AeroChem TP-278

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EVALUATION AND PROGNOSIS

William J. Miller

Technical Report on
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NR092-515/6-15-71[473]

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Prepared for
POWER BRANCH
MATERIAL SCIENCES DIVISION
OFFICE OF NAVAL RESEARCH

AeroChem Research Laboratories, Inc.
SYBRON CORPORATION
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* Invited Review for Fourteenth Symposium (International) on Combustion.

INTRODUCTION

Our knowledge of phenomena involving charged species in flames was last reviewed in Combustion Symposia proceedings by T.M. Sugden[1] in 1964. That was an extremely appropriate time for such a review. Interest in the subject was at its high water mark; several areas of prior investigation had reached the point where definite conclusions could be drawn and several new subjects had been introduced for the first time. Research on ions in flames has ebbed somewhat since 1964. The 10th Symposium included some 20 papers on ionization--this Symposium, fewer than half a dozen. This decrease in volume is certainly not due to a lack of problems in need of further investigation. There are presently more unanswered questions concerning ionization in flames than ever before. The answers to these questions, however, must now be applied to the solutions of a different set of problems than were prevalent in 1964.

Much of the work performed to date in this field has been sponsored by the military establishments of the U.S. and Great Britain. Motivation for this research derived from the need to define the sizes and extents of radar targets, predict the severity of electromagnetic wave attenuation in propulsion and re-entry systems and a host of other related communications problems. In a great many instances, our current knowledge of elementary reaction processes has become sufficient to adequately solve many of these problems or in other cases, serves to indicate that a solution is unattainable. Large areas of uncertainty in our understanding of the above problems still exist however and will, no doubt, continue to stimulate interest in ions in flames research for some time to come.

If a level of effort approaching that attained in this field in 1964 is to be seen again, it will probably be motivated by the recently recognized necessity of controlling the quality of our environment. The relevance of ionization phenomena to problems in this area has already been demonstrated by work on particulates scavenging in electric fields, ion-induced heterogeneous nucleation in flames, control of soot formation and heat transfer in flames via application of electric fields and a number of attempts to control the overall combustion process itself through electrical means. No doubt, as research of this nature progresses, additional applications will suggest themselves.

Whatever the problems motivating research on ionization may be or however their priorities may vary with time, they depend for their ultimate solution on an understanding of the elementary chemical and physical processes involved. The text which follows is an attempt to summarize the status of that knowledge and to indicate the more critical areas of uncertainty. Sugden's review of 1964 provides a convenient point of departure and the emphasis will be on work performed since.

CHEMI-IONIZATION

Ionization in Hydrocarbon Flames

The elementary reaction responsible for ionization in hydrocarbon flames is generally accepted to be

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

There have been flirtations[2] with other mechanisms, most notably with

$$CH^* + C_2H_2 \rightarrow C_3H_3^+ + e \qquad (2)$$

in which CH^* represents $A^2\Delta$ or $B^2\Sigma$. The lack of correlation between the concentrations of these excited states and ion formation rates in flow tubes,[3] flames,[4] shock tubes[5] and a flash photolysis system[6,7] has virtually eliminated this reaction from consideration and indicates a minor role, if any, for other processes involving CH^*. Recently derived evidence in favor of Reaction (1) has been obtained from studies[8] of the $C_3O_2/H/O$ reaction in which CHO^+ is the dominant ion formed upon introduction of H atoms to the C_3O_2/O system. The presence of both H and O atoms are required to produce ions in this case.

The possibility still exists that mechanisms other than Reaction (1) may contribute to ionization in certain flames. Combustion of acetylene and acetylenic compounds yields higher ion formation rates than other hydrocarbons. It has been suggested[9] that this is due to augmentation of the ion formation process via Reaction (1) by an additional reaction--perhaps

$$C_2H + O_2^* \rightarrow CHO^+ + CO + e \qquad (3)$$

Whether this is truly the case or whether C_2H_2 simply oxidizes through a mechanism that produces higher concentrations of CH than do the mechanisms for other hydrocarbons is still conjectural. Of course other reactions may be postulated, as well. For example, it has been noted[10] that ions are produced at very high temperatures (≈ 4100 K) in carbon/oxygen mixtures. This has been attributed to the reaction

$$C_2 + O \rightarrow C_2O^+ + e \tag{4}$$

which is one of many possible alternatives to Reaction (3) in C_2H_2/O_2 flames.

