Ion Formation in the Flame Ionization Detector

A. J. C. NICHOLSON and D. L. SWINGLER

CSIRO Division of Chemical Physics, P.O. Box 160, Clayton, Victoria, Australia 3168

The spatial distribution of positive ions in the flame ionization detector (FID) has been studied by a mass-spectrometric method. Except in the region well upstream from the flame front, the ions formed are the same for hydrocarbons, alcohols, and ketones. A mechanism is proposed for the formation of ions, which leads to the experimentally observed FID relationships connecting ionization with additive structure and concentration.

INTRODUCTION

The work to be described here was initiated with the aim of testing the theory of Bolton and Mc-William [1] which described transport of charge in the flame ionization detector (FID) used in gas chromatography. A mass-spectrometric study [2] showed that the positive charge carriers in the FID (vertical flame with a negative cylindrical collector) are hydrated oxonium ions, $H_3O^+(H_2O)_n$. These travel across the relatively cool gas between the outer edge of the flame and the collector as a group, with values of n corresponding to the equilibrium between the hydrates set by the temperature and the partial pressures of the ions and water vapor. This result tells us little about the primary ion or ions except that the reactions,

primary ions + water $\rightarrow H_3O^+$,

go to completion in the burnt gases.

The above are the ions appearing at some distance from the flame; many more ions [3] can be detected by bringing the flame closer to the sampling orifice leading to the mass spectrometer. The present paper deals with these ions in an attempt to find out what is the primary process of ion formation in such flames, what ion/molecule reactions occur, and what light this knowledge throws on the general combustion process. Because ion/

molecule reactions are rapid, mass identification of a product ion gives an indication of the presence of a reacting free radical which is often more sensitive than direct measurement of the free radical itself [4] (see also Bohme et al. [5]).

It is generally believed that the primary ion in hydrocarbon flames is HCO^+ formed by the reaction

$$CH + O \rightarrow HCO^+ + e^-, \qquad \Delta H = -30 \text{ kJ mol}^{-1}. \tag{1}$$
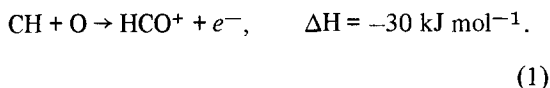
The evidence for this has been summarized by Miller [6]. Since Miller's review, support has been given to this view by the work of Gardner, Vinckier, and Bayes [7] who establish that the primary ion produced in the reaction of oxygen atoms with C_2H_2 is indeed HCO^+, and by the work of Peeters and Vinckier [8] who showed that total ionization in CH_4-O_2 and C_2H_4-O_2 flames is proportional to the concentration product [CH] [O].

Blades [9] has discussed ion formation in the FID, a diffusion flame of hydrogen burning in air, using knowledge obtained from the study of premixed flames. He accepts Eq. (1) as the primary chemi-ionization reaction with a minor modification [10], namely,

$$CH + O \rightarrow HCO^*$$

$$HCO^* + X \rightarrow HCO \cdot X^+ + e^-. \tag{1a}$$
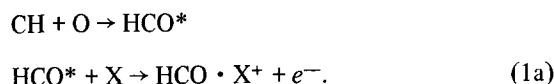
Here the "cluster" ion, $HCO \cdot X^+$, can be formed with less energy than HCO^+ itself when X is either the H_2 fuel or the N_2 or noble gas used as a carrier. This modification gives a rationalization of the changes in the ion current of the FID when different carrier gases are used.

Blades has also pointed out [9, 11] that an ionization reaction involving an excited oxygen molecule is a possibility: it is usually invoked when no hydrogen is present, as in C_2N_2-O_2 flames [12a]. This view has been extended by Sevcik et al. [13] who propose that for all FID flames the ionization steps involve reaction of excited oxygen atoms and molecules with CH_2 and CH_3 as well as with CH. Those of their reactions that involve formaldehyde as an intermediate seem unlikely since formaldehyde itself has almost zero response in the FID. Recently, Bredo, Guillaume, and van Tiggelen [12b] have argued against the participation of excited oxygen in ionization in the C_2N_2 flame and prefer a mechanism involving excited nitrogen atoms. This mechanism is itself questioned in a recent study by Bradley and Metcalfe [30] who show that nitrogen and oxygen atoms in the presence of unsaturated hydrocarbons produce ions in a reaction between excited N_2 and excited NO molecules.

