The enigmatic mechanism of the flame ionization detector: Its overlooked implications for fossil fuel combustion modeling

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Abstract

The flame ionization detector (FID) has been a commercial analyzer now for about 50 years. It still finds significant use as a sensitive quantitative monitor of organic compounds in gas chromatography and for monitoring mixtures of hydrocarbons. Its carbon counting ability to integrate, for example, total unburned hydrocarbon emissions from a source, now is accepted without question. This is especially noteworthy as the fundamental chemistry on which the instrument is based has always been uncertain. Although now largely overlooked, its mechanism has significant implications and suggests that there is an underlying simplicity to hydrocarbon combustion. As a result, in the light of recent discoveries concerning the very rapid formation of a pool of hydrocarbon radicals in hydrocarbon combustion, a re-examination of the chemi-ionization mechanisms in hydrocarbon flames has been undertaken. Many of the previous speculations have been scrutinized and it is confirmed that the primary chemi-ionizing reaction of $CH(X^2\Pi)$ with O atoms is most likely the sole source in combustion including the FID. The oft suggested roles of electronically excited states of CH now are ruled out but with some slight uncertainty remaining on the still unknown importance of the metastable $CH(a^4\Sigma^-)$ state in flames. The reason for the "equal per carbon" response of the FID with any hydrocarbon finally has been resolved. From isotopically labeled studies and measurements of the concentrations of CH and C_2 it is seen, under the same conditions, that different hydrocarbons do produce approximately the same levels of CH on a unit carbon basis. This results from the very rapid destruction and reformulation kinetics in the reaction zone of flames, and formation of a hydrocarbon radical pool that constitutes the unburned carbon. These radicals then are gradually eroded by the continuing oxidation or by soot precursor growth. As a result, the nature of the carbon in a hydrocarbon fuel is mainly irrelevant, only its quantity. The one well-documented exception has always been C_2H_2 but the data now show this so-called anomalous behavior to be no more than a reflection of its uniquely slower combustion nature in the reaction zone. It is not apparent in substituted acetylene fuels. Close to the reaction zone its kinetics produce a larger profile of unburned carbon that is evidenced by enhanced levels observed for CH and C_2. The nature of the specific responses of the FID to other organic structural categories also is a reflection of their primary combustion breakdown and a measure of the initial pool of unburned carbon. Exactly similar responses are seen in both the FID and in soot formation tendencies. The connection though is indirect in that both processes relate to and result from the same pool of non-oxidized carbon, rather than any implied inceptive role. As a result, the observed sensitivities previously recorded with the FID now can be a useful aid in validating the primary dominant steps in combustion mechanisms and the example of dimethyl ether combustion is used as an illustration. At present, this rich analytical database could be particularly useful in modeling the more complex partially oxygenated fuels that now are being extensively studied.
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Keywords: Flame ionization detector (FID); Chemi-ionization; Combustion kinetics; Excited states; Kinetic modeling

Contents

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1. Introduction

To any combustion chemist who is familiar with the performance of the flame ionization detector (FID) there has always remained the puzzling and frustrating enigma concerning its remarkable behavior. This stems from the fact that it essentially monitors and integrates carbon atoms in gaseous hydrocarbon mixtures in such an effective way irrespective of their molecular genesis. With only minor idiosyncrasies, this occurs in an otherwise seemingly complex diffusion flame mode. Although never expressed as such, this has to relate directly to the very fundamentals of fossil fuel combustion. It automatically implies that there is an underlying general chemical behavior in this otherwise kinetically complex system. Even after 50 years, the continuing inability to satisfactorily resolve this dilemma has been ignored mainly because plausible explanations were not forthcoming. Detailed kinetic modeling has never been attempted on such a flame configuration. However, the greater reliability of the databases of some combustion kinetic models now appears to be generating renewed interest in attempting to expand them further to more specifically predict the minor species and any major ion chemistries [1].

In 1958, credit for the FID was mainly given to McWilliam in Australia [2–4], as was also the patent. The simultaneous efforts and prior publication of Harley et al. [5] and Pretorius [6] in South Africa were also commendable and should be equally noted in its history. These developments stemmed not from an interest in combustion but rather from a need for a more sensitive detector for gas chromatography. By chance, this coincided in the field of combustion with the growing interest in the nature of ionization in flames. Whereas the 5th and 6th Proceedings of the Combustion Institute in 1954/1956 had only three and one paper on ionization, respectively, the subsequent meeting in 1958 had 6 and 2 years later there were 14, the opening paper of that meeting being a survey on ions in flames by Eyring and his collaborators [7]. Additionally, the first volume of *Combustion & Flame* appeared in 1957 with three papers on ionization. The electrical nature of flames had been long realized. In fact it was Calcote in 1949

[8] that first noted the high levels of ions in the reaction zone of flames and concluded this was evidence of chemi-ionization. Now, interest was turning from free electrons to the identity in hydrocarbon flames of the specific ions and the nature of their formation and decay mechanisms. The two fields of commercializing the FID analyzer and understanding flame ionization developed in parallel with little interconnection in these earlier years, and it only became apparent later that the emerging suggested mechanisms of ionization in flames were the foundation of the FID's operation [9,10].

The FID instrument design, that has remained hardly changed over the years, burns a small pure hydrogen diffusion flame diluted by N_2 or He in the surrounding air. A typical arrangement is reproduced in Fig. 1 [11].
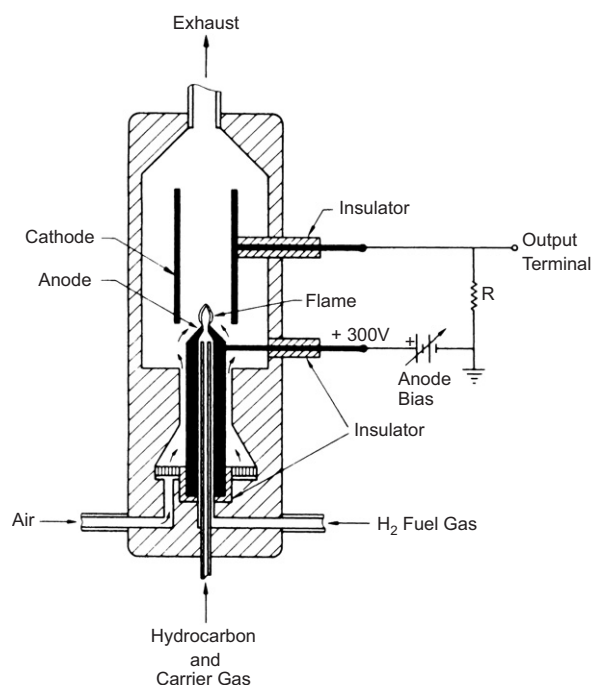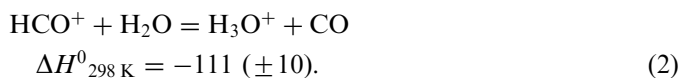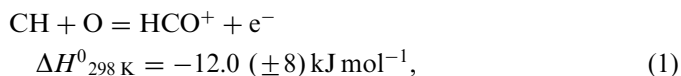

Fig. 1. The typical design of a flame ionization detector. Reprinted with permission of The Optical Society of America from ''Laser-enhanced flame ionization detector'', by T.A. Cool and J.E.M. Goldsmith in *Applied Optics*, 1987, vol. 26, pp. 3542–51 [11].

However, recent years have seen it modified slightly as a fast response instrument for in-cylinder engine development measurements. Such a use was reviewed 10 years ago in this journal [12]. In all cases, the total ion formation rate in the flame is monitored using two electrodes, one generally the burner itself, and operated in a saturation voltage mode that ensures a withdrawal of all flame charge as it is formed. On adding traces of organic vapors to the fuel stream, great monitoring sensitivity is noted that is linear with the concentration of the additive over a wide dynamic range. Additionally, and unexpectedly, the signal to a good approximation was seen to be linearly proportional to the number of carbon atoms in the organic molecule and displayed an insensitivity to its structure.

As will be seen, although many studies of hydrocarbon combustion have been reported, no overall satisfactory explanation of the FID's mechanism yet has emerged. The chemi-ionization step (1), which was suggested from the start of such studies, still is accepted as the primary reaction [13,14]. The parent HCO^+ ion then rapidly reacts further to produce H_3O^+ and other secondary hydrocarbon ions:

$$CH + O = HCO^+ + e^-$$
$$\Delta H^0_{298\,K} = -12.0\ (\pm 8)\ kJ\,mol^{-1}, \tag{1}$$

$$HCO^+ + H_2O = H_3O^+ + CO$$
$$\Delta H^0_{298\,K} = -111\ (\pm 10). \tag{2}$$

However, as to how the system's kinetics manage to maintain the observed linear proportionalities from such a reaction of CH for differing organics, and whether additional ionization channels also contribute, remain the unsolved puzzles to be addressed herein.

2. Recent developments in the analyses of radical behavior in hydrocarbon flames

Recently, using laser-induced fluorescence, measurements were made of the concentrations of CH, C_2 and OH, in a series of seven pre-mixed fuel-rich ($\phi = 1.2$, 1.6 and 2.0) laminar flat-front flames ($C_2H_2/O_2/N_2$) at atmospheric pressure by the author and his colleague [15]. Corresponding H-atom concentrations and temperatures also were monitored. As a function of downstream time from the narrow reaction zone, the CH and C_2 concentration profiles in the seven cases showed a striking resemblance, indicating some mutual interconnection. This was unexpected and not obviously explained as these two radicals have very dissimilar chemical natures and are very rapidly formed and destroyed at different rates by unconnected reactions. As a result, a detailed kinetic analysis was undertaken to examine, as a function of time, each of the major hydrocarbon species known to be present in such flames, namely, C, CH, CH_2, CH_3, CH_4, CHO, CHOH, CH_2O, CH_2OH, CH_3O, CH_3OH, C_2, C_2H, C_2H_2, CHCO, CH_2CO and C_2O. The analysis emphasized the

flame location 50–600 μs downstream from the reaction zone. This is the region where the CH and C_2 were observed. It was immediately apparent that this region reflected that of a hydrogen flame heavily seeded with CO and CO_2 and containing remaining traces of hydrocarbon species. The species H, OH, H_2, H_2O, O and O_2 formed an important controlling radical pool that was in partial equilibrium; the concentrations of each of the hydrocarbon radicals were minor to this pool and on a $\leqslant 1000$ parts per million by volume (ppmv) scale. The known reaction rates implied that the CH and C_2 were formed and destroyed on a time scale much less than a μs, as were also the other hydrocarbon species. As a result, such observed flame profiles as a function of downstream time reflect an extremely dynamic kinetic network and any one hydrocarbon species has but a brief existence and is changing and being reformulated extremely rapidly as long as non-oxidized carbon still exists. The hydrocarbon species all rapidly form steady-state distributions. However, with the exceptions of C, HCO, CHOH and CH_2O, which are being irreversibly oxidized to CO, the others almost instantly produce an interconnected radical pool of hydrocarbon species. Consequently, this hydrocarbon pool exists within the larger hydrogen/oxygen pool, which controls its distribution. In flames that are only slightly fuel rich ($\phi = 1.2$), the oxygen levels are still significant and oxidation reactions rapidly drain the hydrocarbon pool to completion. However, in richer flames, levels of oxygen become extremely low and the pool's life lengthens. With increasing equivalence ratios, as the onset of soot formation is approached, the pool becomes drained more slowly. This is no longer by oxidation but by hydrocarbon–hydrocarbon reactions that lead to the precursors to soot in the now heavily reducing H and H_2 burned gas environment of these fuel-rich flames. It is the existence of this hydrocarbon radical pool that provides the indirect coupling and interrelationship observed between CH and C_2. As the pool drains by radical oxidation or soot precursor growth, the CH and C_2 concentrations rapidly adjust and track each other. This type of behavior now has also been predicted theoretically and shown to be a natural general occurrence in systems with such short time scale constants [16].