It should be noted at this point that even if auxiliary mechanisms like those above are operative in some specific flames, their effects on the overall ion formation process are small. The consistency[11] in ion formation rates per C-atom consumed in hydrocarbon flames regardless of temperature or of fuel structure is impressive. It is upon this principle that the striking linearity and wide applicability of gas chromatographic flame ionization detectors is based. Acetylene exhibits the largest deviation from the nearly constant (maximum) value of 0.25 coulombs/g-atom C observed for all aliphatic compounds and even in this case the deviation is only about 30%.

Unfortunately, this consistent behavior is not displayed in low temperature atomic flame systems. Flow tube studies[3,12-14] of C_2H_2/O, C_2H_4/O and C_nH_{2n+2}/O reaction systems reveal large differences in the number of ions produced. Available data indicate that C_2H_4 is about as efficient in this system as in a high temperature flame, i.e. the consumption of approximately 10^6 C-atoms yields 1 electron. On the other hand, C_2H_2 produces 100-fold more ionization than C_2H_4 and CH_4 about 100-fold less. Obviously, if these reactions share a common ionization mechanism, the proportions of

CH produced in their oxidations must differ considerably. Ion production in the catalytic low-temperature combustion of hydrocarbons on platinum filaments[15,16] is similarly very sensitive to the structure of the fuel molecule. For example, branched paraffins such as $(CH_3)_4C$ and $(CH_3)_3CCH_2CH_3$ are found to produce ion yields per C-atom comparable to those observed in flames, but n-pentane and n-hexane give 30 times smaller yields and response to C_2H_2 is down by more than a factor of 100. Very little is known of the oxidation mechanisms in catalytic combustion and the ionization process is understood even less well. It is clear, though, from the data at hand, that either ionization mechanisms other than Reaction (1) are operative here or, more likely, that the overall oxidation mechanism is sufficiently different in these systems to produce drastically different concentrations of CH and O in the combustion of variously structured fuels. The ions produced are also considerably different from those observed in flames. Because of the much lower temperatures and the presence of unburned fuel molecules, extensive ion clustering takes place resulting in the formation of a wide variety of species[17]--more than half of the ions present have M > 200 amu. Detailed speculation on either the oxidation or ionization mechanisms is not warranted by the meager amount of basic information currently available.

No discussion of Reaction (1) is complete without consideration of its thermochemistry. The quantity in question is ΔH_f for CHO^+; it has decreased considerably in recent years. Early determinations[18] based on electron impact studies resulted in values around 920 kJ mole^{-1}. Taken together with (more accurate) values for $\Delta H_f(CH)$ and $\Delta H_f(O)$, Reaction (1) was computed to be endothermic by some 75 kJ at 2000 K. This relatively high energy of activation was no doubt responsible in large measure for the considerable favor afforded to the participation of excited CH in Reaction (1)--particularly in low temperature systems.[3,12] Recently, photo-ionization studies[19] have led to a value $\Delta H_f(CHO)^+ = 840 \pm 20$ kJ mole^{-1} which renders Reaction (1) nearly thermoneutral (8 ± 20 kJ). This helps explain the apparent insensitivity of hydrocarbon ion-formation processes to changes in temperature and removes historical thermochemical objections to Reaction (1).

Attempts to measure the rate constant for Reaction (1) are complicated, in most cases, by the thinness of typical hydrocarbon flame reaction zones. Reported values[20-22] are in the range $10^{-13} < k_1 < 10^{-11}$ (ml molecule^{-1} sec^{-1}). Theoretical considerations[20] and analogy with other reactions, including the isoelectronic process[21]

$$N + O \rightarrow NO^+ + e \qquad (5)$$

tend to support values at the higher end of this range. The most direct measurement of k_1 would comprise simultaneous determination of [CH], [O] and the ion formation rate. This experiment would also provide a straightforward means of testing the validity of Reaction (1). The only attempt thus far, to perform this study led to results[23] which, in fact, did not correlate with Reaction (1) but several objections[24] to these published results have been raised. The experiments are certainly worth repeating.