Any theory of the FID mechanism must explain the two major features of the device, namely, that ion production is linear with additive concentration and that it is proportional to the carbon number of hydrocarbon additives (often called the equal-per-carbon response and calibrated relative to $CH_4 = 1$). The simplest explanation of these observations is that every hydrocarbon is degraded to the same distribution of single-carbon radicals before ionization takes place. The visible light from an FID flame is due to emission at 431.5 nm from excited $(A^2\Delta)CH$ radicals, and this emission also has the equal-per-carbon and linear response of the ion production [9b]. However, there is evidence [6, 15] that excited CH radicals are not the precursors of the ions. The similarities between light emission and ionization suggest both processes involve ground-state CH radicals. Blades [9a] has shown that the equal-per-carbon response only holds when the hydrocarbon is carried up to the flame in a hydrogen atmosphere. He postulated

a "hydrogen-cracking" mechanism. Hydrogen atoms abstract hydrogen from the additive to give a radical which on collision with another hydrogen atom splits to give two smaller radicals: this process continues until all carbon-carbon bonds have been broken.

The mass-spectrometric work on which the above mechanism (1) is based was carried out with premixed flames burning mostly a H_2:N_2:O_2 mixture containing about 1% of C_2H_2 additive [16]. These premixed flames were larger and hotter than the FID diffusion flames considered here. It seemed useful to make direct measurements on an FID flame and to compare the behavior of additives of different chemical types.

EXPERIMENTAL

In this work the flames burned on a cylindrical jet (0.25 mm I.D.) of stainless steel surrounded by a 2-mm tube which could be used to sheath the flame with air or with a 4:1 argon-oxygen mixture. The blue luminous zone of CH emission was 4-mm long surrounded by a faint violet glow. Thermocouple measurements showed that additives up to 1% of the gas stream did not change the measured temperature. Schaefer [14a] has discussed the difficulties in measuring the temperature in such small flames and calculation, by his method, of the flame giving the mass spectrum of Fig. 1, gives a temperature of 2170°K. Measurements of a similar flame by Ohline, Thall, and Oey [14b] gave 2043°K at the hottest points. These values are appreciably lower than the temperatures of Knewstubb and Sugden's premixed flames [16] which were around 2500°K. The jet could be moved horizontally along the axis of the entrance orifice to a sampling system that guided the ions into a quadrupole mass spectrometer. The sampling system was a version of that described previously [2], modified as follows:

1. The entrance orifice consisted of a 30° cone, expanding inward, in a 3-mm front plate. The entrance was countersunk to 0.25-mm diameter to give 0.1-mm diameter at the narrowest point. This size was about the smallest that could be

easily unblocked by poking with a tungsten wire.

2. Faster pumping (80 dm^3 s^{-1}) was provided in the space between the entrance and the "first cone" electrode so that the pressure in this region was about 22 m Torr (3 Pa) instead of 1.5 Torr (200 Pa) in the previous apparatus.

3. The distance between the entrance orifice and first cone was 1.5 cm instead of 3.5 cm.

4. A focusing electrode consisting of a cylinder split into four segments was placed between the first and second cones.

In our earlier work, as a horizontal jet was brought up to the orifice, the flame "entered the hole" and was eventually extinguished by oxygen starvation. This did not occur in the modified apparatus. Rather, as the jet approached the entrance orifice, the flame changed sharply from a "tongue" to a "mushroom" shape. It proved difficult to position the flame to give reproducible mass spectra at the position where the luminous flame tip just touched the entrance orifice. However, three distinctive types of spectra could be recognized depending on whether the flame tip was distant from, just touching, or spread over the front plate. These three types of spectra give information about the ion composition of the burnt gases, in the flame front and in the unburnt gases, respectively. The temperature of the flame obviously drops as it spreads over the front plate and there is a corresponding drop in ion current. Mass spectra are drawn to show the percentage of total ion current at each molecular mass (m/z).

"Nonflame" Ions Produced in Sampling

It has been known for many years [16] that the sampling device can produce ions that are not present in the flame itself. The most prominent of these are clusters formed by the addition of one or more molecules of water to an ion. We have discussed the formation of cluster ions in the FID previously [2] and for the purpose of the present paper all hydrates of a given ion are considered as one entity.