This finding now is seen to be particularly relevant to the FID. The rapid destruction and oxidation in the reaction zone that spontaneously develops into such a hydrocarbon radical pool establishes the concept of the underlying simplicity that has always been implied. It now provides the insight needed to explain its specific mechanism.

3. The chemi-ionization mechanisms in fossil-fueled flames

Although a general consensus has always accepted Calcote's basic reaction (1) as the primary ionization step in flames [13,17], this has been by piecing together observations from numerous independent techniques, rather than a rigorous direct measure. Loose ends still

surround it. An extensive review in this journal by Fialkov [18] on ions in flames provides an introduction that will be extended herein with respect to the primary process. Chemi-ionizing reactions are not common. This is mainly as a result of their severe energy needs and also invariably due to competition from alternate additional neutral channels. It is for these reasons that the majority of the known cases involve oxide bond formation [19] and in the present FID case it is the HCO^+ ion that provides such a strong bond. This ion is isoelectronic with HCN and N_2 and so is thermally very stable. Its lowest energy dissociation channel to $CO + H^+$ requires $586\,kJ\,mol^{-1}$. Additionally, like HCN and N_2, it has no low-lying electronic states. Theoretical calculations, even though approximate, indicate the lowest $HCO^+(A^3A')$ state to have an excitation energy of at least $500\,kJ\,mol^{-1}$ [20–22].

The instant appeal of reaction (1) was that it satisfied exothermicity requirements, correct flame profile shapes and had the potential, as indicated by reaction (2), for producing by proton transfer to H_2O the subsequent H_3O^+ ion observed in flames. The chemi-ionizing reaction (1) was shown to be theoretically acceptable [23,24] and also to occur in simpler discharge flow systems [25–27]. The most direct study by Peeters and Vinckier [14], using a series of $CH_4/C_2H_4/O_2/Ar$ flames, showed that the saturation current correlated linearly with the integral of the product of the CH and O concentrations. Also, the rate constant so implied was of a reasonable magnitude. This was later repeated at room temperature in a simpler fast flow reactor with C_2H_2 and discharged O_2 that added further credence [28,29]. Also by applying an electric field, Vinckier et al. [30] had distinguished between the primary and secondary ions, concluding that the HCO^+ ion was the main primary ion. The low-temperature discharge flow studies also confirmed that the process had to have minimal activation energy.

Prompt NO formation in flames now is generally accepted as originating from the reaction between CH and N_2 [31]. However, even with this process it is currently being suggested that additional channels, such as the reactions of C_2O or CH_2 with N_2 may be needed for a complete description [32]. Nevertheless, it has been observed that both the concentrations of prompt NO in flames and the chemi-ionization levels are directly proportional to the quantity of carbon atoms present in the hydrocarbon pool [33–36]. This was suggested as support for the role of CH in the two different processes, but in fact may not be a rigorous argument. It is to be remembered that if hydrocarbon radicals are in a kinetically coupled pool, and linearly related, there can be a loss of exact species identity. In other words, CH, CH_2 and C_2O become kinetically indistinguishable in flames. As a result, the interpretation of flame data alone can be insufficient at times in effectively tying down exact mechanisms. H and OH radicals are often so linearly related in many fuel-rich flames. In such cases, mechanistic support for their individual roles has to be obtained from independent non-flame studies. That chemi-ionization in flames may result from reaction (1) was initially surmised primarily from the fact that it is one of exceedingly few energetically feasible reactions. It was this factor in itself that reduced somewhat the level of speculation and uncertainty.

Bascombe et al. [37] and Green and Sugden [38] had noted that the peak concentration of the H_3O^+ ion in their flames implied an approximate value of $k[A][B] = 5 \times 10^{15}$ molecule $cm^{-3}\,s^{-1}$ at 2300 K for the dominant chemi-ionizing reaction between any potential A and B species. Also, that this product had to be first order in C_2H_2 ruled out hydrocarbon radical–hydrocarbon radical reactions. This immediately implied, if the chemi-ionization reaction was kinetically efficient, that the concentrations of A and B could be as small as 1 ppmv each, further hinting that minor species were most likely involved. This condition alone has always imposed a necessary balance between concentrations and rate constant on any proposed alternate choice for the identities of either A or B in the chemi-ionization channel. Larger concentrations have to be offset by a very inefficient interaction. Although this appeared to potentially open the door to highly endothermic reactions, the rate of the chemi-ionization step was found to be insensitive to flame temperature, and proceeded also at room temperature, so necessarily was exothermic or close to thermal neutrality [13,26,39].

Questions that still remain tend to center more on whether the ionization, and possibly even NO formation, is specific only to the $CH(X^2\Pi)$ ground electronic state or whether contributions occur in flames from channels involving $CH(a^4\Sigma^-, A^2\Delta, B^2\Sigma^-)$. The likelihood of such possibilities for ionization is considered below. Moreover, although reaction (1) is satisfactory in general, it has been long known that C_2H_2 fuel appears to be exceptional and shows enhanced ionization implying possibly a second contributing mechanism [10,40].

4. The potential roles of $CH(a^4\Sigma^-, A^2\Delta, B^2\Sigma^-)$ electronically excited states

$CH(X^2\Pi)$ is formed and destroyed very rapidly in flames [15]. Its loss reactions are listed in Table 1. Their reaction rate constant values now are quite well established and indicate that reaction rates in flames are very significant. For illustration, the removal rates are listed for the various channels in an acetylene flame at about 2380 K. These imply a removal half-life in this slightly fuel-rich, atmospheric pressure, acetylene flame of only about 50 ns. This emphasizes the very dynamic kinetics that we know as combustion. Nevertheless, CH still manages to maintain a steady-state concentration on the order of 200 ppmv in and near the reaction zone of such a flame and its decay can be monitored for a fraction of a millisecond in some cases [15]. Consequently, even in such a dynamic formation/loss system, with relatively low O-atom concentrations and a small chemi-ionization rate constant (2.7×10^{-13} at 2000 K) it is possible to observe reasonable levels of ions.

Table 1
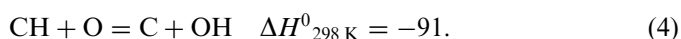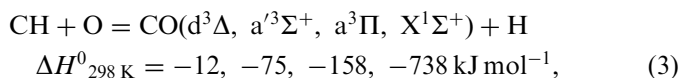Appropriate rate constants for CH removal reactions in flames [15,41,42]

Reaction	$\Delta H_{298\,K}$ kJ mol^{-1}	k^a cm^3 molecule^{-1} s^{-1}	T, K range	$k_{2000\,K}$	Removal rate (s^{-1})^b	Dominant channels	Notes
CH + N$_2$ = HCN + N^c	+12^e	6.0(−12)exp(−11060/T)	1000–4000	2.4(−14)	1.3(5)		Spin forbidden^e
= NCN + H^d	+95						$k(c+d)$
CH + CO$_2$ = CHO + CO	−270	1.1(−16)$T^{1.5}$ exp(360/T)	298–3500	1.2(−11)	4.3(6)	*	
CH + CO = C$_2$O + H	+114	3.1(−13)	2500–3500	3.1(−13)	7.9(4)		
CH + H$_2$O = CHOH + H^f	−36	7.6(−8)$T^{-1.42}$	298–1000	1.6(−12)	2.7(5)		$k(f+g)$
= CH$_2$ + OH^g	+75						
CH + H$_2$ = CH$_2$ + H	+13	2.9(−10)exp(−1670/T)	200–1000	1.3(−10)	4.8(6)	*	
CH + H = C + H$_2$	−97	2.0(−10)	1500–2500	2.0(−10)	3.9(6)	*	
CH + OH = CHO + H^h	−372	5(−11)	1000–2500	5(−11)	1.2(6)		$k(h+i+j)$ estimate
= C + H$_2$O^i	−158						
= CH$_2$ + O^j	+7						
CH + O$_2$ = CHO + O	−304	1.4(−10)	2200–3500	1.4(−10)	3.5(6)	*	Major only for $\phi = 1.2$
CH + O = CO + H	−738	6.6(−11)	298–2000	6.6(−11)	5.5(5)		
= C + OH	−91	2.5(−11)exp(−2380/T)?	1600–2000	7.6(−12)?	7.6(4)?		
= HCO$^+$ + e$^-$	−12	4.2(−13)exp(−850/T)	298–2500	2.7(−13)	2.4(3)		
CH + CH$_4$ = C$_2$H$_4$ + H	−251	2.2(−8)$T^{-0.94}$ exp(−29/T)	160–750	1.7(−11)	8.9(3)		
CH + C$_2$H$_2$ = C$_3$H$_2$ + H^l	+44	3.1(−10)exp(61/T)	200–700	3.2(−10)	2.0(5)		$k(l+m)$
= c−C$_3$H$_2$ + H^m	−130						

*Dominant channels in $\phi = 1.2$, 1.6, 2.0, C$_2$H$_2$/O$_2$/N$_2$ flames.
^{a}Read 6.0(−12) as 6.0×10^{-12}, and 1.3(5) as 1.3×10^5.
^{b}Illustrative values of removal rates, k[M] (where M is the reactant), at 0.2 ms downstream in an atmospheric pressure premixed flame at 2380 K, C$_2$H$_2$/O$_2$/N$_2$ (1.2/2.5/10 unburned gas volume ratios), assumes CH$_4$ and C$_2$H$_2$ concentrations of 200 ppmv [15]. The average collisional removal half-life for CH with all flame species is about 50–120 ns, respectively, at 0.2 ms in seven $\phi = 1.2$–2.0 acetylene flames [15].

For C$_2$H$_2$ ($\phi = 1.2$ to 1.6) flames, the fraction of the CH that channels to an ion is seen to be about 10^{-4}. This low efficiency arises partly from the O atom concentration (collisionally contributes about 3% to the total CH removal), but mainly from the additional internal branching ratio that is occurring within the CH + O reaction (only 0.5% producing electrons). As seen in Table 1, the alternate branching channels (3, 4) are exothermic, neutral, and dominate over chemi-ionization formation. Reaction (3) is kinetically quite efficient and also correlates theoretically to a variety of possible product states [43]:
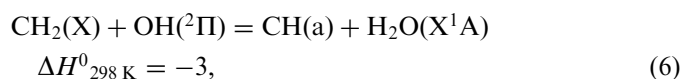
$$CH + O = CO(d^3\Delta,\ a'^3\Sigma^+,\ a^3\Pi,\ X^1\Sigma^+) + H$$
$$\Delta H^0_{298\,K} = -12,\ -75,\ -158,\ -738\,\text{kJ mol}^{-1}, \qquad (3)$$

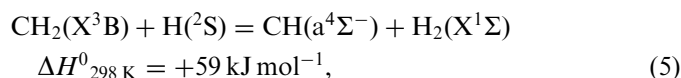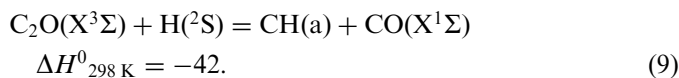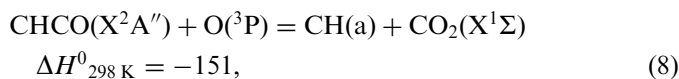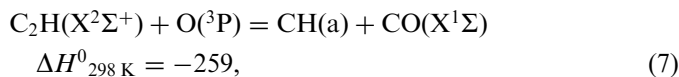$$CH + O = C + OH \quad \Delta H^0_{298\,K} = -91. \qquad (4)$$

As a result, any role by CH's electronically excited states in possibly modifying this fractional branching to ions obviously merits a detailed consideration.