Ionization in Cyanogen Flames

These flames hold considerable promise as an experimental medium for the study of high temperature reactions, but thus far they have not been extensively characterized. Flames of C_2N_2 supported by O_2 exhibit[25] temperatures in excess of 4800 K at 1 atm. Because of the very high temperatures and the presence of large amounts of NO (I. P. = 9.5 eV) in the combustion products, equilibrium considerations[26] lead, typically, to the prediction of very high ion concentrations; for example, a stoichiometric (with respect to formation of CO and N_2) mixture of C_2N_2/O_2 at 1 atm yields 10^{13} ions ml^{-1}. In view of these considerations it is perhaps surprising that studies of these flames reveal ion formation kinetics characteristic of chemi-ionization[27] rather than collisional ionization. Moreover, the ionization levels are frequently found to achieve values below their equilibrium values despite the fact that considerable time for reaction is allowed for by making measurements far downstream of the flame front. This behavior is in contrast to that observed for hydrocarbon flames in which the ion concentration attains above-equilibrium values in the flame front and then relaxes to near equilibrium in the burnt gases.

Bulewicz and Padley,[27] working in low pressure C_2N_2 flames, noted that the electron concentration scaled with p^2 indicating a molecular ion formation process. Their work yields the following empirical relationship for the maximum electron concentration as a function of pressure:

$$n_e = 3 \times 10^7 p^2$$

where p is the pressure in Torr. Extrapolation of this relationship to 1 atm indicates $n_e = 6 \times 10^{12}$, still somewhat lower than the equilibrium value of 1×10^{13}. The elementary reactions considered[27,28] to be most plausible for ion formation in these flames are

$$NO + N + N \rightarrow N_2 + NO^+ + e \qquad (6)$$

and

$$CN + O + O \rightarrow CO + NO^+ + e \qquad (7)$$

Reaction (6) is exothermic by 136 kJ and $\Delta H_7 = -53$ kJ mole^{-1}.

The observation[29] of copious ionization upon the addition of small amounts of C_2N_2 to CO/O_2 flames ($T \approx 2500$ K) has been cited as evidence in favor of Reaction (7) but flow tube studies[30, 31] lend considerable support to Reaction (6) which need not necessarily proceed in a single step as written. Indeed both of these processes may occur through the formation of an excited reaction intermediate--CNO^* or metastable N_2^*. The ionization accompanying the recombination of N and O atoms in the presence of carbonaceous gas phase catalysts in flow tubes[30] is in fact thought to proceed through these or similar intermediates. Clearly more experimental data should be obtained before much further mechanistic speculation will become worthwhile.

Ionization of the Alkali Earth Metals

In 1955, Sugden and Wheeler[32] noted that the addition of Ba or Sr salts to $H_2/O_2/N_2$ flames can produce higher electron concentrations than a corresponding amount of Na salt. Subsequent investigations[33,34] of this ionization have revealed that the ion produced is $MeOH^+$ (where Me = Ba, Sr or Ca), which arises from either the reaction

$$Me + OH \rightarrow MeOH^+ + e \qquad (8)$$

or from the indistinguishable process

$$MeO + H \rightarrow MeOH^+ + e \qquad (9)$$

The data in Table I[34] may be used to demonstrate that the ionization of these metals may be of considerable importance in many practical systems. For example a total atom fraction of $\approx 10^{-5}$ Ba in a $H_2/O_2/N_2$ (3.5:1.0:3.0) flame at 2250 K yields 10^{11} electrons ml^{-1}.

The kinetics of these reactions have not yet been examined in any detail. Limiting values have been derived by Jensen[34] from his 1-atm data but even these limits are semi-quantitative in nature. They suggest, however, that the activation energies of these reactions are approximately equal to their endothermicity; the (upper) limiting values for their pre-exponential factors are about 2×10^{-10} ml molecule^{-1} sec^{-1}. It is interesting to note that neither (8) nor (9) can be operative in "dry" CO/O_2 flames; indeed, in these flames, the rates of ionization for the alkaline earths exhibit[35] much larger activation energies--on the order of the ionization potentials for the respective metal atoms.