Ions can also be recorded in the mass spectrometer which have been formed by ion/molecule reactions during expansion through the entrance orifice or in the relative high pressure region following it. A full discussion is given by Peeters, Vinckier, and van Tiggelen [15] for an extraction system almost identical with the one used in our work. They suggest that exothermic reactions during expansion can only add a small fractional contribution to the same reactions occurring in the flame but that endothermic reactions that do not occur in the flame can occur in the first chamber. Such reactions can be identified, since the ratio of product ion current to H_3O^+ ion current plotted against the voltage across the first chamber increases with voltage for an endothermic reaction occurring there. Of the ions observed in our work, only CH_3^+ increased when this test was applied.

RESULTS

Figure 1 shows the ions from a "distant" flame with the flame tip 1 mm from the entrance orifice. Of the ion mass spectrum, 99.1% was made up of $H_3O^+(H_2O)_n$ ions and the spectrum including the minor ions was the same for all the additives tested (paraffins, aromatics, alcohols, and ketones). In this particular example the gas flowing to the jet was 1.5 cm^3 s^{-1} H_2, 0.56 cm^3 s^{-1} N_2 and 0.025 cm^3 s^{-1} CH_3OH. We showed in an earlier paper [2] that over 90% of the ions at m/z 18 and 36 were NH_4^+ and $NH_4^+(H_2O)$, respectively, and that $m/z = 30$ was NO^+; these nitrogen-containing ions will not be discussed here. We identify the other minor ions as m/z 15, CH_3^+; 29, HCO^+; 33, $CH_3OH_2^+$; 39, $C_3H_3^+$; 43, CH_3CO^+; 45,
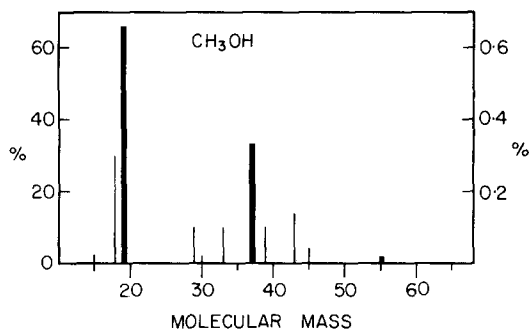

Fig. 1. Positive ion mass spectrum of a flame with tip 1 mm from the entrance orifice. The thick lines refer to the left-hand ordinate. The additive is CH_3OH, but all additives give the same spectrum.

$CH_3COH_2^+$. There is no doubt that the peaks at m/z = 39 and 43 contain more than one carbon atom, but the extensive polymerization [16] observed for acetylene-containing premixed flames did not occur in any of our flames. For both CH_3COCH_3 and C_6H_6, deuteration showed that the ion giving the m/z = 43 peak contained only three hydrogen atoms.

Figure 2 is a typical ion mass spectrum obtained when the flame tip was just touching the entrance orifice. This particular spectrum is for acetone as additive, but the same mass peaks were observed for C_6H_{14} and C_6H_6. The most remarkable feature is that the $C_3H_3^+$ ion dominates the spectrum. A small peak was observed at m/z = 27 which must be the $C_2H_3^+$ ion. Most of the peaks at higher m/z fit into hydrate series—27, 45, 63; 29, 47, 65; 33, 51, 69; 43, 61, 79. A homologous series, 39, 53, and 67, is formed with formulae established by deuteration as $C_3H_3^+$, $C_4H_5^+$, and $C_5H_7^+$.

It is only when the ions come from the unburnt gas that mass spectra characteristic of the additive are obtained. Figure 3 shows such spectra from mushroomed flames with the jet 1 mm closer to the orifice than that giving the spectrum shown in Fig. 2. The dominant ions found for the three gases were the protonated molecules, $CH_3OH_2^+$, $CH_3COHCH_3^+$, and $C_6H_7^+$, respectively. The 79 peak in Fig. 3 corresponded to a

Fig. 3. Positive ion mass spectra of mushroomed flames (1 mm closer than that of Fig. 2). The thick line refers to the left-hand ordinate.

current of 2 × 10^{-11} A at a steady C_6H_6 flow of 50 μg s^{-1}. The noise was 1 × 10^{-13} A and there was no 79 background peak when no C_6H_6 entered the flame. The limit of detectability (twice the noise) is therefore 0.5 μg s^{-1} for observation of a recognizable M + 1 peak. This compares unfavorably with the limit of detectability for the FID itself: a representative figure for propane is 10^{-6} μg s^{-1} [17]. No protonated molecules were observed for hydrocarbons with a proton affinity less than that of CO.

