_{2}H_{2} \\ C_{4}H_{2} = C_{11}H_{9}^{+} \end{cases}$ $C_{9}H_{7}^{+} + \begin{cases} C_{2}H_{2} = C_{11}H_{9}^{+} \\ C_{4}H_{2} = C_{11}H_{7}^{+} + C_{2}H_{2} \\ C_{4}H_{2} = C_{13}H_{9}^{+} \end{cases}$ etc.

 Table 1. Proposed Ion-Molecule Soot Nucleation Reactions

 (from Ref. 4)



Fig. 5 Ionization potentials of soot particles.

### 111. ION CONCENTRATION FOR SOOT NUCLEATION

It is frequently assumed that the ion concentration in sooting flames is too small to account for the observed concentration of soot, This question arises for two reasons: (1) the available ion concentration data are not definitive and (2) the argument has not been thoroughly analyzed. Several measurements of ionization in sooting flames have been reported but, unfortunately, these have not always been performed under comparable experimental conditions with those for soot concentrations. Some data for a well-studied premixed flame are shown in Fig. 6. The flame is an acetylene-oxygen flame at an equivalence ratio  $\phi = 3.0$ , a pressure of 2.7 kPa, and an unburned linear gas feed velocity of 50 cm<sup>-1</sup> except as noted. The curve untitled "soot" is a combination of data obtained by Bonne et al.<sup>7</sup> and The curve marked "Yeung '73""," was obtained using a molecular beam sampling system similar to those used in molecular beam mass spectrometer sampling of flames with the ions collected by a Faraday cage. The curve marked "Homann '79" was obtained by a simi-lar technique. The probe curve is a recently obtained set of data from AeroChem<sup>10</sup> obtained by a Langmuir probe technique using the continuum electrostatic probe theory of Clements and Smy<sup>11</sup> which in the past has given very reliable absolute ion concentrations in nonsoating flames. In obtaining this curve we have used the molecular weight increase through the flame measured by Homann." The close



Fig. 6 Number density of ions, soot, and charged soot particle profiles. Acetylene-oxygen,  $\phi = 3.0$ , P = 2.7 kPa, u = 50 cm s<sup>-1</sup>, (except where noted). Soot from Wersborg et al.<sup>6</sup> and Bonne et al.<sup>7</sup>; charged soot particles from Prado and Howard<sup>6</sup>; Yeung '73 represents a molecular beam total ion sampling<sup>6,6</sup> for u =38 cm s<sup>-1</sup>; Homann '79 is a similar type measurement<sup>6</sup> for  $\phi =$ 2.9, 44 cm s<sup>-1</sup>; the probe curve represents total ion concentration measured by Gill et al.<sup>10</sup> with a Langmuir probe.

agreement between the AeroChem probe data and the molecular beam data of Homann are encouraging. Certainly it remains an important task to identify the absolute concentration of individual ions and small charged particles as a function of position in the flames and equivalence ratio.

Diffusion flames also contain large concentrations of ions, Fig. 7. This set of data was taken on a 3.3 kPa ethylene-oxygen flame. The soot is as visually observed; the temperature was measured with a radiation corrected coated thermocouple and the curve indicated as "probe current" is the actual probe current obtained with a Langmuir probe 0.305 cm long and 0.0127 cm radius. The indicated ion concentrations were deduced from the probe current assuming an average mass of 50 amu at 1 cm and 1000 amu at 3 cm. The ions > or < 300 amu were obtained from mass spectrometric flame sampling. The peaks in the  $C_2$  and CH emission have been indicated as obtained photographically using a combination of light filters and film to isolate their



Fig. 7 Ionization in sooting diffusion flames. Ethylene-oxygen, P = 3.3 kPa; fuel burner diam = 2.4 cm; fuel flow =  $39 \text{ cm s}^{-1}$ ; oxygen flow = 50 cm s<sup>-1</sup> (Ref. 10).

emission spectra. Some striking feature. of this set of data are their close similarity to those from premixed flames, the large amount of reaction occurring in the center of a diffusion flame (note, however, the low pressure), and the relatively large concentration of ions at low temperature.