4.1. CH($a^4\Sigma^-$)

The lowest-lying excited state of CH has ($a^4\Sigma^-$) symmetry and so is metastable having long collision-free radiative lifetimes of about 12 to 8 s for its $v = 0$ to 2 levels, respectively [44]. No optical spectral transitions have ever been observed, but its far infrared laser magnetic resonance spectrum has been reported [45]. Its

71.6 kJ mol^{-1} electronic excitation energy was established by laser photoelectron spectroscopy of CH$^-$ [46]. A purely thermal distribution would imply a ratio of about 1.4% for CH(a)/CH(X) in flames. CH(a), the spectroscopic abbreviation for CH($a^4\Sigma^-$), undoubtedly will be formed chemically in flames but necessarily at a rate reduced from that of CH(X). For example, the reactants CH$_2$ and H of reaction (5) can only channel to CH and H$_2$ products. From the measured rate constant value of 2×10^{-10} cm^3 molecule^{-1} s^{-1} (298–3000 K) for all product channels, this magnitude automatically implies that the dominant product must be CH(X) due to the necessary endothermicity for CH(a) production. The reaction of CH$_2$ and H is in fact the major source of CH(X) in flames. Consequently, any parallel branching to CH(a) by reaction (5) will be severely modified both by the adverse enthalpy needs and the now quartet nature of the transition. Of the other sources of CH(X) [15], that may also channel to the CH(a) state, reactions (6)–(9), these are similarly spin allowed but are on quartet surfaces with as yet unknown reactive efficiencies:

$$CH_2(X^3B) + H(^2S) = CH(a^4\Sigma^-) + H_2(X^1\Sigma)$$
$$\Delta H^0_{298\,K} = +59\,\text{kJ mol}^{-1}, \qquad (5)$$

$$CH_2(X) + OH(^2\Pi) = CH(a) + H_2O(X^1A)$$
$$\Delta H^0_{298\,K} = -3, \qquad (6)$$

$$C_2H(X^2\Sigma^+) + O(^3P) = CH(a) + CO(X^1\Sigma)$$
$$\Delta H^0{}_{298\,K} = -259, \tag{7}$$

$$CHCO(X^2A'') + O(^3P) = CH(a) + CO_2(X^1\Sigma)$$
$$\Delta H^0{}_{298\,K} = -151, \tag{8}$$

$$C_2O(X^3\Sigma) + H(^2S) = CH(a) + CO(X^1\Sigma)$$
$$\Delta H^0{}_{298\,K} = -42. \tag{9}$$

Of these, reactions (6)–(8) also should be remembered as being only one of possibly three or four alternate product channels with such reactants. For example, reaction (8) has been studied and found to have only a 6% overall efficiency in spite of its exothermicity for the branching to the combined $CH(a^4\Sigma^-$ and $X^2\Pi)$ states at room temperature [47]. As a result, formation rates of CH(a) will be significantly below those of CH(X).

The reactivity of CH(a) has only been studied at room temperature. The source used was multi-photon dissociation of $CHBr_3$, any CH(X) formed being scavenged by its quite rapid reaction with CH_4. In spite of its electronic energy, the high multiplicity of CH(a) decreases its reactivity in many cases. Rate constant values that are available were obtained and summarized by Hou and Bayes [48]. With closed shell singlet states such as CO, CO_2, H_2O, H_2, N_2, N_2O or CH_4 that are relevant to flames, any interaction has to occur on a quartet surface that in some cases may only couple to products via non-adiabatic spin-forbidden transitions. The only measured reactants displaying room temperature reactivity were with the multiplet state molecules $NO(X^2\Pi)$ and $O_2(X^3\Sigma)$. The latter has a rate constant of magnitude $2.6 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$. However, as seen above, the reverse of reactions (5) and (6) with H_2 and H_2O are exothermic or about thermoneutral and are potentially rapid and allowed reactive channels for CH(a) in flames. Liu et al. [49] did examine theoretically the reactive chemical quenching of CH(a) with H_2 (reaction (−5)) and predicted a rate constant at 2000 K of order $(1–5) \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$. That with CO, measured as 8×10^{-13} at room temperature is too large a value to relate to the endothermic reaction (−9) and most likely refers to physical electronic quenching of CH(a) to CH(X) [48]. This contention is supported by theory that indicates channels facilitated by a CHCO* intermediate complex [50,51]. Although not measured, correlation diagrams with H-atom indicate that CH(a) may be effectively converted to $C + H_2$. Also, whether H-atom can physically quench the CH(a) state via a CH_2 transition state remains unknown. Additionally, the CH(a) + O chemi-ionizing channel also has alternate branches that correlate to either $C(^1D) + OH$ ($\Delta H = -41\,kJ\,mol^{-1}$) or to $CO(A, I, d) + H$ ($\Delta H = -35$, -37, -84) [43].

Supporting evidence has been claimed for the existence of CH(a) in C_2H_2/O reaction cell studies using chemi-electron and chemi-ion spectral analysis methods. However, the interpretation of the chemi-electron energies remains vague but was related to reaction (10) in such systems [22]. It did positively identify reaction (1) and there appears to be little doubt that HCO^+ is the primary ion product:

$$CH(a^4\Sigma^-) + O(^3P) = HCO^+(X^1\Sigma) + e^-$$
$$\Delta H^0{}_{298\,K} = -84\,kJ\,mol^{-1}. \tag{10}$$
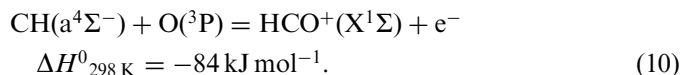
Although still somewhat uncertain, they did conclude that one of the chemi-electron bands could be assigned to reaction (10). The question remaining is whether this reaction plays any role in flames at about 2000 K. Currently, a reliable answer still is not available. The exact formation and loss rates remain unknown. If losses are limited mainly to reactions with H_2 ($k = 2.5 \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$) and O_2 (5×10^{-11}), this could imply a 10–100-fold longer-lived CH(a) species than for CH(X). Therefore, a steady-state concentration not too different from that of CH(X) might even be plausible from the combination of both slower formation and loss channels. Reaction (10) has been examined theoretically [23,24] and discussed further by Dyke et al. [22]. They suggest that a more detailed theoretical examination might expect a larger barrier in the entrance channel with CH(a) than with CH(X). Its multiplicity also can require some non-adiabatic coupling of states that will reduce its efficiency. The magnitude of the chemi-ionization rate constant, which is attributed to reaction (1), reflects an inefficient channel (Table 1). The value was derived from flame and flow studies and could actually refer to either state. Consequently, although uncertainties surround the actual concentrations of CH(a) relative to CH(X), there appears to be little reason to suppose any significant improvement in the branching ratio to the ion within the CH(a) + O reaction. More will be said later on this possibility but if the branching ratio was significantly higher, even a concentration of CH(a) in equilibrium with CH(X) might produce a competing flux. As a result, until these innumerable uncertainties are resolved or the concentration of CH(a) in flames is measured, although considered somewhat unlikely, it might be appropriate to rewrite the chemi-ionization reaction as reaction (11) and assume that CH(a) may be making an as yet unknown contribution:

$$CH(a,\ X) + O = HCO^+ + e^-$$
$$\Delta H^0{}_{298\,K} = -84,\ -12\,kJ\,mol^{-1}. \tag{11}$$
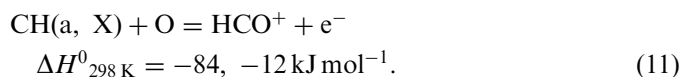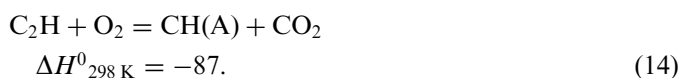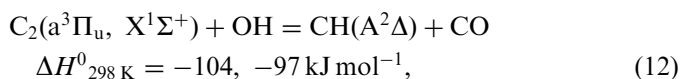
Presently, the rate constant listed in Table 1 for reaction (1) therefore more rigorously represents that for reaction (11).

4.2. CH($A^2\Delta$)

From the start of combustion science, chemi-luminescent reactions have been a curiosity. Due to their emissive nature they have found many uses. However, from the

viewpoint of basic flame chemistry they invariably constitute minor branching channels of low efficiency. As with chemi-ionization they are limited in number by the simple fact that they require energetically rich interactions. In flames, the $CH(A^2\Delta–X^2\Pi)$ blue chemi-luminescence with its strong 431 nm (0, 0) band is well known. CH(A) has a natural collision-free radiative lifetime of about 530 ns [52] and an electronic excitation energy of 277.2 kJ mol^{-1}. On examining all the known flame species and the energies of all their potential reactions it has been long realized that $CH(A^2\Delta)$ production is limited to only three possible formation channels:

$$C_2(a^3\Pi_u, X^1\Sigma^+) + OH = CH(A^2\Delta) + CO$$
$$\Delta H^0{}_{298\,K} = -104, \ -97 \, \text{kJ mol}^{-1}, \tag{12}$$

$$C_2H + O = CH(A) + CO$$
$$\Delta H^0{}_{298\,K} = -53, \tag{13}$$

$$C_2H + O_2 = CH(A) + CO_2$$
$$\Delta H^0{}_{298\,K} = -87. \tag{14}$$

Although reaction (12) was favored in earlier years [53], and apparently supported by flame studies of Porter et al. [54], Bulewicz et al. [55] and Peeters et al. [56], its role now is largely discounted for numerous reasons that have been presented and summarized by Devriendt and Peeters [57]. Previous arguments that it is the only reaction that can produce $CH(C^2\Sigma^+–X)$ chemi-luminescence (102.9 kJ mol^{-1} larger energy content than CH(A)) are no longer valid with current thermochemical values. As can be seen, reaction (14) will be but 16 kJ mol^{-1} endothermic to a CH(C) product and this is a negligible energy deficit at flame temperatures. The $C_2(X^1\Sigma^+)$ reactant in reaction (12) theoretically correlates only to CH(X), and it would probably be the very low-lying $C_2(a^3\Pi_u)$ state that would produce CH(C, B, A, a). The reaction can also have alternate product channels to $C_2O + H$, $C_2H + O$ and C + HCO.

The alternate reactions (13) and (14) were subsequently suggested by Hand and Kistiakowsky [58]. Reactions (12) and (14) obviously are complex interactions involving multi-bond rearrangements and for this reason alone are not expected to be efficient [59]. In addition, possibly moderating their efficiencies further, all of these reactions have three or four alternate product channels and of course can also produce CH in its lower or even higher electronic states.

Although some minor uncertainties still remain, the combination of modeling and specific measurements of the rate constants of reactions (13) and (14) now provides a reasonable understanding. It is an interesting example of the difficulties encountered in resolving even between three potential reactions! By modeling the measured CH(A–X) chemi-luminescent intensities in three low pressure (33/40 mbar, 25/30 Torr) pre-mixed CH$_4$/air flames ($\phi = 0.8$, 1.07, 1.28), Smith et al. [60] did show that

reaction (12) could not be making a noticeable contribution. By adding more data from a later study [61] examining CH$_4$/N$_2$O flames that have very different O$_2$/O ratios, they confirmed that both reactions (13) and (14) can contribute. Their relative importance is controlled by the specific O$_2$/O ratio. This had been surmised earlier by Matsuda et al. [62] in studies of the induction period of shock-heated C$_2$H$_2$/O$_2$/Ar mixtures, where they noted the less likely reaction (14) as being dominant.