COLLISIONAL IONIZATION

Alkali Metal Additives

Studies of the ionization of alkali metals in both $H_2/O_2/N_2$ flames[36] and $CO/O_2/N_2$ flames[37] indicate that the operative mechanism for ion production is

$$Me + M \rightarrow Me^+ + M + e \tag{10}$$

Mechanisms involving the reactions

$$Me + e \rightarrow Me^+ + 2e \tag{11}$$

$$Me + OH \rightarrow Me^+ + OH^- \tag{12}$$

or

$$Me + H_2O \rightarrow MeH_2O^+ + e \tag{13}$$

can now be rejected with a fair degree of certainty.

The rates of alkali metal ionization are anomalously fast. Measurements of their rate constants made either directly or via measurement of the recombination coefficient (reverse of Reaction 10) and calculation[38] of k via the equilibrium constant, yield activation energies very close to the respective ionization potentials. Pre-exponential factors for these reactions are therefore very high and lead in turn to reaction cross sections 100 to 1000 times larger than simple gas kinetic predictions. The magnitude of these cross sections has led to the suggestion[38,39] that excited metal atoms are involved in the rate-limiting ionization step. Typical values of the cross sections (σ), measured activation energies (Ea), and ionization rate constants (k_i, defined by $d[e^-]/dt = k_i[A]$) for Na, K and Cs are given in Table II for both $H_2/O_2/N_2$ and $CO_2/O_2/N_2$ flames.

Electron Impact Ionization and Electron Temperatures

The question of whether or not ionizing collisions of the type

$$e^* + A \rightarrow A^+ + 2e \qquad (14)$$

involving hot electrons (e^*), are of significance in flames is inextricably tied to the older question of whether or not electron temperatures in fact exceed overall flame gas temperatures and if so by how much. Recent works by Porter[40] and Bradley[41,42] and co-workers have clarified these problems considerably. It is now quite certain that collisions of the second kind producing "hot" electrons do, indeed, occur in flames and that this effect is due to the presence of highly vibrationally excited molecules in the vicinity of the flame front. It has further been observed[43] that high electron temperatures are restricted to flames containing carbon; the effect is absent or negligible in hydrogen flames. Theoretical considerations[41] indicate that the most probable energy transfer process for electron superheating is

$$CO_2^* + e \rightarrow CO_2 + e^* \qquad (15)$$

where CO_2^* represents CO_2 vibrationally excited to above equilibrium levels. This proposal correlates quite well with observations of the location and magnitude of electron excitation.

von Engel and Cozens[44,45] have suggested that the excess ionization exhibited by hydrocarbon flames is due to electron impact ionization involving the hot electrons produced in reactions such as 15 above. This suggestion is based on reported observations of electron temperatures of 10,000 K or higher. At temperatures on this order, electron impact ionization can, indeed, account for observed ionization rates in many situations. The question then, is whether or not electron over-heating can produce values of T_e this high; recent work indicates that it cannot. The maximum in T_e given by Bradley and Sheppard[42] is $\approx 2\ T_g$ in a CH_4/air flame and Porter[40] finds T_e to exceed T_g by only 200 K or so. It would appear therefore that the possibility that this mechanism can account for non-equilibrium ionization in hydrocarbon flames can now be set aside.

ION-MOLECULE REACTIONS AND ELECTRON ATTACHMENT

Ion-Molecule Reactions

The tremendous variety of ions produced in hydrocarbon flame fronts[46] coupled with the complexity of the neutral gas composition give rise to a discouragingly large number of possibilities for ion-neutral interactions. It is therefore somewhat surprising that so many of these processes have been studied in detail. A description of even a small proportion of these investigations is beyond the scope of this review; the interested reader is instead referred to any of a number of excellent reviews on the subject (e.g. Ref. 47). For purposes of this discussion we will simply present an overview and qualitative description of the types of reactions observed.