In Fig. 4 the variation in ion current is plotted as a function of distance from the orifice with zero corresponding to the flame tip touching the orifice. The additive was C_6H_6. The peaking of the $C_3H_3^+$ current at (or very close to) the flame tip is shown clearly. Although not shown clearly in this diagram, CH_3CO^+ was found to peak just measurably downstream from the $C_3H_3^+$ peak. The lesser ions are difficult to measure accurately, but in all flames m/z = 27, m/z = 29, and m/z = 33 also peaked very close to the flame tip. With CH_3OH additive the $CH_3OH_2^+$ ion peaked near the flame tip, passed through a minimum, and
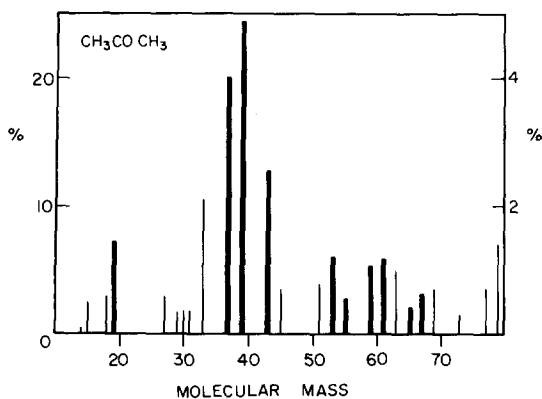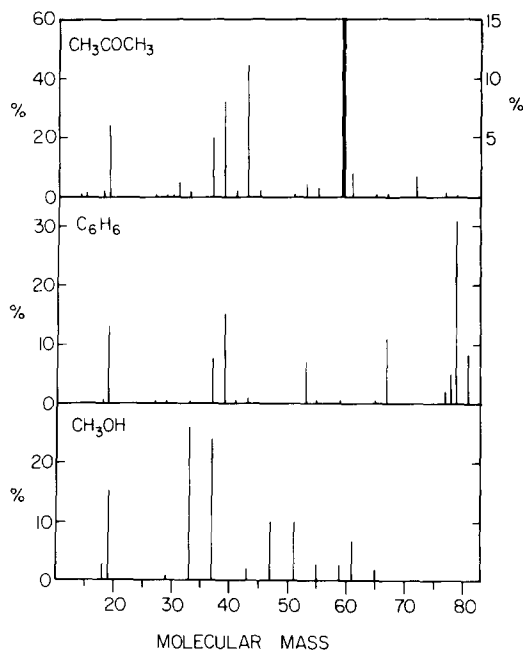

Fig. 2. Positive ion mass spectrum of a flame with the tip of the flame just touching the entrance orifice. The thick lines refer to the left-hand ordinate. The additive is CH_3COCH_3, but all additives give a similar spectrum.
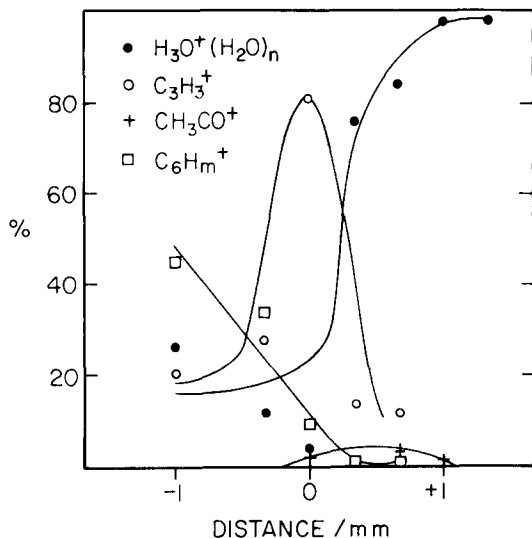
Fig. 4. Plot of percentage ion current at particular molecular masses against distance of the jet from the orifice. Zero corresponds to the flame tip just touching the orifice; positive distances indicate the distance the jet has been withdrawn from the zero position (to give a "downstream" spectrum). The additive is benzene.

then increased again as the unburnt gases were sampled; the same occurred for the CH_3CO^+ ion with CH_3COCH_3 as additive. This is taken to indicate that the same ion can be formed by different reactions in different parts of the flame. In all flames $CH_3OH_2^+$ is formed close to the flame tip: in flames with methanol additive, it is also formed upstream by protonation of the intact molecule. Similarly, CH_3CO^+ is formed close to the flame front in all flames, but is formed by another mechanism upstream in flames containing acetone.