Values for the rate constants, derived in simpler flow reactor systems, are $k_{13} = 2.4 \times 10^{-11} \exp(-230/T) \, \text{cm}^3$ molecule^{-1} s^{-1} in the 290–925 K range ($k_{2000\,K} = 2.1 \times 10^{-11}$) [57]. This is considered to be accurate to within a factor of two and the extrapolation to 2000 K is acceptable. The rate constant for reaction (14) has been reported in a recent pulsed laser photolysis study as $k_{14} = 1.0 \times 10^{-27} T^{4.4} \exp(1150/T)$, 316–837 K, $k_{2000\,K} = 5.9 \times 10^{-13} \, \text{cm}^3$ molecule^{-1} s^{-1} [63]. As stated therein, although the pronounced temperature dependence is well characterized within its measured range, the absolute rate constant at any specific temperature is accurate only to within an order of magnitude and extrapolation to 2000 K questionable. Nevertheless, although complex, this implied rate constant value at flame temperatures appears reasonable and is consistent with modeling [61]. Consequently, in stoichiometric or slightly rich CH$_4$/air flames that can have O$_2$/O ratios of about 20, this ratio can offset the difference in rate constants and both reactions (13) and (14) can contribute. However, reaction (13) will be dominant in CH$_4$/N$_2$O [61] or rich C$_2$H$_2$/O$_2$/N$_2$ flames [15], where this ratio falls below 4 and even below unity in the latter case.

In the present context, such finer points are somewhat irrelevant. The major issue here is the rate of formation of CH(A). The fact that it depends on the O and O$_2$ concentrations immediately implies that its formation rates have to be very limited compared to those of CH(X) in any stoichiometric or fuel rich condition.

It is now known that CH(A) is a very reactive species; its quenching rate constants for physical and chemical channels are listed in Table 2 for various flame reactants. These values are now quite reliably established. All the major flame species are seen to quench it with high efficiencies. As an illustration, the removal rates are listed for a $\phi = 1.2$ acetylene flame and imply values in this case 14-fold faster for CH(A) than for CH(X) under similar conditions. Such a figure represents a reasonable fraction of the total gas kinetic collision rate. Measurements of the lifetimes of CH(A) in several low-pressure CH$_4$/O$_2$/N$_2$ flames have been shown to be consistent with such a quenching database [70–72]. Their quoted quenching rates are smaller than for the acetylene example used here due to their reduced pressure flames.

This analysis therefore shows quite clearly that a chemi-ionization role for CH(A) in flames is rather unlikely under normal conditions. Not only is its rate of formation small but its loss rate can be huge implying a very small steady-state concentration. This conclusion is consistent with the

Table 2
Appropriate rate constants for CH(A$^2\Delta$) removal reactions in flames

| Reaction	$k\,cm^3\,molecule^{-1}\,s^{-1}$	T, K range	$k_{2000\,K}$	Quenching rate (s^{-1})[a,b]	References
CH(A) + N$_2$	$7.5(-17)T^{1.7}\exp(-520/T)$	300–2160	3.0(−11)	9.4(7)	[64]
CH(A) + CO$_2$	$4.0(-25)T^{4.3}\exp(+850/T)$	300–1800	9.6(−11)	5.5(7)	[65]
CH(A) + CO	$2.0(-10)\exp(-345/T)$	300–1300	1.7(−10)	4.4(7)	[66,67]
CH(A) + H$_2$O	$5.1(-12)T^{0.5}$	300–2160	2.3(−10)	5.2(7)	[64]
CH(A) + H$_2$	$6.7(-12)T^{0.5}\exp(-686/T)$	300–2160	2.1(−10)	9.1(6)	[64]
CH(A) + H	$1.7(-10)$	300	1.7(−10)	3.3(6)	[52]
CH(A) + OH	?			$\leqslant 1(7)$	Upper limit
CH(A) + O$_2$	$4.0(-18)T^{2.1}\exp(+870/T)$	300–1300	5.3(−11)	1.8(6)	[65]
CH(A) + O[c]	$\leqslant 2(-10)$	300	$\leqslant 2(-10)$	$\leqslant 1.7(6)$	[52]
CH(A) + CH$_4$	$3(-11)$	300	8(−11)	5.2(4)	[68]
CH(A) + C$_2$H$_2$	$1.6(-10)$	300	1.6(−10)	1.0(5)	[69]

[a]Illustrative values of the physical and/or chemical quenching rate at 0.2 ms downstream in an atmospheric pressure premixed flame, C$_2$H$_2$/O$_2$/N$_2$ (1.2/2.5/10 unburned gas volume ratios), assuming CH$_4$ and C$_2$H$_2$ concentrations of 200 ppmv [15].
[b]CH(A) collision-free radiative lifetime 530 ns [52] (1.9(6) s^{-1} rate).
[c]CH(A) + O = HCO$^+$ + e$^-$, $k = 1(-10)$ suggested (see text).

several quantitative assessments that have been published for the ratio of CH(X)/CH(A) in various flames. Joklik et al. [72] estimated this ratio to be about 1300 or larger in low-pressure acetylene/oxygen flames ($\phi = 0.6$ to 1.4) at 1800 K. Walsh et al. [73] in a diffusion CH$_4$/N$_2$ jet flame in air derived a 2000-fold estimate. More recent measurements and modeling studies in low-pressure methane flames indicate that this ratio can be as large as 10^5 with CH(A) concentrations being no more than $10^7\,cm^{-3}$ [61,74]. Consequently, this confirms the results obtained 40 years ago that the level of ionization in flames does not correlate in any way with CH(A) or the [CH(A)] [O] concentration product [75–78].
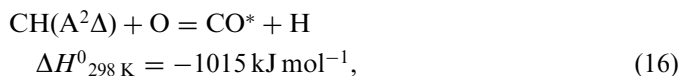
Nevertheless, the interest in a possible role for CH(A) was resurrected by the elegant measurements of Cool et al. [11,79]. Initially, by using a short pulse-length excimer-pumped tunable dye laser (4 ns), the individual CH(A–X) P$_{1dc}$(7) transition was saturated in absorption at 434.8 nm in reduced pressure CH$_4$ and C$_2$H$_4$ flames. Conditions were such that the pulse-length was shorter than the collision frequency. By scanning the laser over the entire (0, 0) band they recorded its absorption spectrum by monitoring the induced level of chemi-ionization. Previous studies of saturated laser-induced fluorescence have shown that such excitation wavelengths and power levels are non-perturbing and should not noticeably modify the carbon balance in the flame to produce additional CH [80,81], nor have any effect on the basic flame species such as the O atom concentrations. As a result there seems little doubt that their measurements confirmed in this simple manner that enhanced saturated levels of CH(A) did significantly enhance chemi-ionization. Extracting an accurate measure for a rate constant for reaction (15) from their data is difficult and necessarily approximate:

$$CH(A^2\Delta) + O(^3P) = HCO^+(X^1\Sigma) + e^-$$
$$\Delta H^0_{298\,K} = -289\,kJ\,mol^{-1}. \qquad (15)$$
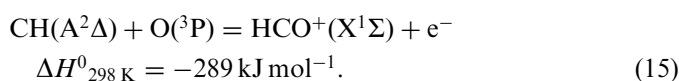
It is derived from an assessment of the onset limit of saturation and requires absolute concentrations of O atom and CH, total quenching rates for CH(A), and an estimate of the flame volume pulsed by the laser [79]. An approximate enhancement factor of 2000-fold was implied by the value obtained for k_{15} over that for the normal chemi-ionization reaction (1). Accepting the value in Table 1 for k_1 they suggested a value of $k_{15} = 8(\pm 6) \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$, essentially a gas kinetic collisional efficiency of unity. Additional work applying this concept to an FID [11] indicated that this may have been slightly too large an estimate. From the quenching rates of Table 2, the fraction of CH(A) removed by O atom in this flame is of the magnitude of about 2% of its total quenching. This is similar to the 3% or so seen for CH(X). Therefore, the observed enhancement has to result from a change in the internal branching within the CH + O reaction. Additionally, even under such saturation conditions only about 1% of the total CH is present as CH(A), yet the substantial effect was noted. This in itself implies and is consistent with a significant increase in the value for k_{15} over that of k_1. Because of the lack of low-lying states, reaction (15) necessarily has to produce HCO$^+$ in its ground state. This undoubtedly indicates, due to the minimal number of connecting surfaces, that non-adiabatic transitions will be involved with an expectation of some subsequent reduction in efficiency below that of a unit collisional rate. Consequently, accepting that the enhancement originates solely from reaction (15), the initially quoted estimate for k_{15} may be slightly too large. A magnitude of about $1 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$ might be more appropriate to accept for the present until it can be more accurately remeasured. The intriguing much enhanced branching ratio to the ion of reaction (15) rather than to neutrals has to relate in some manner to the more energetic nature of the reaction. It is unexpected and an

interesting observation that remains neither explained nor addressed theoretically.

The alternate neutral and competing branching channels of reaction (15), namely reactions (16) and (17) also are highly energetic:

$$CH(A^2\Delta) + O = CO^* + H$$
$$\Delta H^0_{298\,K} = -1015\,kJ\,mol^{-1}, \tag{16}$$

$$CH(A^2\Delta) + O = C + OH$$
$$\Delta H^0_{298\,K} = -369. \tag{17}$$

In fact, reaction (16) was considered as the possible source for the vacuum ultraviolet chemi-luminescence of CO from C_2H_2/O flow systems [82] that exhibit radiation down to 124.6 nm (960 kJ mol^{-1} excitation energy) [83]. However, the fact that a comparable chemi-luminescence could be reproduced in C_3O_2/O low-pressure reactive flows confirmed that it resulted predominantly from reaction (18) as initially suggested by Becker and Bayes [84–86] and not from reaction (16):

$$C_2O + O = CO^* + CO$$
$$\Delta H^0_{298\,K} = -851\,kJ\,mol^{-1}. \tag{18}$$
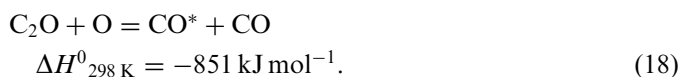
Reaction (18) now has been shown to be sufficient to populate all the singlet and triplet electronically excited states up to $CO(A^1\Pi)$ [87]. Whether reactions (16) or (17) occur to any degree or whether the chemi-ionization channel is totally dominant remains to be seen. It is clear though that the concentrations of CH(A) and CH(X) are much below those of C_2O in flames and their contribution to CO chemi-luminescence is minor.

Consequently, in spite of this noteworthy finding by Cool and Tjossem [79], conditions in flames are such that even the enhanced rate constant for chemi-ionization is more than offset by the normally encountered much lower steady-state concentrations of CH(A) that result from its reduced formation rate, high collisional quenching values and at reduced pressure its short radiative lifetime. As a result, this is why reaction (15) cannot contribute to flame ionization under normally encountered conditions in spite of its more significant branching ratio to the ion. In certain flames it may not be that much below such a contributing limit but its role remains negligible. Consequently, its early suggestion, although not borne out, did hold particular merit and has led to this most interesting observation of changes in the branching ratios for the CH + O reaction due to extra electronic reactant energy. This needs to be examined further theoretically.

4.3. CH(B²Σ⁻)

Arguments against any ionization roles for CH(B) follow the same logic as just outlined above for CH(A). The CH(B) state has a natural collision-free lifetime of about 330 ns [88] and an electronic excitation energy of 307.4 kJ mol^{-1}. Formation rates again are very limited
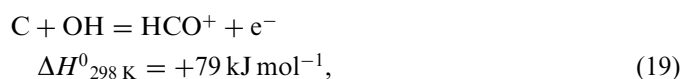
and similarly are by the corresponding reactions to (12)–(14). For a CH(B) product, these all remain exothermic with $\Delta H^0_{298\,K}$ values of −74, −67 for (12), and −23 and −57 kJ mol^{-1} for (13) and (14), respectively. Their rate constants are not known. However, collisional removal rates have been measured at room temperature for individual partners and for the overall rates in flames. These tend to reflect the reactive nature of CH(A), and CH(B) is efficiently quenched by the major flame species N_2, H_2O, CO and CO_2, and only at slightly lesser rates by H_2 and O_2 [68,89–91]. Rensberger et al. [92,93] noted that the overall quenching rate in low-pressure hydrocarbon flames was 70% faster for CH(B) than for CH(A) and at 1800 K had an overall rate constant of $2.5 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$. It was also noted that about 20% of this rate represented cross-relaxation from the B- to A-state [94]. Consequently, the concentration of CH(B) in flames will be even less than that of CH(A) and any chemi-ionization role is very unlikely.
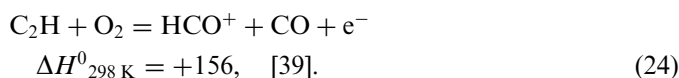
Similarly, although the corresponding study of saturated absorption but with CH(B) instead of CH(A) also showed a large enhancement of ionization [79], and a similar change in the nature of the branching ratio to ionization, it cannot contribute significantly to ion formation in normally encountered flames.