Proton transfer processes of the type

$$AH^+ + B \rightarrow BH^+ + A \qquad (16)$$

are responsible for the formation of nearly all the naturally occurring ions in hydrocarbon flames. The end product of these reactions is H_3O^+ which comprises the only ion of significance in the burned gas region. These reactions are apparently all very fast. The reaction

$$CHO^+ + H_2O \rightarrow H_3O^+ + CO \qquad (17)$$

is frequently chosen to represent the overall H_3O^+ formation process and several measurements[21,22,47] of its rate have been made. The results give $k_{17} = 1.5 \pm 1.0 \times 10^{-8}$ ml molecule^{-1} sec^{-1}. A large variety of reactions similar to (17) have now been studied[48,49] in low-pressure, room temperature flow tube systems. In general they are found to be <u>very</u> fast or <u>very</u> slow--i.e. they possess rate constants on the order of 10^{-9} ml molecule^{-1} sec^{-1} or they do not proceed at a measurable ($k \geq 10^{-14}$) rate. Under the thermally equilibrated low temperature conditions of most flow tubes, it has become commonplace to make thermochemical judgments concerning these reactions on the basis of their kinetics--if a reaction proceeds at all, it is judged to be exothermic. Endothermic processes are "forbidden". This criterion must be largely relaxed at the high temperatures prevalent in flames. Products of ion-molecule reactions with large activation energies are quite common. This is particularly true of reactions of the type

$$H_3O^+ + Me \rightarrow Me^+ + H_2O + H \qquad (18)$$

The heat changes and rate constants associated with a number of metals reacting as in (18) are given[47] in Table III. Despite their endothermicities, these reactions are very fast and, as a result, they produce $[Me^+]/[Me^+]_{equil}$ ratios much greater than unity in typical hydrocarbon flames. The magnitudes of these rate coefficients and their relatively large activation energies predicate very large pre-exponential factors--typically 10^{-7} ml molecule^{-1} sec^{-1}. As in the case of alkali metal ionization, the participation of excited states is a likely explanation for these large reaction cross sections.

Negative Ion Formation and Reaction

Mass spectrometric examinations[46, 50] of hydrocarbon flames have established the presence, in the reaction zone, of the negative ions C_2^-, C_2H^-, O^-, O_2^-, OH^- and a wide variety of $C_xH_yO_z$ species. The concentrations of these ions are not known, nor are their formation mechanisms. It is doubtful that negative ion concentrations ever exceed the electron concentration, even in the flame front where attachment is most extensive; a short distance downstream of the flame front, the electron is certainly the dominant negative charge carrier. The relative concentrations of electrons and negative ions in the burned gases appear[51] to correspond quite closely to their equilibrium values. Although the overall concentration of charged species is considerably above equilibrium, the species e, OH^-, O^- and O_2^- are in equilibrium with one another and with the neutrals involved; i.e. the reactions

$$e + H_2O = OH^- + H \qquad (19)$$

$$OH^- + H = O^- + H_2 \qquad (20)$$

$$O^- + OH = O_2^- + H \qquad (21)$$

are balanced throughout the region of ion decay.

The rapidity of negative ion formation in the flame front and the absence of pressure effects characteristic of three-body attachment processes strongly suggest that the operative mechanism is one of dissociative attachment to some carbon-containing intermediate. Its identity is still unknown.

The addition of electrophilic materials such as Cl_2 or Br_2 to hydrocarbon flames produces additional electron attachment.[52] This also occurs in the flame front and is quantitatively accounted for on thermodynamic grounds. Substances such as C_2N_2, NH_3 and H_2S which produce electrophilic combustion products and/or reaction intermediates also yield negative ions.[52] The specific attachment reactions responsible in these cases however are also unknown as are the identities of the ions produced.

The $H_2/O_2/N_2$ flames employed in the aforementioned studies of metal atom ionization have also served as convenient media for a series of investigations[53-56] of negative ion thermodynamics. It has been found that a number of metals will produce negative ions of extraordinary stability. The attachment mechanism for these species is thought to be dissociative attachment of the type

$$e + HA \rightarrow A^- + H \qquad (22)$$

The thermodynamic parameters for the species studied to date are give in Table IV. It may be seen that the electron affinities of the oxyhydroxides and oxides in many cases exceed those of the halogens which themselves are considered highly electrophilic.