At the closest distance of approach the ion mass spectrum is dominated by ions with mass one above the molecular mass and by ions from fragment of the molecule. These spectra are very much what would be expected for chemical ionization spectra with HCO^+ and/or H_3O^+ as reactant ions.

No cluster ions containing N_2, O_2, or Ar were ever observed either from flames or in the few experiments in which an electron beam was used to ionize the gas that had flowed into the orifice from an unlit jet. Because the measured ion current at $m/z = 29$, HCO^+, was always small, failure

to detect $HCO \cdot X^+$ does not necessarily disprove Blades's mechanism.

DISCUSSION

On the basis of the work described here and the generally accepted mechanism of ion formation in hotter flames, a picture can be drawn of the processes in FID flames as follows. It is convenient to discuss the three parts of the flame separately.

Upstream from the Flame Front

The simplest explanation of the FID relationships, the equal-per-carbon response and the linearity of response with additive molecules, is to postulate that all additive molecules are broken down to the same distribution of single-carbon free radicals before ionization takes place. The experimental evidence given here supports this view, since it is only well upstream of the flame front that any ions characteristic of the additive can be detected.

Let us consider whether the reactions occurring are fast enough for this to be achieved. A typical FID flame consists of a stream of $3:1/H_2:N_2$, flowing at 2 cm^3 s^{-1}, carrying a discrete amount, say, 5×10^{-4} g, of hydrocarbon. This amount is at the upper limit of linearity for propane [17] and by the time it reaches the FID it makes up about 1% of the gas flow. According to Ohline et al. [14b], the "boundary" of the unburnt gas for a similar flame lies about 0.75 mm upstream of the hottest part of the flame and has a temperature of $1800°K$. If we consider a cylindrical annulus 1 mm in diameter, 4-mm long and 0.1-mm thick at this boundary, the residence time of the flowing gases is 4×10^{-4} s. Table 1 shows the lifetimes for possible reactions with ethane as additive at $1800°K$. The total gas concentration, [M], is 4×10^{18} molecules cm^{-3}, $[H_2] = 3 \times 10^{18}$ molecules cm^{-3}, the initial $[C_2H_6] = 3 \times 10^{16}$ molecules cm^{-3} and the rate constants and equilibrium constants used are from Jensen and Jones [18].

The rate of Reaction (2) is too slow to establish the $H_2 \rightleftharpoons 2H$ equilibrium, but it can be established via Reactions (3) and (4). Thus the hydrogen atom concentration is constant and equals 1.25×10^{15} atoms cm^{-3}. The concentration of

<div style="text-align:center">

TABLE 1

Lifetimes at 1800°K for the Removal of the first Molecule or Radical in the Given Equation

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Reaction	Rate (molecules cm^{-3} s^{-1})	Lifetime (s)
(2) $H_2 + M \rightarrow 2H + M$	$[M][H_2]$ $7.9 \times 10^{-6}T^{-1}$ exp $(-52,650/T)$	287
(3) $C_2H_6 \rightarrow 2CH_3$	$[C_2H_6]$ 1.1×10^{16} exp $(-43,380/T)$	2.7×10^{-6}
(4) $CH_3 + H_2 \rightarrow CH_4 + H$	$[CH_3][H_2]$ 3.0×10^{-11} exp $(-7,500/T)$	7.2×10^{-7}
(5) $C_2H_6 \rightarrow C_2H_5 + H$	$[C_2H_6]$ 1.1×10^{16} exp $(-48,430/T)$[a]	4.4×10^{-5}
(6) $C_2H_5 \rightarrow C_2H_4 + H$	$[C_2H_5]$ 4×10^{12} exp $(-17,600/T)$	4.2×10^{-9}
(7) $C_2H_5 + H_2 \rightarrow C_2H_6 + H$	$[C_2H_5][H_2]$ $2.3 \times 10^{-18}T^2$ exp $(-4640/T)$	5.9×10^{-7}
(8) $H + C_2H_5 \rightarrow 2CH_3$	$k_8[C_2H_5][H] = ?$	

[a] Estimated.