5. Other potential contributing primary ionization channels in fossil-fueled flames

From Calcote's early paper on the formation of ions in flames, published in the first volume of *Combustion & Flame* [95], there have been continuing hints of a secondary channel contributing to the chemi-ionization. This has been sustained by the apparently anomalous behavior of acetylene that produces about 30% more electrons per carbon than other hydrocarbon fuels. Otherwise, as stated by Miller [96] in his review, "the consistency of ion formation per carbon atom consumed in hydrocarbon flames regardless of temperature or fuel structure is impressive."

Calcote had noted that a hydrocarbon fuel was needed for ionization [9], and shock tube experiments had additionally shown that oxygen had to be present [97]. Consequently, that HCO^+ was the major primary ion was undisputed as was reaction (1). Discussions therefore centered only on the nature of any possible contributing channels or any role for electronically excited states of CH. Although several alternate reactions generally based on CH, C_2 or C_2H have been suggested over the years their energetics and need for electronic excitation in the reactant, coupled to a lack of any specific evidence, has always ended in their elimination. These include as examples reactions such as

$$C + OH = HCO^+ + e^-$$
$$\Delta H^0_{298\,K} = +79\,kJ\,mol^{-1}, \tag{19}$$

$$CH + O_2 = CHO_2^+ + e^-$$
$$\Delta H^0{}_{298\,K} = -7, \quad [18, 98], \tag{20}$$

$$C_2 + CH_3 = c\text{-}C_3H_3^+ + e^-$$
$$\Delta H^0{}_{298\,K} = +106, \quad [22], \tag{21}$$

$$C_2 + O_2 = CO^+ + CO + e^-$$
$$\Delta H^0{}_{298\,K} = +309, \quad [78], \tag{22}$$

$$C_2 + O = C_2O^+ + e^-$$
$$\Delta H^0{}_{298\,K} = +360, \quad [96, 99], \tag{23}$$

$$C_2H + O_2 = HCO^+ + CO + e^-$$
$$\Delta H^0{}_{298\,K} = +156, \quad [39]. \tag{24}$$
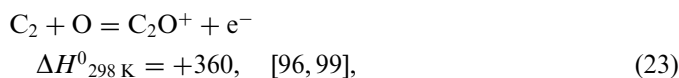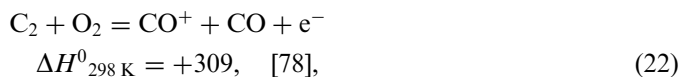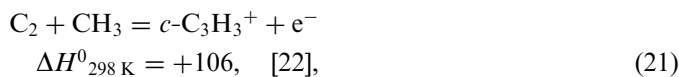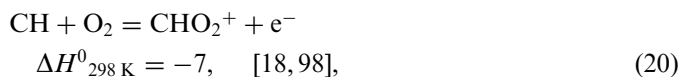
Reaction (19) seems not to have been suggested previously. Although recently identified as a species irreversibly exiting from the hydrocarbon radical pool that forms in flames, the C atom still has a steady-state concentration that reflects the concentration of CH [15]. OH does not have the variation of concentration range of O atom in rich flames but does have a higher concentration to compensate for the adverse reaction enthalpy and so could retain a reasonable reaction flux. However, the need for a somewhat energy neutral reaction rules out many such suggestions quickly. In addition, even if such reactions could contribute, these are of little use in explaining the different behavior of acetylene.

The reaction most discussed in that regard as the possible secondary ionizing channel is reaction (25) with either CH(B) or CH(A) electronically excited states [100,101]:

$$CH(B, A) + C_2H_2 = c\text{-}C_3H_3^+ + e^-$$
$$\Delta H^0{}_{298\,K} = -56, \; -25\,\text{kJ mol}^{-1}. \tag{25}$$
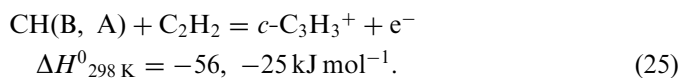
This was first suggested by Knewstubb and Sugden [102] in 1958 after noting that $C_3H_3^+$ was a major flame ion. Soon after, it became apparent from shock tube and flame studies that this reaction could play at the most only a very minor role [75,76,103–106]. Nevertheless, Hayhurst and collaborators [101,107,108] have at least until 1987 continued to espouse a contributing role for it in fairly fuel-rich flames (sooting) with [C]/[O] > 0.9. Its second-order nature with respect to C_2H_2 might be acceptable if it were indeed only minor [104]. Now, the latest evidence for its final elimination is reported in the study by Cool and Tjossem [79]. This involved the laser saturated absorption of CH to these two electronically excited states in methane and ethylene flames. The $CH_4/O_2/Ar$ and $C_2H_4/O_2/Ar$ low-pressure flames examined in their study were known to have differing C_2H_2 concentrations in their flame front regions. However, a comparison of their relative ionization levels, that appeared to be similar, ruled out altogether any role for reaction (25) as a source of ions even under saturated absorption conditions that significantly enhanced the levels of CH(A, B). Under normal flame conditions, the steady-state concentrations of CH(B) or CH(A) are much smaller and rates for reaction (25) will be well below the threshold for any contribution.
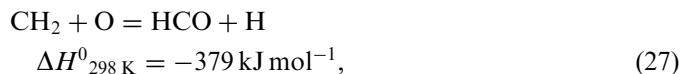
Consequently, it does not appear that any of the previous suggestions can provide any alternate chemi-ionization mechanism in the FID. There is nothing to challenge reaction (1) as the dominant chemi-ionization channel nor be a plausible candidate reaction to support the presence of a secondary channel in the case of acetylene fuel. Consequently, the most appealing proposal is that made by Miller [96] 30 years ago. He suggested the possibility that C_2H_2 is unique and oxidizes differently in flames from other hydrocarbons and simply produces a higher level of CH radicals. This concept and further evidence for it will be outlined below.

6. Aspects of the CH + O reaction dynamics

The basic interaction of CH with O atom to form an HCO transition state is extremely energy rich as indicated by the reaction:

$$CH + O = HCO(X^2A')$$
$$\Delta H^0{}_{298\,K} = -802\,\text{kJ mol}^{-1}. \tag{26}$$
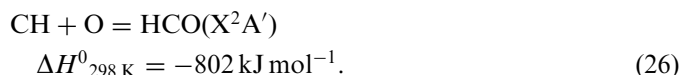
This reaction energy has the potential to produce excited states of HCO^*, by collisional stabilization, up to and above its ionization potential of about $790\,\text{kJ mol}^{-1}$. Such an energy corresponds to a spectral emission of about 150 nm and so is far more energetic than required for the documented chemi-luminescent Vaidya band emission of HCO in flames in the 250–410 nm range [109,110]. Moreover, studies to establish the most probable excitation mechanism for HCO* chemi-luminescence do not rule out reaction (26) completely but instead suggest reactions (27) and (28), respectively [111,112]:

$$CH_2 + O = HCO + H$$
$$\Delta H^0{}_{298\,K} = -379\,\text{kJ mol}^{-1}, \tag{27}$$

$$CHCO + O = HCO + CO$$
$$\Delta H^0{}_{298\,K} = -493. \tag{28}$$

Metropoulos and Mavridis [23] and Metropoulos [24] have estimated the surfaces for reaction (26) in this high-energy range and have illustrated the complexity. The dispensation of such energy is most intriguing as the chemi-ionization channel to HCO^+, which is close to being resonant in energy with the reactants, has the very low collisional efficiency of only about 0.02%. The dominant channel, which is quite efficient, is dissociation to various states of CO and H products (Table 1 and reaction (3)). Nevertheless, as already mentioned, it is reaction (18)), the reaction of C_2O with O atom, and not this channel to CO and H (reaction (3)) that is the major source of electronically excited CO in flames. This is interesting in that reaction (3) is highly exothermic ($738\,\text{kJ mol}^{-1}$) and kinetically efficient. It has the ability to produce CO up

to its $d^3\Delta$ excited state and most probably does. Consequently, the observation implies that the C_2O species in flames must have a more significant concentration than CH to minimize the contribution of reaction (3) to the CO chemi-luminescence. Not generally included in previous chemical models [42,113] or kinetic rate date evaluations for combustion modeling [41], it is now becoming apparent that the C_2O radical requires more consideration. It was in fact included in a recent model by Smith et al. [74].

As outlined in detail already, there now appears to be no doubt for the CH(B,A) states that the branching ratios for their reactions with O atom significantly change from that of CH(X). Elevating the available reaction energy in this manner above the threshold for chemi-ionization to HCO^+ appears to significantly enhance ionization such that it becomes the dominant reactive channel. As a result, it might be plausible to consider whether the corresponding chemi-ionization reaction with CH(a) might also reflect this behavior. Its $71.6\,kJ\,mol^{-1}$ of electronic excitation now elevates the reactive energy to about $84\,kJ\,mol^{-1}$ above the threshold for HCO^+ formation. However, a corresponding enhancement in the ionization branching channel of two orders of magnitude or so might even go unnoticed if CH(a) has only its equilibrium population with respect to CH(X). Therefore, depending on the still uncertain steady-state levels of CH(a) and this possible enhancement factor, some role of CH(a) in chemi-ionization cannot be fully ruled out.

To add further to this discourse on the interaction between CH and O, both in FID observations [114–116] and also in a discharge flow system involving C_2H_2/O [28], a curious enhancement of ionization has been reported that remains difficult to explain. In the flow system, typical pressures were 4 mbar (3 Torr) He, and 4 µbar (3 milliTorr) each of C_2H_2 and O atoms. On replacing some of the helium with an equivalent pressure ($\leqslant 0.13$ mbar (100 mTorr)) of a non-reactive gas, a significant enhancement in ionization occurred. In other words replacing the helium with only 1 or 2 percent of CF_4, CO_2, N_2, CO or Ar, for example, produced a linearly increasing level of ionization with additive concentration. The relative magnitude of the effect was largest for CF_4 and the smallest for Ar. Similar effects were recorded in the FID with these species but indicated some slight differences in the specific ordering of their relative effectiveness. Its occurrence in the two very different experimental systems tended to rule out any flow artifact and pointed to the chemistry [117]. The flow study [28] measured both the level of ionization using the saturated current method and also the intensity of the vacuum ultraviolet chemi-luminescence due to CO. The two quantities were seen to be linearly dependent on C_2H_2 concentration and clearly illustrated that the two processes had close mechanistic similarities. The ionization results from $CH + O$ (reaction 1) and the chemi-luminescence from $C_2O + O$ (reaction 18). Their linear relationship again can only stem from their being present in the same pool of connected radicals. The enhancement effects, seen also to a

different degree with the chemi-luminescent emission have to imply that reaction complexes are initially formed that can be collisionally conditioned. In the case of the FID, collision-induced ionization becomes favored, and energy transfer occurs in the case of the CO chemi-luminescence. These observed effects need further study and obviously convey details of the chemi-ionization dynamics.