We now address the problem of the relationship between ion concentration and soot number density observed in flames with respect to the premise that ions are the key element in the nucleation step. Consider one of the first reactions in the proposed scheme

$$C_3H_3^+ + C_2H_2 \rightarrow C_5H_3^+ + H_2 \tag{6}$$

If this is the first reaction in an ion-molecule growth sequence, we can deduce the rate of formation of  $C_3H_3^+$  from the rate of its disappearance; thus

$$\frac{d(C_{3}H_{3}^{+})}{dt} = -\frac{d(C_{3}H_{3}^{+})}{dt} = k(C_{3}H_{3}^{+})(C_{2}H_{2})$$
(7)

For this reaction we will assume, for the sake of argument, an ion concentration of  $C_3H_3^+$  of 10° ions cm<sup>-3</sup> which is conservatively low compared with the values reported, for example, in Fig. 6. The rate coefficient k has recently been measured by Ausloos and Lias<sup>12</sup> to be 10°° cm<sup>3</sup> s<sup>-1</sup> and the temperature coefficient was estimated to be

negligible. The acetylene concentration is taken from the work of Homann and Wagner<sup>13</sup> in a flame similar to that described in Fig. 6. This equation would lead to a rate of  $C_0 H_1^+$  formation (and disappearance) of about  $10^{15}$  ions cm<sup>-3</sup> s<sup>-1</sup>. In the most simplistic interpretation of our theory the  $C_0 H_0^+$  ion would then sequentially add acetylene molecules in a large number of steps to produce charged soot particles of (assumed for this discussion) 5 nm diameter. This would require approximately  $10^3$  steps:

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$$C_{3}H_{3}^{+} \xrightarrow{} C_{2}H_{2}^{+} \xrightarrow{} p^{+}(5 \text{ nm})$$
(8)

This overestimates the number of steps but ignores some loss of ions through ion-recombination reactions. If we assume the rate coefficient for each step is the same as that for Reaction (6), then the total time required for the  $10^3$  steps will be approximately 6 x  $10^{-5}$  s. This is a short time on the time scale of the flame and is consistent with the observation that very large ions are observed early in the flame front.

The charged soot particles will be neutralized by recombination with free electrons

$$P^+(5 \text{ nm}) + e^- \rightarrow P(5 \text{ nm}) \tag{9}$$

The rate coefficient for this reaction is<sup>14</sup>:

$$k = \frac{\pi d^2}{4} \overline{c}_e S\left(1 - \frac{e^2}{CkT_e}\right)$$
(10)

where d is the particle diameter;  $\overline{c}_e$  is the mean electron velocity, S is a sticking coefficient assumed to be l; e is the charge on an electron, C the electrical capacitance of a planar disk (the assumed shape for small particles);  $C = 4\varepsilon_0 d$ , where  $\varepsilon_0$  is the dielectric constant of free space and Te is the electron temperature assumed to be equal to the gas temperature. For particles of 5 nm diameter, k is approximately 10<sup>-5</sup> cm<sup>9</sup> s<sup>-1</sup>. Thus, assuming that the concentration of charged particles is equal to the initial concentration of ions because of the rapidity of Reaction (8) and neglecting any recombination of loss in this chain, the characteristic time for Reaction (9) is about 10<sup>-3</sup> s, again a fairly short time but not nearly so short as the time at which the ions grow to produce charged particles. The rate of charged particle recombination increases rapidly with charged particle diameter. The rate of particle production through this sequence of reactions would be equal to the initial ion production rate which gives 10<sup>15</sup> particles cm<sup>-3</sup> s<sup>-1</sup>. Wersborg et al.<sup>15</sup> observed a particle production rate in the same flame of 1013 particles cm<sup>-3</sup> s<sup>-1</sup> and a particle concentration of 10<sup>10</sup> cm<sup>-3</sup>. Thus it is possible, using reasonable values to have a considerably lower ion than particle concentration and still have the ions be the primary source of particles. For example, in the above calculation

 $(C_3|l_3^+) = 10^6$  cm<sup>-3</sup> which is much less than  $(P) = 10^{10}$  cm<sup>-3</sup>. The above example clearly demonstrates that particle concentrations and ion concentrations per se are not important for the argument but that the rate of ion formation and the rate of particle formation are really the important parameters which should be addressed. The ion concentration is, of course, important in that it is rate controlling for some of the steps in the process.

### IV. ALTERNATIVE SOURCES OF LARGE MOLECULAR IONS

In our interpretation of the observation of large molecular ions in sooting and nearly sooting flames, we have assumed that these ions were produced by a continuing sequence of ion molecule reactions producing larger ions. To substantiate that argument it is necessary to eliminate other possible mechanisms by which these large molecular ions could be produced. We attempt to do that in this section for six different mechanisms:

- 1. Thermal ionization of large molecules.
- 2. Charge transfer from particles to molecules.
- 3. Proton transfer from particles to molecules.
- 4. Hydride transfer from molecules to particles.
- 5. Chemi-ionization of large molecules.
- 6. lon-molecule equilibria.