C_2H_5 radicals, determined by the equilibrium of Reactions (7) and the reverse Reaction (−7), is 0.017 $[C_2H_6]$. Although C_2H_4 is produced by the fast Reaction (6), in equilibrium its concentration is proportional to $[C_2H_5]$ and hence to $[C_2H_6]$. Once this equilibrium has been attained, C_2H_4 is removed as fast as C_2H_6 which is itself removed by the sequence, Reaction (3), followed by Reaction (4) where the slower step, Reaction (3), will control the rate. Since the residence time is about 150 lifetimes, C_2H_6 will be completely removed to give an equilibrium between Reaction (4) and its reverse Reaction (−4).

Blades [9a] has suggested that the main cracking is Reaction (8), but little is known about its rate constant. If we take the value of k_8 to be a "collision frequency", about 5×10^{-10} cm^3 molecule^{-1} s^{-1}, then the maximum value of $k_8[H][C_2H_5]$ is $10^4[C_2H_6]$ s^{-1}. This is smaller than the rate of Reaction (3) which is $3.75 \times 10^5[C_2H_6]$ s^{-1}. Although this reaction might be faster than Reaction (3) at lower temperatures, invoking it as a major cracking pathway is unnecessary.

For a paraffin of higher molecular weight than ethane the reaction corresponding to Reaction (3) will be faster than Reaction (3) because the C–C bond strength decreases with increasing molecular weight. Although there would be more steps in the decomposition, the overall rate would still be enough to decompose higher hydrocarbons in the time available. The final result is the equilibrium of Reactions (4, −4) with both $[CH_3]$ and $[CH_4]$ proportional to the initial amount of hydrocarbon and to its carbon number. If it is further assumed that similar equilibria

$$CH_3 + H \rightleftharpoons CH_2 + H_2$$

$$CH_2 + H \rightleftharpoons CH + H_2$$

$$CH + H \rightleftharpoons C + H_2$$
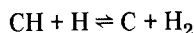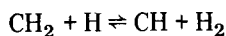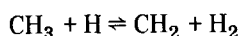
are established, any of the single-carbon radicals could be one partner in the reaction producing ions.

The essential feature of this mechanism, that the cracking has taken place before the hydrogen has been appreciably decomposed (or burned up), is what enables radical recombination reactions to be neglected relative to hydrogen abstraction reactions. This is reasonable, since under the conditions given above the steady-state methyl radical concentration is 6×10^{14} molecules cm^{-3} and the rate of Reaction (−3) is 5×10^{18} molecules cm^{-3} s^{-1}, whereas that of Reaction (4) is 8×10^{20} molecules cm^{-3} s^{-1}.

Support is given to this mechanism by Blades's observation [9a] that the equal-per-carbon response only occurs when the additive is brought up to the flame in a hydrogen atmosphere and by McWilliam's observation [19] that the response is no longer linear in additive in an FID burning pure carbon monoxide as fuel.
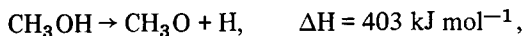
"Effective" Carbon Number

The equal-per-carbon response holds fairly accurately for hydrocarbons, but the response for a hydrocarbon with substituent groups is always less
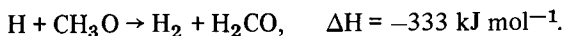
than that of the parent hydrocarbon. There have been several attempts [20] to develop systems in which an "effective" carbon number is allotted to each carbon joined to a hetero-atom for calculation of the molecular response. The effective carbon number is zero for a carbonyl group or for one of the carbons joined to an ether oxygen and about 0.7 for an alcohol group. We suggest that the response of a group is related to the speed with which the group can be reduced to a CH_n radical compared with any other available reaction. For the carbonyl group there is no reaction leading to a CH_n radical that is competitive with that leading to CO. For methanol the reaction

$$CH_3OH \rightarrow CH_3 + OH, \qquad \Delta H = 376 \text{ kJ mol}^{-1}$$
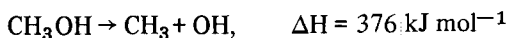
will occur but more slowly than the C–C bond breaking in a hydrocarbon. It might, too, be in competition with

$$CH_3OH \rightarrow CH_3O + H, \qquad \Delta H = 403 \text{ kJ mol}^{-1},$$

followed by

$$H + CH_3O \rightarrow H_2 + H_2CO, \qquad \Delta H = -333 \text{ kJ mol}^{-1}.$$

It is tentatively suggested that this last reaction is fast enough to account for the zero response of the ether group: its activation energy does not seem to have been measured but might be estimated as 30 kJ mol^{-1}, giving a lifetime of about 10^{-5} s.