Almost nothing is known of the kinetics of these processes. Even the rate of electron attachment to HCl via

$$e + HCl \rightarrow Cl^- + H \tag{23}$$

is poorly known, and of reactions of the type, this is the most extensively studied. The works of both Buchel'nikova[57] and Christophorou[58] indicate an activation energy for Reaction (23) of about 75 kJ mole^{-1}, the endothermicity of the reaction. However, the pre-exponential factors from these two studies differ by nearly an order of magnitude. If this activation energy and the equilibrium constant at 300 K are used to compute the pre-exponential factor for Reaction (23) from kinetic data[48] for the reverse (dissociative attachment) reaction, a value greater than 10^{-7} ml molecule^{-1} sec^{-1} results. Clearly, these reactions must be much better understood kinetically before predictions of their effects in practical systems can be made.

ELECTRIC FIELD EFFECTS

Observations of alterations in flame geometry and burning velocities in the presence of applied electric fields comprise the earliest evidence of the presence of charged species in flames. Excellent accounts of the historical development of this field have been given in several places (e.g. see Ref. 59) and no attempt to repeat this story will be made here. Many of these older observations can now be quantitatively accounted for in terms of ion mobilities and ionic wind effects based on current knowledge of ion concentrations and identity; many other effects are still unexplained.

The relevance of these phenomena to modern day problems is demonstrated by a number of studies in which soot and smoke formation have been reduced, heat exchange enhanced, flame ventilation altered, and flammability limits increased via the judicious application of electric fields. The effects of fields on soot formation are an integral part of an evolving controversy concerning the role of ions in carbon formation and are discussed separately below. Other work in this area has, for purposes of discussion, been divided into "physical" and "chemical" effects.

Physical or Ionic Wind Effects

When a strong longitudinal field is applied to a rising column of combustion product gases, the relatively massive positive ions (compared to the electron) are accelerated toward the cathode. Collisions between these ions and neutral gas molecules transfer momentum to the bulk gas resulting in a directional body force. The magnitude of this effect is determined by gas density, ion concentration and mobility, temperature and field strength. The latter must be limited to values below that necessary for breakdown. A comprehensive analysis of the interactions and the maximum possible effects attainable under a variety of flame conditions have recently been set forth by

Lawton and Mayo.[60,61] The equations presented in these studies facilitate the computation of optimum electrode gauze geometries and provide the means for predicting enhanced rates of air entrainment and increases in gas flow velocities.

When the voltage impressed between two flame-immersed electrodes is modulated at audio frequencies, the flame can be made to act as an extremely high-fidelity speaker or amplifier.[62] This and similar effects have provided a novel source of entertainment for several investigators but it is unlikely to have any significant impact on the sound reproduction industry. These findings do have an intriguing corollary however: If acoustical effects can be induced by electric fields perhaps their naturally occurring analogs can be eliminated in a similar way. The most frequently cited potential applications of this effect are in the suppression of acoustic instabilities in jet engine and solid propellant rocket motor exhausts.

If a heat exchanger in contact with a flame is negatively biased with respect to its surroundings, increased heat transfer rates are obtained.[59, 63] The potential practical importance of this effect is obvious. Similarly, considerable advantage may be envisaged in the field-induced modifications of flame stabilities observed in a number of studies.[64-66] Strong fields (on the order of 1-2 Kvolt cm^{-1}) have been seen to produce greater apparent flame strengths in opposed jet diffusion flames,[66] broader extinction limits in bunsen-type flames,[64] and increased burning velocities in premixed systems.[67] It is doubtful (see below) that all these effects can be attributed purely to the ionic wind phenomenon.

Chemical Effects

Jaggers and von Engel[68] have recently found that flame propagation velocities can be considerably enhanced by impressing high frequency (5 MHz) ac fields on ion-containing flames. Frequencies this high are incapable of inducing sufficient ionic motion to influence burning velocities[68] and an explanation for the observations has therefore been sought in electron-molecule interactions rather than ionic wind effects. As the electrons, "overheated" by the field, undergo collisions with chain propagating free radicals in the flame front they produce vibrational excitation which has been previously shown[69] to accelerate chemical kinetic rates of reaction. Since the electron concentration peaks in the flame front, the effect maximizes there. Since this is also where radical concentrations and their gradients are highest, it is not difficult to envision large variations in flame velocity induced by relatively low electrical power inputs in this region.