1. Thermal ionization can be calculated by Saha's equation which for both large molecules and particles takes the form<sup>14</sup>

$$K = \frac{\frac{N^{+} N}{p} e}{\frac{N}{p}} = G\left(\frac{\frac{2\Pi m kT}{e}}{h^{2}}\right)^{3/2} \exp\left(-\frac{\Phi}{kT}\right)$$
(11)

where G is taken as 2 because the statistical weights of the initial and final states of the particles or large molecules and ions will be equal,  $N_p^+$ ,  $N_p$ , and  $N_e$  are the concentrations of charged particles or molecules, neutral particles or molecules and electrons, respectively;  $m_e$  is the mass of an electron, k is Boltzmann's constant; h is Planck's constant, and  $\phi_p$  is the ionization potential of a large molecule or the equivalent work function for a particle where  $\phi_p$  for a particle is given by  $\phi + e^2/2C$ , with  $\phi$  the work function of graphite.  $\phi_p$  is displayed in Fig. 5 as a function of particle diameter. As already pointed out, it is possible to account for the concentration of charged particles as being in thermal equilibrium with neutral particles by the use of this equation. However, it is clear that this cannot be true for most of the large molecules especially in lower temperature flames such as the diffusion flame reported in Fig. 7. Some typical ionization potentials of large polycyclic molecules are: 7.97 eV for phenanthrene  $C_{14}I_{10}$ ; 7.52 eV for pyrene  $C_{16}I_{10}$ ; and 7.43 eV for coronene  $C_{24}H_{12}$ .<sup>16</sup> For the same flame as in Fig. 6 the mass concentration of large molecules peaks at about  $2 \times 10^{-9}$  g cm<sup>-9</sup> at about 2.5 cm above the burner where the flame tempcrature is 2120 K.<sup>4</sup> Assuming the molecular weight of coronene this is equivalent to  $4 \times 10^{19}$  molecules cm<sup>-9</sup>. If ion and electron concentrations are equal Eq. (11) gives  $3 \times 10^7$  ions cm<sup>-9</sup>. This is considerably less than the observed ion concentration, Fig. 6.

Another compelling reason for rejecting thermal ionization of large molecules is that the ions observed in flames have odd numbers of hydrogen atoms and the neutral species observed have even numbers.<sup>1</sup> Of course this does not eliminate the possibility that there may be large concentrations of free radicals with odd numbers of hydrogen atoms. Assuming these are in about the same concentration as the large molecules and that the ionization potential is roughly the same as for large molecules, a reasonable assumption, then the above equiibrium calculation shows that only minor amounts of ions containing an odd number of hydrogen atoms could be produced by thermal ionization.

2. Charge transfer from a particle to a molecule

 $\mathbf{P}^{\mathsf{T}} + \mathbf{M} + \mathbf{P} + \mathbf{M}^{\mathsf{T}} \tag{12}$ 

can also be easily eliminated by reference to Fig. 5 in which it can be seen that as particle size increases the ionization potential decreases so one would expect the equilibrium to be heavily weighted to the left. Again, another compelling argument aginst this mechanism is that quoted above: the ions have odd numbers of hydrogen atoms and the observed large molecules have even numbers.

3. It is also conceivable that a proton could be transferred from a particle to a molecule

 $PH^+ + M + P + MH^-$ (13)

This possibility can be eliminated by reference to Fig. 8 which shows the calculated proton affinity as a function of a particle diameter.<sup>14</sup> The validity of this calculation is supported by observing that for small particle diameters the curve extrapolates very satisfactorily through the proton affinities<sup>14</sup> for a number of large polycyclic aromatic compounds indicated on the figure. For this extrapolation the diameter of the large molecule was estimated as the diameter of a circle with the equivalent cross sectional area as the large molecule. In addition, for the large diameter particles the curve can





be smoothly extrapolated to the bulk graphite value derived by Meot-Ner.<sup>16</sup> From Fig. 8 it is easy to see that Reaction (13) will be highly biased towards having the proton remain on the particle rather than on the molecule because of the very rapidly decreasing proton affinity as a molecule or particle increases in size.