7. The FID's carbon counting ability

Very soon after its development, it was realized that not only was the FID a sensitive detector of organic materials, linear with concentration over a significant range, but also that it related in a pronounced manner to specific carbon content. The instrument became known as an effective carbon counter especially for hydrocarbons. Although not understood, it was realized that the electron precursor was generated with essentially a constant efficiency per carbon atom, independent of the hydrocarbon injected into the hydrogen diffusion flame of the FID. Estimates for the ion yield of propane in an FID were constant and measured as 2.5×10^{-6}/carbon input over four orders of magnitude change in the propane addition rate [40]. In other studies of a $\phi = 1.1$, $H_2/O_2/N_2$ flame, Peeters et al. [56] noted this yield as about 2×10^{-6} for injections of numerous different hydrocarbons. Shock tube studies of $C_2H_2/O_2/Ar$ and $CH_4/O_2/Ar$ at several equivalence ratios and temperatures quoted values of 2×10^{-6} to 1×10^{-8} [105], and 6.3×10^{-6} [118], respectively. Such observations led to a flurry of studies tabulating the exact relative response factors per unit carbon with FIDs for all categories of hydrocarbons and many other organic groupings. As an illustration of this remarkable consistent behavior, Table 3 lists the relative molar responses for a wide range of C/H/O organic structures in an FID. Additional values for long lists of other molecules can be found in additional references that are not included in the table [134–139]. Measurements with hydrocarbon samples immediately indicated the strikingly similar values for all alkanes, alkenes, aromatics and polycyclic aromatic hydrocarbons irrespective of their specific structures. Such responses require great care in measurement and any variations from the effective number of carbons in a structure tended to be more measurement error than real divergences. Acetylene, however, was seen to be exceptional and generally counted as about 1.3/carbon. In other words, three acetylene molecules (7.8 carbon count) were not equivalent to one of benzene (a 6 carbon count). Consequently, with this exception, the fact that a very different range of hydrocarbon structures can produce a corresponding level of CH per carbon atom has to convey significant implications for hydrocarbon combustion chemistry.

As seen further in Table 3, partially oxidized organics fall into different categories depending on their structure. The factor that is immediately apparent is that the presence of one oxygen atom in a structure such as for ketones, aldehydes or ethers lowers the apparent carbon count by

Table 3
Measured FID relative molar response factors for a range of organic (C/H/O) molecules of differing structures

Structure	Molecule	Formula	Structure	Effective FID carbon number	Non-contributing carbons	References
Alkanes	Ethane	C_2H_6	CH_3CH_3	1.97	0	[40,119,120]
	n-Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	5.04	0	[40,119]
	i-Pentane	C_5H_{12}	$(CH_3)_2CHCH_2CH_3$	4.99	0	[40,119]
	n-Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	6.10	0	[40,119,121]
	2,2-Dimethylbutane	C_6H_{14}	$(CH_3)_3C\ CH_2CH_3$	6.13	0	[40]
	Methylcyclopentane	C_6H_{12}	c-$C_5H_9CH_3$	5.93	0	[40]
	Cyclohexane	C_6H_{12}	c-C_6H_{12}	6.04	0	[40]
	n-Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	7.83	0	[122]
	n-Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	10.05	0	[122]
Alkenes	Ethylene	C_2H_4	CH_2CH_2	1.99	0	[40,120,123]
	1-Butene	C_4H_8	$CH_2CHCH_2CH_3$	4.00	0	[121]
	2-Methylpentene	C_6H_{12}	$CH_2C(CH_3)C_3H_7$	5.76?	0	[40]
	Cyclohexene	C_6H_{10}	c-C_6H_{10}	5.61?	0	[40]
	1,3-Butadiene	C_4H_6	$CH_2CHCHCH_2$	4.00	0	[121]
Alkynes	Acetylene	C_2H_2	$CHCH$	2.2–2.6[a]	−(0.2–0.6)	[40,121]
	Methylacetylene	C_3H_4	CH_3CCH	$\approx$3.4?[a]	−(0.4)	[10]
	Ethylacetylene	C_4H_6	C_2H_5CCH	$\approx$4.0	0	[10]
	Diphenylacetylene	$C_{14}H_{10}$	$C_6H_5CCC_6H_5$	12.77?	1.2?	[123]
Aromatic hydrocarbons	Benzene	C_6H_6	c-C_6H_6	6.00	0	[40,119,121]
	Toluene	C_7H_8	$C_6H_5CH_3$	7.00	0	[40,119]
	1,2,4-Trimethylbenzene	C_9H_{12}	$C_6H_3(CH_3)_3$	9.09	0	[124]
	Naphthalene	$C_{10}H_8$	$C_{10}H_8$	10.01	0	[123]
	Biphenyl	$C_{12}H_{10}$	$C_6H_5C_6H_5$	11.79	0	[123]
	Bibenzyl	$C_{14}H_{14}$	$C_6H_5CH_2CH_2C_6H_5$	14.11	0	[123]
Ketones	Acetone	C_3H_6O	CH_3COCH_3	2.03	1	[40,123]
	2-Butanone	C_4H_8O	$CH_3COC_2H_5$	3.18	1	[40,122]
	i-Butylmethylketone	$C_6H_{12}O$	$(CH_3)_2CHCH_2COCH_3$	4.97	1	[123]
	2-Hexanone	$C_6H_{12}O$	$CH_3COC_4H_9$	4.99	1	[122,124]
	c-Hexanone	$C_6H_{10}O$	c-$C_6H_{10}(=O)$	5.04	1	[123,124]
	3-Methylcyclopentanone	$C_6H_{10}O$	c-$(CH_3)C_5H_7(=O)$	5.00	1	[124]
	Acetophenone	C_8H_8O	$C_6H_5COCH_3$	7.13	1	[124]
	2,3-Pentadione	$C_5H_8O_2$	$CH_3COCOC_2H_5$	3.69?	1.3?	[125]
	2,4-Pentadione	$C_5H_8O_2$	$CH_3COCH_2COCH_3$	3.38	1.6	[125]
	1,4-Naphthoquinone	$C_{10}H_6O_2$	$C_{10}H_6(=O)_2$	8.34	1.7	[124]
Aldehydes	Formaldehyde	CH_2O	$HCHO$	0.0	1	[126]
	Butanal	C_4H_8O	C_3H_7CHO	3.04	1	[123,125]
	i-Butanal	C_4H_8O	$(CH_3)_2CHCHO$	2.83	1	[40]
	Octanal	$C_8H_{16}O$	$C_7H_{15}CHO$	6.99	1	[123]
Ethers	Diethylether	$C_4H_{10}O$	$C_2H_5OC_2H_5$	3.00	1	[40]
	i-Propylether	$C_6H_{10}O$	$((CH_3)_2CH)_2O$	5.01	1	[40]
	c-Trimethylene oxide	C_3H_6O	c-$(CH_2)_3O$	1.99	1	[126]
	2,3-Benzofuran	C_8H_6O	C_8H_6O	7.01	1	[124]
	1,4-Dioxane	$C_4H_8O_2$	c-$O(CH_2)_4O$	2.2	2	[125]
	Diethyleneglycol	$C_4H_{10}O_3$	$O(CH_2CH_2OH)_2$	1.9	2.1	[125]
Alcohols Primary	Methanol	CH_4O	CH_3OH	0.52	0.5	[123]
	Ethanol	C_2H_6O	C_2H_5OH	1.59	0.5	[40,123]
	Propanol	C_3H_8O	C_3H_7OH	2.48	0.5	[40,122,123]
	i-Butanol	$C_4H_{10}O$	$(CH_3)_2CHCH_2OH$	3.59	0.5	[40]
	Hexanol	$C_6H_{14}O$	$C_6H_{13}OH$	5.41	0.5	[122]
	Ethylene glycol	$C_2H_6O_2$	$HOCH_2CH_2OH$	1.10	1	[127]
Secondary	*i*-Propanol	C_3H_8O	$(CH_3)_2CHOH$	2.22	0.8	[40,123]
	2-Butanol	$C_4H_{10}O$	$CH_3CH(OH)C_2H_5$	3.36	0.6	[40]
	2-Hexanol	$C_6H_{14}O$	$CH_3CH(OH)C_4H_9$	5.32	0.7	[124]
Tertiary	*tert*-Butanol	$C_4H_{10}O$	$(CH_3)_3COH$	3.78?	0.2	[40]
	Phenol	C_6H_6O	C_6H_5OH	5.21	0.8	[124]
	1-Naphthol	$C_{10}H_8O$	$C_{10}H_7OH$	9.06	0.9	[124]
	Catechol	$C_6H_6O_2$	$1,2$-$C_6H_4(OH)_2$	4.94	1	[124]

Table 3 (continued)

Structure	Molecule	Formula	Structure	Effective FID carbon number	Non-contributing carbons	References
Acids	Formic acid	CH_2O_2	HCOOH	0	1	[128]
	Acetic acid	$C_2H_4O_2$	CH_3COOH	1.01	1	[123]
	Hexanoic acid	$C_6H_{12}O_2$	$C_5H_{11}COOH$	5.11	1	[123]
Esters	Methyl formate	$C_2H_4O_2$	$HCOOCH_3$	0.87	1.1	[129]
	Ethyl formate	$C_3H_6O_2$	$HCOOC_2H_5$	1.79	1.2	[129]
	Methyl acetate	$C_3H_6O_2$	CH_3COOCH_3	1.57	1.5?	[129]
	Ethyl acetate	$C_4H_8O_2$	$CH_3COOC_2H_5$	2.62	1.5?	[40,123,124,129,130]
	n-Propyl acetate	$C_5H_{10}O_2$	$CH_3COOC_3H_7$	3.80?	1.5?	[40,124,125]
	Methyl propionate	$C_4H_8O_2$	$C_2H_5COOCH_3$	2.49	1.5	[127,129]
	Ethyl propionate	$C_5H_{10}O_2$	$C_2H_5COOC_2H_5$	3.5[b]	1.5	[129,130]
	Methyl butyrate	$C_5H_{10}O_2$	$C_3H_7COOCH_3$	3.55	1.5	[129]
	n-Propyl propionate	$C_6H_{12}O_2$	$C_2H_5COOC_3H_7$	4.63	1.5	[129]
	i-Butyl acetate	$C_6H_{12}O_2$	$CH_3COOCH_2CH(CH_3)_2$	4.57	1.5	[40,128]
Double esters	Dimethyl oxalate	$C_4H_6O_4$	$(-COOCH_3)_2$	1.26	2.7	[125,131]
	Diethyl oxalate	$C_6H_{10}O_4$	$(-COOC2H_5)_2$	3.46	2.5	[125,131]
	Dimethyl succinate	$C_6H_{10}O_4$	$(-CH_2COOCH_3)_2$	3.33	2.7	[125,131,132]
	Diethyl succinate	$C_8H_{14}O_4$	$(-CH_2COOC_2H_5)_2$	5.43	2.6	[125,131]
	Dibutyl maleate	$C_{12}H_{20}O_4$	$(=CHCOOC_4H_9)_2$	9.5[b]	2.5	[133]

[a] Exceptional enhanced value.
[b] Estimated value.

one. The C=O structure is retained in combustion, not permitting the carbon to enter into any radical chemistry. It behaves as though it is already oxidized to CO and hence to CO_2. That ethers behave similarly suggests that these proceed in combustion via an aldehyde intermediate that contains the required C=O and not via an alkoxy (RO) grouping. This is true for aromatic structures as well as for aliphatic. As seen in Table 3, although combustion of double ethers such as dioxane adhere to this breakdown, double ketones like diones and quinones may introduce alternate branching channels as slightly less than the expected two carbons are ineffective. The single bonded oxygen in alcohols behaves differently. With primary alcohols it consistently shows close to a reduction of one-half of a carbon. Obviously branching occurs whereby the C–OH carbon partly exhibits its oxidized nature and partly participates in the hydrocarbon radical pool. This branching ratio modifies in secondary alcohols losing about three-quarters of a carbon to pre-oxidation. The behavior of tertiary alcohols remains unclear. In the case of aliphatic t-butanol, if values are reliable, the presence of the oxygen appears to have minimal effect on the carbon structure. However, for aromatics such as phenol, the oxygen is very effective at staying linked to a carbon so that it has a five-carbon count. This may relate to the relative ease with which each of these structures can modify to have a C=O intermediate structure and so tie up the adjacent carbon. If there are two oxygens in a structure as in esters (RCOOR′) the number of effective carbons contributing to the ionization is quite consistently reduced by about one and a half. The oxygens behave as ketonic and alcoholic and so have difficulty in producing CO_2 directly. Organic acids have one oxidized carbon as might be expected but this seems to carry somewhat also into formate esters. Other esters are surprisingly similar and must have corresponding breakdown mechanisms that effectively leave one and a half carbons of the structure as essentially pre-oxidized. Double esters are intriguing in showing a specific pattern of 2.5–2.7 pre-oxidized carbons and not quite the three expected from two separate single esters. Such behavior has to be a reflection of the primary combustion breakdown mechanism and a clear indicator of whether a specific carbon is participated in producing CH or not. As a result, it is clear that particular organic classes of structure indicate a significant commonality in their combustion channels.