When dc fields are imposed, it is difficult to separate "chemical" effects such as the above from ionic wind effects and, indeed, in this case, the differentiation is more convenient than real. For example, changes in rotational and electronic excitation characteristics observed[70] in the reaction zone may be qualitatively accounted for by either or both of these mechanisms. If any systematically designed systems are to be realized for the alteration of burning velocities through the application of electric fields, a great deal more information on these phenomena will have to be collected. The success attained[71, 72] in mathematical modeling of simple ionic wind effects on flame chemistry and heat release profiles to date however, offers considerable promise in this area.

CARBON FORMATION AND HETEROGENEOUS NUCLEATION

It is now a well established fact that soot particles formed in rich hydrocarbon flames are electrically charged.[73, 74] It has also been clearly demonstrated that the rate of carbon deposition and the nature of the material formed can be drastically altered by the impression of an electric field on the flame.[73,75] The question at this point concerns the time in its history at which the carbon particle acquires its charge. If ion-induced heterogeneous nucleation is responsible for carbon formation, the particles would have been charged at birth. Alternatively, charge may accumulate by diffusion of ionic species to the surface of previously formed particles. Ionic nucleation is a well known phenomenon and classical theory[76] predicts nucleation rates via this mechanism that are much larger than those for homogeneous nucleation.

A recent study by Mayo and Weinberg[75] of the effects of electric fields on carbon formation rates indicates strongly that both nucleation mechanisms occur. The relative importance of each cannot be quantitatively assessed from the work however, nor, as the authors point out, do the results apply directly to carbon formation in the absence of a field. However, this work as well as that of Wersborg et al[77] has shown that each particle bears but a single charge and that very young particles are charged. These findings suggest strongly that ionic nucleation plays a very important if not a dominant role. Further evidence[73] for this hypothesis may be derived from the fact that strong fields which quickly remove potential ionic growth centers, reduce the amount of carbon formed by 90% or more. An equally if not more impressive body of cross-correlated evidence has been compiled over the years, however, based on theories involving only neutral species (see e.g. Ref. 78).

Studies of the effects of additives on carbon formation provide little but further obfuscation of the picture. This is due in no small part to the fact that each of these studies is performed in a different flame, each worker chooses a different criterion by which to evaluate the effectiveness of a given material, and seldom do two investigators select the same materials at the same or similar concentrations.

Table V is excerpted from the work of Addecott and Nutt[79] and is intended to show a satisfying correlation between flame front ion concentrations and the smoke reduction abilities of a number of metals. The explanation for this correlation may lie in the fact that hydrocarbon ions such as $C_nH_m^+$ which are known to be present[80] are potentially efficient centers for carbon particle nucleation and are reduced in concentration upon introduction of ionizable metal atoms or compounds. This occurs through charge transfer of the type

$$C_nH_m^+ + M \rightarrow M^+ + C_nH_m \tag{24}$$

and/or the enhancement in $C_nH_m^+/e$ recombination produced by an increase in [e].

All of these metals have also been studied by Cotton et al.[81] This investigation produced a significantly different order of relative efficiencies but in this case the threshold value of the equivalence ratio at which soot is produced was chosen as the correlation parameter. The mechanism cited is one in which the metals increase the rate of neutral nuclei combustion by catalyzing the reaction

$$H_2O \xrightarrow{Me} H + OH \tag{25}$$

or its equivalent. The resultant higher radical concentrations, particularly [OH], increase the consumption rate of heavy hydrocarbon radicals or particles. Unfortunately these two studies (Refs. 79 and 81) cannot be compared directly. The amount of soot produced and the ion concentrations are missing from the latter; the change in soot point produced by the various metals was determined in the former. However, since the amount of soot produced and the stoichiometry at which soot is first observed will depend on quite different processes, it is not surprising that the same additive rankings fail to emerge from both studies. The alkaline earth metals appear to be highly efficient in both regards however, and their efficiencies in reducing soot are in the order Ba > Sr > Ca.

The structure of the fuel molecule also appears to be of considerable importance. Although the alkaline earths reduce soot formation in the above studies with predominantly aliphatic fuels, this is apparently not the case for aromatics. In fact, when Ba, Ca, or Sr are added to the aromatic fuel stream in industrial carbon black furnaces, an increase in yield is produced.[82] This observation forms the basis of a process patent held by the Cabot Corp. Clearly we are far from achieving a satisfactory picture of elementary carbon-forming chemistry.