4. Hydride transfer from a molecule to a particle represented by

 $P^+ + MH \rightarrow PH + M^+$ (14)

can also be considered as a possible mechanism for production of large molecules by summarizing the individual steps which thermodynamically make up this process:

MH	+	<b>P</b> <sup>+</sup>	•	нţ	+	PH	240
P	Ŧ	H	+	PH			-420
<b>P</b> +	+	e"	+	P			-440
M			+	Mŧ	+	e <sup>-</sup>	680
MH			+	M	+	H	420
							AH, kI

The large endothermicity of this process argues against its being an important mechanism for large molecular ion formation.

5. Another possible mechanism for production of large ions is chemi-ionization of large molecules. This mechanism cannot be eliminated out-of-hand because the following reactions involving large molecules can readily be written down.

				•			AH, kJ mol <sup>-1</sup>	
C3H7	+	C10H2	+	C13H9+	+	e"	-370	(15)
Callz	+	C <sub>e</sub> H <sub>2</sub>	+	C13H9+	+	e-	-290	(16)
C., H.	+	C,H,	+	(C1 2H	+	e_	-210	(17)
C∈H	+	C13H10	+	C1.H11+	+	e_	-160	(18)
ก บ		C . 11		c v +		•-	-20	(10)

It is somewhat difficult, however, to envision the energy from such large molecular reactions involving complex rearrangements ultimately residing in the electronic state needed to ionize the molecule. Nevertheless, because of the large exothermicities involved in some of these reactions they will require further consideration. For example, how does the rate production of ions by such processes compare with the measured rate of ion production?

6. Ion molecule equilibria might also allow for production of larger ions. In fact, it would be just such reactions that we consider in our scheme to produce the larger ions. There are several types of ion molecule equilibrium which one might consider. The most obvious is, of course, proton transfer

 $mH^{T} + H \ddagger m + MH^{+}$  (20)

where m represents a small molecule and M a large molecule.

Two examples of such equilibria are

 $C_4H_9^+ + C_{12}H_8 \ddagger C_4H_2 + C_{12}H_8^+ K \approx 10^{-2}$  (22)

In both of these examples the equilibrium constant is estimated to be far to the reactant side.

Another class of ion molecule equilibria would be hydride transfer from the large molecule to a small ion

 $m^+ + MII \ddagger mH + M^+$  (23)

Two examples of this type of reaction are:

$$C_{3}H_{3}^{+} + C_{8}H_{8} \neq C_{3}H_{4} + C_{6}H_{7}^{+} K \gtrsim 10^{-3}$$
 (24)

$$C_{3}H_{3}^{+} + C_{12}H_{10}^{+} + C_{3}H_{4}^{+} + C_{12}H_{9}^{+} + K^{2}_{1}10^{-3}$$
 (25)

Again the equilibrium constants indicate that the reaction would be favored toward the left.

Another type of ion molecule equilibria would involve the transfer of  $C_3H^2$ . For example in the equilibrium

$$C_3H_3^{\dagger} + C_2H_2 \ddagger C_3H_3^{\dagger} + H_2 \qquad (26)$$

This reaction, in fact, is one of the assumed steps in our proposed mechanism. The heat of formation of  $C_3H_3^+$  is not well known; assuming the heat of formation derived from Ref. 17, the equilibrium constant would be  $10^{-1}$  while using the heat of formation recently derived from flame measurements by Michaud et al.<sup>3</sup> the equilibrium constant would be  $10^{-1}$ . This reaction has been observed to be very rapid in the forward direction when the linear isomer of  $C_3H_3^+$  is assumed.<sup>12</sup> Another type of ion molecule reaction which again is a part of our assumed mechanism is the CH<sup>+</sup> transfer which is typified by reactions:

 $C_{3}H_{3}^{+} + C_{3}H_{4} \stackrel{?}{\downarrow} C_{4}H_{3}^{+} + C_{2}H_{2} K \gtrsim 10^{3}$  (27)

$$C_{3}H_{3}^{+} + C_{32}H_{6}^{+} + C_{33}H_{6}^{+} + C_{2}H_{2} - K_{2}^{+} 10^{6}$$
 (28)

In both of these reactions the equilibrium is favored toward the larger product ion.

In summarizing this discussion of alternate sources of large molecular ions, none of them seem nearly as attractive and reasonable as the assumption that the large molecular ions arise by ion molecule reactions in which the product mass exceeds the reactive mass of the ion, i.e., the scheme we have championed for the nucleation step in soot formation.