The values of the enthalpy used in this paper are for 298°K, taken from Rosenstock et al. [21].

Flame Front

As the flame front is approached, the ions found are the same whatever the additive. This follows from the postulated mechanism but, in addition, the molecular products observed are those produced by the combination and oxidation of CH, CH_2, and CH_3 radicals, namely, C_2H_2, H_2CO, CH_3OH, and perhaps a trace of C_2H_4. In a few experiments with electron impact ionization of the flame products, small peaks at m/z 26, 29, and 30 were observed, which are attributed to C_2H_2 and H_2CO molecules. These products are also found in the diffusion flame [22] of CH_3OH. Finally, the ions with concentrations peaking around this point in the flame, m/z 27, 31, and 33, are attributed to protonated C_2H_2, H_2CO, and CH_3OH, respectively, since all these molecules have higher proton affinities than CO.

Ionization

If the decomposition mechanism given above is accepted, the FID relationships can be obtained if any of the single-carbon radicals react with a particle that does not contain carbon in a reaction energetic enough to give an ion. The evidence supporting Reaction (1) for hydrocarbon premixed flames is strong and the fact that CH emission gives the same FID relationships as ionization seems to us to establish that Reaction (1) is a primary ionizing reaction in our diffusion flame. It would take place where the CH radicals meet oxygen atoms between the blue luminous zone where [CH*] is at a maximum (presumably [CH] also) and the position, farther downstream, of maximum temperature [14b] where [O] is at a maximum. The ion concentration reaches a maximum in the violet zone of the flame [31], that is, downstream of the blue zone.

Even if Reaction (1) is the main primary ionizing reaction, others may occur. For example,

$$CH_2 + (A^3\Sigma)O_2 \rightarrow HCO^+ + OH^-,$$

$$\Delta H = -142 \text{ kJ mol}^{-1} \qquad (9)$$
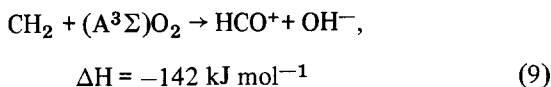
was suggested by Sevcik [13] and seems to have been accepted in recent gas chromatograph reviews [23]. This particular reaction would not give a rate of ionization proportional to [O]. While the possibility of additional primary ionizing reactions cannot be ignored, we see no reason for abandoning Reaction (1) as the main primary reaction, nor any experimental evidence requiring Reaction (9).

$C_3H_3^+$ Formation

The mechanism of $C_3H_3^+$ formation requires special consideration since, in a limited region of space close to the flame front, it is the major ion whatever the additive. This ion has been observed so consistently in hydrocarbon flames that it has in the past been proposed [23] as the primary ion.

This postulate fell from favor for many years, but evidence has been advanced recently [24, 25] that it might be an additional primary ion in acetylene flames. However, $C_3H_3^+$ cannot be the only primary ion in FID flames. If it were, either the per-carbon response would be much less than 1 or the ionization rate would be proportional to additive concentration raised to a power greater than 1 [9].

As a secondary ion, $C_3H_3^+$ could be formed by

$$C_3H_2 + HCO^+ \rightarrow C_3H_3^+ + CO.$$
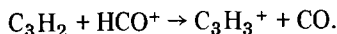
Hayhurst and Kittelson [24] proposed this reaction since they detected both $C_3H_2^+$ and $C_3H_2^-$ in hot acetylene flames and inferred from this that the radical C_3H_2 is also present.

Alternatively, C_3H_3 itself could be formed by

$$CH + C_2H_2 + M \rightarrow C_3H_3 + M,$$

where either the CH or the C_2H_2 might be excited, and ionized by charge transfer. Jones and Bayes [26] observed C_3H_3 molecules produced in the reaction of atomic oxygen with C_2H_2 and postulated reaction of C_2H_2 with an excited intermediate which could have been any one of the CH_2, HCCO, or CH_2CO observed in their system. In our system it is possible that $C_3H_3^+$ is produced catalytically. Decarpo, McDowell, Johnson, and Saalfeld [27] have shown that $C_3H_3^+$ is the primary ion in the catalytic combustion of 2,2-dimethyl butane at temperatures around $1023^\circ K$. They found it was produced on platinum but not on gold: we found no difference in ionic mass spectra whether the entrance orifice was brass, mild steel, or titanium. Whatever the mechanism of $C_3H_3^+$ production, the pronounced maximum observed in its concentration very close to the point where the flame tip touches the front plate suggests that [CH] is also at a maximum at this point. Since this too occurs for all additives, it supports the postulate that all additives have been broken down to single-carbon radicals before they reach the hottest part of the flame. For C_3H_3 to be ionized by charge transfer, it would have to have an ionization energy close to that of HCO^+ which lies between 820 and 836 kJ mol^{-1}, according to choice of the heat of formation of