CONCLUSIONS

An attempt has been made here only to summarize the status of our understanding of a variety of high temperature charged species phenomena and to point out the greatest areas of uncertainty. It is hoped that the material included will provide the novice in the field with a basic key to the available literature and an appreciation of those aspects of the field which bear on current air quality problems arising from combustion.

The long awaited rekindling of interest in combustion research motivated by concern for our environment has so far been slow materializing. At least that seems to be the opinion of most researchers in the field. That this revitalization will take place seems inevitable--particularly in view of society's almost certain dependence on fossil fuels as an energy source for years to come. That this effort will include a concomitant increased interest in flame ionization also appears inevitable.

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TABLE I

Thermodynamic Data* for Ionization

via Me + OH = $MeOH^+ + e$

Me	ΔH^o_o (kJ mole^{-1})	K_{equil}
Ca	146 ± 42	1.8×10^{-3} exp(-18000/T)
Sr	105 ± 34	2.0×10^{-3} exp(-13000/T)
Ba	25 ± 42	1.7×10^{-3} exp(-3000/T)

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* from Ref. 34

TABLE II

Rate Data for the Ionization of Alkali Metals*

	$H_2/O_2/N_2$‡			$CO/O_2/N_2$†		
Metal	k_i (sec^{-1})	σ (10^{-12} cm^2)	E_a (kJ $mole^{-1}$)	k_i(sec^{-1})	σ (10^{-12} cm^2)	E_a (kJ $mole^{-1}$)
Na	7.2	9	481 ± 20	8.0	1.4	489 ± 13
K	280	8	414 ± 17	190	0.6	418 ± 13
Cs	4000	11	385 ± 25	400	0.15	376 ± 13

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* both flames at 2250 K

‡ from Ref. 36

† from Ref. 37

TABLE III

Kinetic and Thermodynamic Data for Metal Atom Charge Transfer*

$(Me + H_3O^+ = Me^+ + H_2O + H)$

Metal	ΔH(kJ mole^{-1})	k(ml molecule^{-1} sec^{-1})
Pb	+100	1×10^{-9}
Mn	+100	8.5×10^{-10}
Cr	+44	8.0×10^{-10}
Zn	+290	1.0×10^{-10}
Li	-100	7.5×10^{-10}
Na	-125	1.1×10^{-8}
K	-203	5×10^{-8}

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* from Ref. 47

TABLE IV

Thermodynamic Data for Metal-Containing Negative Ions

Ion	Reaction	K_{equil}	Electron Affinity (kJ mole^{-1})	Ref.
BO_2^-	$HBO_2 + e = BO_2^- + H$	1500 exp(-10000/T)	393 ± 20	53
$HMoO_4^-$	$H_2MoO_4 + e = HMoO_4^- + H$	24 exp(500/T)	410*	55
MoO_3^-	$HMoO_4^- + H = MoO_3^- + H_2O$	0.85 exp (10400/T)	250 ± 50	55
HWO_4^-	$H_2WO_4 + e = HWO_4^- + H$	25 exp (1300/T)	400*	54
WO_3^-	$HWO_4^- + H = WO_3^- + H_2O$	0.87 exp(5700/T)	351 ± 50	54
CrO_3^-	$HCrO_3 + e = CrO_3^- + H$	2500 exp (-13400/T)	229 ± 50	56
$HCrO_3^-$	$CrO_3^- + H_2 = HCrO_3^- + H$	1.7 exp (-9900/T)	390 ± 50	56

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* Error limits undefinable due to uncertainty in H—O bond dissociation energy.

TABLE V

Correlation of Ion Concentration and Smoke Reduction*

Metal	% Smoke Reduction	Ions (10^{13} ml^{-1})
Ba	13.3	5.8
Pb	12.8	5.4
Cs	12.0	6.7
K	12.0	2.8
Sr	5.7	3.4
Ca	3.1	2.1
Mg	2.6	1.9
Na	2.6	1.4

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* from Ref. 79