The fact that this is not solely a behavior specific to the FID configuration was dispelled by low-pressure pre-mixed flame studies. Bulewicz and Padley [10] examined 29 different organic fuels measuring their relative trends in total ionization levels. These followed the same patterns of carbon atom counting as noted in Table 3. They confirmed the exceptional behavior of acetylene but differing from the FID studies they also examined the unknown ionization behavior of methyl acetylene (CH_3CCH) and ethyl acetylene (C_2H_5CCH). This was particularly noteworthy by illustrating that unsubstituted acetylene was unique. On introducing a degree of saturation into its structure by substitution, the anomalous behavior decreased significantly for methyl-substitution, and disappeared altogether for ethyl substitution. In fact, per carbon atom, the response for methyl acetylene was not too dissimilar from those of C_2H_4 or C_6H_6. Ethyl acetylene (C_4H_6) was seen to be identical to butadiene (C_4H_6). Their results help to

isolate C_2H_2 as a unique case and support also the argument for only one dominant chemi-ionization reaction for all the other organic molecules.

It now appears that the implications of this extensive body of data relating to this remarkable behavior in the FID and in low-pressure flames has been overlooked and forgotten. These same structural observations now are being rediscovered but with respect to the kinetic modeling of oxygenated fuels and their soot formation tendencies [140–143]. This eerie similarity [140] between ionization and soot formation, and even prompt NO, indicates a somewhat unexpected relationship that provides additional confirmation for the recently reported suggestion that the formation of a hydrocarbon pool of radicals is formed quite generally in such flames [15]. Now, with the new level of understanding, this connection between the three processes of chemi-ionization, soot formation tendency, and prompt NO formation is seen to originate from their parallel dependences on the extent of free unburned carbon. The ionization and prompt NO result from the CH concentration in the hydrocarbon radical pool and the soot relates to all the interconnected unburned hydrocarbon radicals in the same pool. The interesting corollary of this loose and indirect connection between ionization and soot formation is that it in essence shows that not only CH, but also all of the other hydrocarbon species in the radical pool, might be said to be equally important precursor species in soot formation!

Over the years, two opposing views of soot formation, namely the ionic [144] and the free radical mechanisms [145,146] have given rise to controversy. Whether a direct link between ionization and soot formation does occur is beyond the scope of the present discussion. However, the indirect connection between the two, as discussed above, may be very relevant. In such kinetic relationships a false impression can easily arise that two processes are directly connected whereas it is due simply to an aspect that is common to both.

8. The mechanism that explains the FID's performance and its connection to soot formation tendencies

The "equal per carbon response" of the FID has posed severe difficulties in previous attempts to derive a kinetic model for the functioning mechanisms. The observations demand a general scheme that on burning a hydrocarbon can produce amounts of CH proportional to the number of carbons in its structure whether it be a saturated or unsaturated aliphatic, or aromatic in nature. Furthermore it also has to extrapolate and explain the behaviors of other organic compounds. For example, why ketones, aldehydes or ethers appear to have one carbon in their structure that is ineffective in producing CH, and why primary alcohols reflect an apparent deficit of one-half of a carbon. Blades [120] initially summarized the difficulties relating to early suggested concepts such as that based on pyrolysis with cracking and stripping in the hydrogen-rich pre-heating

zone of a flame, or alternatively one accepting some kind of oxidative degradation. Several years later, as mentioned earlier, Hayhurst and Vince [33,34] noted in a series of premixed laminar flames that 'prompt' NO formation and hydrocarbon-induced chemi-ionization both were similarly dependent on CH and the number of carbon atoms in a hydrocarbon fuel. This was a noteworthy observation confirming to some degree that both processes are pivotal on the CH radical. It was also very intriguing in that these are not parallel processes in that 'prompt' NO formation depends on reaction with N_2, while chemi-ionization requires reaction with an O-atom. Consequently, they can be occurring in different regions of the flame, either pre- or post-combustion. They extended the concept of H-cracking in the pre-heat zone and suggested the establishment of a partial equilibration between CH_3, CH_2, CH and C radicals forming a limited pool of these before any major onset of oxidation. Such a pool was required to form with 100% conversion before combustion. Thereafter the CH maintained linearity during combustion. This concept was pursued further by Nicholson [147] for the FID diffusion flame mode. He showed that the kinetics were in fact sufficiently rapid for alkanes. However, with C_2H_4 and C_2H_2, for example, difficulties arose as these do not easily degrade quantitatively to CH_4. More recently, Holm et al. [148–150] have reiterated that pyrolysis in the hydrogen environment prior to combustion would reduce hydrocarbons to CH_4. However, the experiments of Wagner et al. [151] tended to rule out all such suggestions. They interchanged the flows of an FID, having instead an O_2 jet, containing the additive, flowing into an environment of H_2 that entered the detector cell with combustion at the diffusion interface. Consequently, the trace additive went in one case from being in its normal hydrogen-rich environment to one having an oxygen-rich condition prior to combustion. In this latter case, although sensitivities were reduced, the equal per carbon response remained the same for numerous alkanes and also showed the behavior expected with an ether. This simple experiment immediately implied that the exact mechanism had to involve also the combustion zone and the burned flame gases directly, rather than having a dependence on a pre-heating hydrogenation or cracking mechanism. There is little doubt that such pre-heating modifications will occur to some degree with any organic compound prior to combustion. However, their contribution is not important or relevant and cannot be the controlling fundamental mechanism that locks the available carbon into a more complex coupled reaction network wherein the level of CH is prescribed solely by the amount of combustible carbon and the flame parameters [15].

A number of combustion studies on soot formation have used ^{13}C or ^{14}C labeling. These can now be seen to also have a direct bearing on the FID's mechanism. Ever since the 50-year-old pioneering papers of Ferguson [152,153] with ^{13}C-labeled acetylene and propane, it has been accepted that such hydrocarbon structures are rapidly

fragmented in the initial stages of oxidation in the reaction zone. The carbon atoms lose their specific identity. This early work was extended later by Homan and Robbins [154] with ^{14}C labeling. In both diesel engine and laminar wick diffusion flame measurements using #2 diesel fuel, they concluded that all the carbon atoms in the fuel could contribute equally to the soot formed. Baumgartner et al. [155] also examined soot formation in pre-mixed flames burning a wide variety of hydrocarbon fuels. For the same temperatures, structural effects were found not to be a basic factor in the chemistry of hydrocarbons. However, with partially oxidized fuels such as ethanol-1-^{14}C and -2-^{14}C, Lieb and Roblee [156] showed that in diffusion flames, soot is preferentially formed from the non-hydroxy-carbon. Schmieder [140] confirmed the same pattern of behavior with regard to the presence of oxygen in organic structures that had been reported for ionization in the FID many years earlier but now with respect to soot formation. This similarity between the two unrelated and unconnected topics appears to have gone unnoticed. Namely, that carbon doubly-bonded to oxygen plays neither a role in chemi-ionization nor soot formation, and hydroxylated carbon (–COH) counts essentially as a half a carbon. The carbons in benzene, toluene or *c*-hexane are essentially equivalent. Sorek and Anderson [157,158] confirmed this but used a mixture of fuels. Their most insightful experiment was with ^{14}C-labeled CH$_3$OH in a mixture with unlabeled toluene. CH$_3$OH is known to have great difficulty in forming soot, but burned in such a mixture its carbons also were found in the soot product. Recent studies [142,143] have similarly labeled various carbons in the oxygenated fuel dibutyl maleate ($=$CHCOOC$_4$H$_9$)$_2$ in an attempt to unravel its primary combustion channels. To a significant degree their results reflect those predicted by the FID response factor measurements in Table 3. However, their conclusion that CO$_2$ is a primary product is not fully compatible with FID measurements. As noted in Table 3, two and a half carbons in its structure avoid the unburned carbon radical pool which means that some butyl alcohol must result from the ester breakdown.

In the present context, it is certainly apparent for the conditions within the FID, that total breakdown, oxidation and redistribution will be very rapid. The kinetics are extremely fast and CH will establish itself as a member of the pool of radicals in the amount of its apportionment of the available non-oxidized carbon [15]. One consequence of the production of a radical pool is that it creates a specific buffering effect on such a distribution. Slight differences that might be occurring in the kinetics will be shared among the pool members and be further minimized. Therefore, it would seem that for the fixed flame configuration of the FID, small additions of hydrocarbon that are instantly broken down and reformulated to unburned carbon fragments in such a manner provide the basis of its mechanism. Similar behavior has been observed in pre-mixed fuel rich hydrocarbon flames [10] and in the quite different arrangement of the FID, which introduces

small organic samples into an H$_2$/O$_2$ diffusion flame. This has to be a consequence of the remarkably fast kinetics that are common to all hydrocarbon flames. As was noted in Table 1, the CH radical can have a half-life of 50–100 ns, a value that is not exceptional for a hydrocarbon radical. Consequently, steady-state distributions and radical pools form almost instantly and minimize the differences between fuels and flow configurations.