HCO. Unfortunately, there is no reliable information available on the ionization potential of C_3H_3, although the heat of formation $C_3H_3^+$ is known to be 1079 kJ mol^{-1}. Thus the heat of formation of C_3H_3 would be about 250 kJ mol^{-1} which is close to the value for C_2H_2. Lossing [29] has established that the cyclopropenyl structure for this ion is appreciably more stable than the isomeric structures $HC\equiv C\text{-}CH_2^+$ or $H_2C=C=CH^+$. For this reason, the ion in flames is assumed to have the cyclic structure. Whenever $C_3H_3^+$ ions are found in the flame, ions at $m/z = 53, 67$, and 81 are also seen, and it is possible that these are homologues of the cyclopropenyl ion.

Downstream from the Flame Front

Just a little downstream from the flame front, the $m/z = 43$ ion current reaches a maximum and we have shown that this ion has the formula C_2H_3O. At this point, radicals can first react with CO, for example,

$$CH_3 + CO + M \rightarrow CH_3CO + M$$

$$CH_2 + CO + M \rightarrow CH_2CO + M.$$
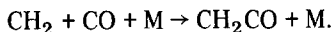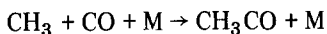
This is in the violet zone of the flame, and it is known that light from the CO + O continuum is at a maximum in the violet. Both these radicals would form ions by reaction with HCO^+:

$$CH_3CO + HCO^+ \rightarrow CH_3CO^+ + HCO$$

$$CH_2CO + HCO^+ \rightarrow CH_3CO^+ + CO.$$
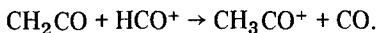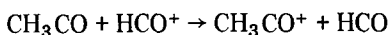
Small peaks are also observed at m/z 41 which might be $CHCO^+$ formed in a similar way. Well downstream from the flame, as in the drift space of the FID, the major ions are oxonium, H_3O^+, and its hydrates. The reaction

$$HCO^+ + H_2O \rightarrow H_3O^+ + CO,$$
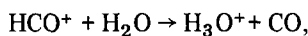
$$\Delta H = -113 \text{ kJ mol}^{-1}$$

is exothermic, and even endothermic ion/molecule reactions giving H_3O^+ will occur here because the concentration of H_2O molecules is so high.

CONCLUSIONS

It has been shown that the FID relationships connecting ionization with additive structure and concentration follow from the postulate that additives decompose to the same distribution of CH_n radicals upstream of the region where hydrogen is appreciably decomposed to hydrogen atoms or oxidized, and before the ionizing reaction has occurred. Although some rate constants are not known very accurately, calculations for a typical FID system show that there is time for this to occur. For hydrocarbons their rate of decomposition by C–C bond breaking is adequate without invoking Blades's [9a] atom-cracking mechanism. Our observations that all the additives we have studied give the same ions, together with our studies of the nature of these ions and of the variation in ion content observed as the flame is moved relative to the sampling orifice, all support this postulate. We suggest that the diminished response of oxygen-containing molecules is due to the slowness of reactions leading to CH_n relative to those leading to CO or H_2CO.

Reaction (1) between CH and O is believed to be the primary ionizing reaction in premixed flames and we see no reason for replacing it by any other in FID diffusion flames. The FID relationships cannot be obtained if $C_3H_3^+$ is formed to any extent in a primary process.

When this work was started, it was hoped that an atmospheric pressure mass spectrometer might be used as an adjunct to the FID to identify the molecule eluted from a gas chromatograph. In the event, a molecular weight can be recognized, but only for flames close to the orifice with additive concentrations at the upper end of the useful range of the FID. One obtains a chemical ionization spectrum of the additive with HCO^+ or H_3O^+ as reagent, overlaid by the traces of the downstream FID ion spectrum and the limit of detection is many orders worse than obtainable in a conventional FID.

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