### V. SUMMARY AND CONCLUSIONS

In summary: ionic mechanisms appear to be important in the nucleation step in which chemi-ions react by ion molecule reactions to produce increasingly larger ions and in the coagulation step where charged particles are produced by thermal ionization. It has also been demonstrated that comparison of the absolute concentration of ions and particles is not a significant argument for or against an ionic mechanism except insofar as these concentrations indicate rates of reaction. It is important to demonstrate that the rate of ion production is equal to or greater than the rate of particle production. It is difficult to explain the appearance of large ions except by ion molecule growth reactions in which the molecular weight of the product ion exceeds the molecular weight of the reactant ion.

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# APPENDIX D

ION AND CHARGED PARTICLE CONTRIBUTION TO SOOT FORMATION IN FLAMES

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# EXTENDED ABSTRACT

The prospect of using synfuels with larger carbon to hydrogen ratios-and thus greater tendencies to soot--than for petroleum-derived fuels has stimulated a flurry of interest in the mechanism of soot formation in flames. This mechanism is not well understood and there are many competing ideas and different interpretations of the same data. Both molecular ions and charged particles may play significant roles in the nucleation and agglomeration steps of the sequence forming mature soot particles.

The precursor for the nucleation step is postulated to be the chemi-ion  $C_3H_3^+$ . This ion then grows by the addition of such flame species as acetylene and diacetylene through a series of very rapid ion-molecule reactions to become an incipient soot particle. During this growth period the charge on the ion or particle is neutralized by recombination with the electrons produced in the reaction generating the original chemi-ion. The growing electrically neutral particle may then become ionized, by e.g., thermal ionization. The charge on particles--either positive or negative--will have a significant effect on the rate of coagulation and/or agglomeration. It thus becomes important to understand and to quantify the various mechanisms by which soot particles may gain or lose electrical charges in sooting flames. This is also necessary to demonstrate that the small and large molecular ions observed in the early stages of soot formation are indeed produced by the chemi-ion, ion-molecule nucleation mechanism and are not a by-product of the formation of thermally charged particles.

The various means by which soot particles may become charged or discharged in a flame have thus been considered. The objective has been to formalize the rates of the various processes in terms of rate coefficients and species concentrations which can be quantitatively evaluated to compare with experimental observations.

The important mechanisms for charging soot particles and neutralizing charged particles (P and M symbolize particles or molecules, respectively) are:

Thermal Ionization or Thermionic Emission:

 $p = energy p^+ + e^-$ 

This will be the dominant process in producing charged soot particles.

Diffusive Charging:

 $P + M^+ \rightarrow PM^+$ 

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This process will be important when chemical additives of low ionization potential are used to influence soot formation.

Electron Attachment:

 $P + e^{-} \rightarrow P^{-}$ 

Charged Particle-Electron or Ion Recombination:

 $P^+ + e^- \rightarrow P$  $P^+ + M^- \rightarrow PM$ 

Because negative ion concentrations are usually much smaller than electron concentrations and the rate coefficient is smaller, only electron attachment is considered of importance.

Proton or Hydride Ion Removal from Charged Particles:

 $PH^+ \Rightarrow P + H^+$  $PH^- \Rightarrow P + H^-$ 

For energetic reasons this process would be considered only in a reaction in which the proton or hydride ion becomes attached to a molecular species. The process then becomes equivalent to an ion-molecule reaction:

 $PH^+ + M \rightarrow P + MH^+$ 

for which the rate coefficient will be very large if the overall process is exothermic. To estimate this rate coefficient the energetics of the proton or hydride ion removal from charged particles have been calculated. The above processes are defined; the rate coefficients and relevant equilibrium constants are calculated for typical flame conditions, and where possible, compared with experiments.

The rate of coagulation or agglomeration is calculated for spherical particles of equal diameters, d, which are small compared to the mean free path, by the equation:

 $\frac{dN_{p}}{dt} = k_{c} N_{p}^{2}$ 

where:

$$k_{c} = 0.866 \ d^{1/2} \left(\frac{kT}{\rho_{p}}\right)^{1/2} G \cdot \alpha \cdot S$$

in which  $\rho_p$  is the density of the particle, G is a factor which takes into account particle dispersion and electrostatic forces,  $\alpha$  is the collision integral for a self-preserving size distribution, and S is a sticking coefficient.

Application of the above equations to specific systems demonstrates the nature of the role that ions and charged particles play in soot formation.



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