Accepting that the chemi-ionization results from the CH radical, FID studies show for a specific flame condition that an amount of unburned carbon has to generate a fixed amount of CH. In other words, for any hydrocarbon the amount of carbon that gets oxidized in the reaction zone is approximately the same for a fixed equivalence ratio and flame parameters, and that the FID creates CH in a fixed ratio from any carbon source. Although this has always been an abstruse concept it is in fact fully supported by experimental data. First, reliable quantitative laser-induced measurements have been made in CH$_4$, C$_2$H$_4$, C$_2$H$_6$ low-pressure pre-mixed flames ($\phi = 1.02$ and 1.28) burned with O$_2$ and N$_2$ in the temperature range of 1540–1930 K [74,159]. Based on conservation of total carbon, unburned gas flows, and the flame parameters, it is possible to calculate the total amount of carbon that exists in a unit volume of the burned gases in each of their flames. A comparison with their measured CH concentrations shows an approximately constant ratio of CH produced per initial carbon input at a fixed equivalence ratio. For example, in the three $\phi = 1.02$ flames, this ratio is calculated to be 7.5×10^{-5} for CH$_4$, 5.6×10^{-5} for C$_2$H$_6$, and 5.4×10^{-5} for C$_2$H$_4$. For the corresponding $\phi = 1.28$ flames it is 1.4×10^{-4}, 8.3×10^{-5} and 7.7×10^{-5}. This is further supported by earlier work by Williams and Pasternack [160] who similarly measured the relative levels of CH with stoichiometric flames of the same fuels as above but also with C$_2$H$_2$. These flames were at low pressure (13 mbar, 10 Torr), adjusted to have similar temperatures, and had not too dissimilar OH profiles. As reproduced in Fig. 2, they noted very similar levels of CH with the first three fuels but higher levels of CH in the acetylene flame. This larger magnitude with acetylene also was reflected in their corresponding measured C$_2$ concentration profiles in the same flames. Similar calculations as above indicated that the total carbon content was almost the same in the burned gases of each of these four flames (1.23, 1.30, 1.39, 1.25×10^{16} total carbon atom content/cm^3, for CH$_4$, C$_2$H$_6$, C$_2$H$_4$, C$_2$H$_2$, respectively). From their approximate scaling factor to place the CH measurements on an absolute scale, the corresponding ratio of CH produced per unit carbon is about 4.8×10^{-5} for CH$_4$ and obviously very similar for C$_2$H$_6$, C$_2$H$_4$ but much larger for C$_2$H$_2$. Clearly there was more remaining non-oxidized carbon in the near burned gases for the latter to produce more CH initially. However, as seen in Fig. 2, this initially larger pool of unburned carbon then is rapidly consumed. By 8 mm above the burner, the burned gases of the acetylene flame again become indistinguishable from the other flames. Additional
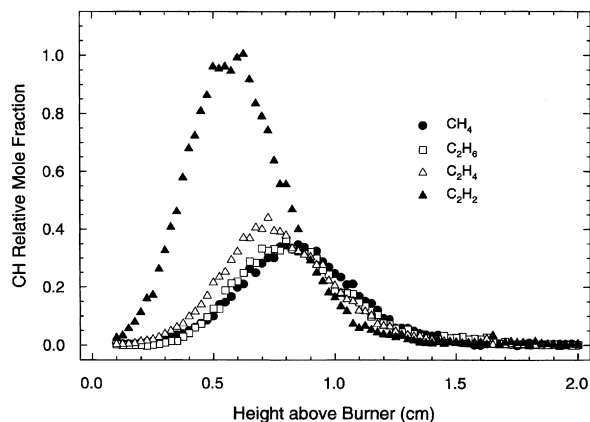
Fig. 2. Measured CH profiles for the different stoichiometric flames at 1800 K, normalized to the maximum in the acetylene flame. Reprinted by permission of Elsevier Science from "The effect of nitric oxide on premixed flames of CH_4, C_2H_6, C_2H_4 and C_2H_2," by B.A. Williams and L. Pasternack in *Combustion & Flame*, vol. 111, pp. 87–110, Copyright 1997 by The Combustion Institute [160].

measurements by Bernstein et al. [161] compared CH concentrations in stoichiometric mixtures of CH_4, C_2H_6, $C_2H_4/O_2/Ar$ flames at 27 mbar (20 Torr) also finding significant similarities for their CH concentration profiles.

These supporting data, taken together with the performance of the FID itself, appear to strongly support one conclusion. This is that the combustion reactions of hydrocarbon fuels proceed very similarly for a fixed equivalence ratio and produce similar quantities of CH per unit carbon input. This then results in the same levels of electrons per unit carbon input. Also, this automatically implies that the oxygen in hydrocarbon combustion consumes the same amount of available carbon in the reaction zone irrespective of its structural form. The remaining unburned carbon becomes distributed over a radical pool such that a fixed quantity of CH is produced. This not only satisfies the mechanistic needs of the FID but also appears to hold the answer to the long sought different behavior of acetylene. Its uniqueness arises in oxidizing at a slightly slower rate in the reaction zone and for a while has a larger pool of unburned carbon. It therefore appears to be as simple as was hinted by Miller [96] 30 years ago that acetylene oxidizes differently from the other hydrocarbons having a larger pool of hydrocarbon radicals. No secondary ionization channel is involved or required.

9. The mechanistic value of the FID for kinetic models

By serendipity, the FID's mode of operation now is seen to originate from the very nature of combustion. It should be remembered that it is not an accurately exact instrument but even so is usually approximate to well within 10% of the carbon content of a hydrocarbon mixture. As with many such analytical instruments care also has to be taken to ensure compatible conditions for the measurement and calibration. The FID is no different; the nature of the diluent of a sample and that of the calibration gas has to be allowed for [162,163]. The "effective carbon number" of a response to a specific molecule will only approximate to unity, but it does so surprisingly well. This has been illustrated by the extensive use of the FID in gas chromatographic analyses of mixtures where this characteristic is the foundation for quantitatively calibrating the individual spectral peaks. Artificial neural network models now have become available to them for predicting FID response factors for a wide range of organic compounds [164,165]. Such modeling, for example, can even predict what might be expected in the combustion of complex organic structures as aryl ether polyethoxylates [166]. The reliability of applying such standard relative response factors for specific structural groups is the very foundation of quantitative chromatography. It has enabled the otherwise difficult analyses encountered in the oil and fats industries such as with complex mixtures of long-chain fatty acid esters and glycerols [167–169]. Moreover, in intercomparisons between different type analytical instruments that monitor hydrocarbon mixtures, the FID has remained the reliable benchmark technique [170]. This is quite remarkable for an instrument the fundamental mechanism of which has never been fully understood.

This wealth of ionization response factors has to be a useful mechanistic supplement for kinetic modeling and has remained overlooked. It is particularly relevant to combustion now that interest is turning to the greater use of partially oxidized fuels. Any proposed mechanism will have to be consistent with the fact that ketonic, aldehydic, ether or acidic type-oxygens will not permit one of the connected carbons to enter any radical pool. Organic esters will in essence behave as though one and a half carbons in their structure are pre-oxidized. Alcohols will be able to partially recycle part of the carbon attached to oxygen and only lose a fraction to pre-oxidation.

An example by Blades [126] in this regard is an interesting illustration of the possible value of the FID in gaining some insight into the primary mechanism of combustion. Initially, on examining the FID response to the molecule oxetane (trimethylene oxide), that contains the C–C–C–O four atom ring structure (c-$(CH_2)_3O$), it was seen to behave normally as an ether and count as of two carbon status. However, on examining trioxane, the six-membered ring trimer of formaldehyde, which has $–CH_2–O–$ linkages $((CH_2O)_3)$ this unexpectedly gave an ionization response equivalent to half a carbon instead of the predicted zero. In other words although known to pyrolyze at 400 °C to formaldehyde a different mechanism had to be occurring in the flame to produce a non-formaldehyde product. Reaction (29) or a corresponding reaction that produces CH_2OH would appear to be most likely and consistent with the FID observation.

$$(CH_2O)_3 + H = CH_2OH + 2CH_2O. \tag{29}$$
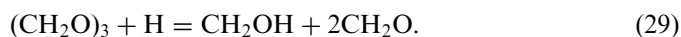
Although seemingly trivial, such exercises can aid in validating the mechanistic suggestions for oxygenated fuel

combustion. This is appropriate to the recent study of Kaiser et al. [141] that examined dimethyl ether flames. For this, cleavage in some manner to CH_3 and CH_3O might be thought possible, but based on the FID this cannot be the case. The FID predicts that only one of the two carbons will behave as a free carbon. On comparing a methane flame with a dimethyl ether flame of the same equivalence ratio their study reported two noteworthy observations. First, that the levels of the C_2 product species were the same in the two flames, and also that the level of CH_2O was 5–10 times larger in the ether flame. The C_2 product species observation tends to imply that the amount of unburned carbon is similar in the two flames. If they had measured the total flame ionization, this would also have been the same, as predicted by the FID database. As seen already, CH_2O is essentially an oxidized form of carbon on a direct route to CO [15, Table 3]. It is no longer a participant in the hydrocarbon radical pool and cannot return to it. Consequently, it can be predicted solely from FID observations that the combustion kinetics of CH_3OCH_3 has to produce CH_3 and CH_2O in the primary step with no CH_3O or CH_3OH. A recent shock tube study has in fact measured the rate constant values for reaction (30) and the corresponding reaction with O-atom.

$$CH_3OCH_3 + H = CH_3OCH_2 + H_2. \qquad (30)$$
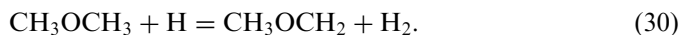
These are seen to be very rapid and are undoubtedly the dominant primary steps in this combustion with subsequent fragmentation of the product radical to CH_3 and CH_2O [171].

Combustion mechanisms of more complex fuels, such as investigated in the recent labeled study of the double ester di-butyl maleate ($=CHCOOC_4H_9)_2$ [142,143] have been mentioned already. At present, it is quite possible that the FID might be of significant help in establishing the primary steps and predict sooting tendencies in two other very interesting recent studies of oxygenated fuels. These compared the behaviors of methyl butanoate and ethyl propanoate, both of formula $C_5H_{10}O_2$ [172], and methyl acetate and ethyl formate, both being $C_3H_6O_2$ [173]. In the first case the behavior of both molecules in FIDs is very similar and as seen in Table 3 each will behave as though one and a half carbons are pre-oxidized. However, this is seen to be inconsistent with the initial modeling attempts that predict the major channel for ethyl propionate produces propanoic acid and ethylene, a loss of only one carbon to oxidation [172]. The FID data would predict instead an initial channel to C_2H_5CO and C_2H_5OH. Moreover, corresponding C_3H_7CO and CH_3OH products are needed in methyl butanoate combustion for consistency. This also differs quite notably from its suggested kinetic models [143,174,175]. Such disagreements raise significant concerns at present over the chemical accuracy of such models.

The second study [173] is interesting in that formates in an FID appear to behave more like an acid than an ester. Consequently, differences might be expected between methyl acetate and ethyl formate. FID predictions would suggest CH_3CO and CH_3OH as initial products for the acetate but possibly $HC(O)O$ plus C_2H_4 for the formate.

The present dilemma is that even in such cases as dimethyl ether, the kinetic modeling of its combustion tends to rapidly race ahead of the chemical understanding. The models become highly detailed, complex, and change into mathematical algorithms. In the case of this ether, it has resulted in a model with 351 reactions and 82 species [176]. That for methyl butanoate ($C_3H_7COOCH_3$) combustion now encompasses 295 chemical species and 1498 reactions [175]! As a result, because the FID reflects the levels of CH and unburned carbon in any fossil fuel combustion system, a comparison with FID predictions has to be an additional important new approach in the initial construction of these complex networks of chemical reactions.

10. Conclusions

An examination of chemi-ionization mechanisms in flames especially that relating to the FID has been presented in detail. This finally resolves many of the speculative suggestions that have appeared over the years. It is now conclusively established that the $CH(B, A)$ electronically excited states play no role in the chemi-ionization normally encountered in flames. The original mechanism of ground state CH with atomic O still remains the dominant and sole reaction. This is now possibly modified slightly in that the relevance in flames of the metastable $CH(a)$ state still cannot be resolved and the functioning reactant for the present should be written more accurately as their combined contributions $CH(a, X)$. From the monitoring of CH and C_2 species in numerous flames of differing fuels it is apparent that the anomalous behavior of C_2H_2 in the FID is no more than a reflection of its unique combustion oxidation kinetics that differ from all other hydrocarbon fuels. It is the very nature of combustion, namely the rapid destruction and reformulation of radicals and molecules that removes the structural identity of differing hydrocarbons and leads to the "equal per carbon response" that is seen in the FID. The essentially forgotten structural dependences of the FID previously recorded for oxygen-bearing organics have significant implications for present day kinetic modeling. They can establish the requirements of the dominant mechanisms in the combustion of oxygenated fuels and be an additional aid that is being neglected by the modelers. Moreover, the same structural relationships seen in the FID parallel those observed in soot formation trends. It is obvious that the formation of the hydrocarbon pool of radicals not only is the source of ions from CH, but also when sufficiently fuel-rich, of soot. Consequently, to the enigmatic question of whether CH, C_2, or some other hydrocarbon radical plays an important role in flames or in soot formation the answer has certainly got to be yes. However, it can equally be argued that they are all of equal importance.

Acknowledgments

I am indebted to the eight reviewers for their time and conscientiousness in thoroughly examining this paper. The most pre-examined and edited work I have ever written. They helped mold it into form, corrected various historical factors and removed hopefully all the errors. For younger readers I hope it conveys the richness of information in the older literature that still can have significant value and implications for present day research. It also helps to remind us that our depth of understanding is much less than we would generally like to conceive.

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