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Mass spectrometry of flames

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A quadrupole mass spectrometric analyser for use in flame ionization is described, together with its application to the ions produced by traces of sodium, added as chloride, in premixed hydrogen-air flames.

Negative ions (Cl^- and OH^-) appear to be of subsidiary importance in the main ionization processes, which rather proceed through direct production of electrons. Nevertheless, it is established that the appearance of Cl^- ions is consistent with dissociative attachment

$$HCl + e^- \rightarrow Cl^- + H,$$

rather than by three-body attachment

$$Cl + e^- + M \rightarrow Cl^- + M.$$

Hydroxyl ions probably are formed in the same way.

The ratios of the amounts of A^+ (alkali) and $A^+.H_2O$ (alkali monohydrate) ions have been measured in the cases of lithium, sodium and potassium. Equilibrium constants for the reaction

$$A^+.H_2O \rightleftharpoons A^+ + H_2O$$

are obtained and heats of monohydration of 44, 28 and 17 kcal/mole deduced respectively for $A \equiv$ Li, Na, K.

Small amounts of H_3O^+ appear in the reaction zone because of traces of hydrocarbon impurities in the flame gas supplies. These are severely reduced by alkali addition, apparently by an exchange reaction

$$A + H_3O^+ \rightarrow A^+ + H_2O + H,$$

with a rate constant of $1{\cdot}1 \times 10^{-8}\,cm^3/s$ at 2000 °K, rather than by recombination with electrons produced by direct ionization of alkali

$$H_3O^+ + e^- \rightarrow H_2O + H.$$

In contrast with the steady production of A^+ ions in the burnt gases by reactions of the type

$$A + M \rightarrow A^+ + e^- + M,$$

there is an anomalously high rate of production in the reaction zone. This appears difficult to explain without introduction of processes involving 'hot' electrons.

1. Introduction

Previous mass spectrometric investigations of ions in flames have largely been directed at the problem of the anomalously high amount of ionization found in the reaction zones of hydrocarbon flames, and have met with fair success (see, for example, Green & Sugden 1963). The purpose of this paper is to describe the application of the method to the ionization of alkali elements in flames. Earlier work in this field has largely been confined to the measurement of concentrations of free electrons (for a review see Sugden 1963), the nature and abundance of other ionic species being obtained by inference. Such a procedure is not fully satisfactory in dealing with questions of mechanism of ionization, where direct evidence on the other ionic species is required. This paper describes experiments aimed at providing

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such evidence, using a quadrupole mass spectrometric analyser in conjunction with hydrogen flames at atmospheric pressure. The ion sampling technique was otherwise similar to that used by Knewstubb & Sugden (1960).

2. Experimental

(*a*) *The quadrupole mass spectrometer*

The mass spectrometer was constructed on the electrostatic quadrupole principle developed by Paul and collaborators (Paul & Steinwedel 1953; Paul & Raether 1955; Paul, Reinhard & von Zahn 1958). The ions, as a continuous stream, enter axially into the space between four parallel rods, of circular cross section, arranged symmetrically so that their axes have a square section. A potential $(U + V\cos\omega t)$ is applied to one pair of diagonally opposite rods, and a similar potential of opposite sign to the other pair, U being a d.c. component and $V\cos\omega t$ an a.c. component of frequency $(\omega/2\pi)$. Under these conditions the ions may settle into a 'stable' oscillatory motion of finite amplitude between a pair of opposed rods, or they may have an 'unstable' motion, in which the amplitude tends to infinity. The type of motion is determined by U, V, ω, $2r_0$ (the closest distance of approach of two opposed rods), and by the (mass/charge) ratio of the ions. The use of opposed pairs of rods in a quadrupolar system leads to an intermediate range of (mass/charge) with stable motions. Only these ions appear at a detector placed at the exit end of the system. The width of the detectable range is determined by the ratio U/V, and must be narrow for high resolving power of the instrument. Variation of the position of this range along the (mass/charge) scale can be effected by altering V and U at constant ω, or by changing ω at fixed V and U.

For optimum resolution it has been shown that V and U are given by

$$V = 7{\cdot}219(Av^2r_0^2)\ \text{volts}, \qquad U = 1{\cdot}212(Av^2r_0^2)\ \text{volts},$$

where A is the mass number of the (singly charged) stabilized ion, v is the frequency of the a.c. component in megacycles/second and r_0 is in centimetres. The a.c. power required is given by

$$\text{power} = 6{\cdot}5\times10^{-4}\left(\frac{CA^2v^5r_0^4}{Q}\right)\ \text{watts},$$

where C is the capacitance of the quadrupole rod assembly in picofarads and Q is the selectivity of the coupling circuit supplying the energy.

The actual resolution, R, defined by (peak height/half peak width) is determined under these conditions by the diameter, d, of the entrance aperture, according to

$$d = r_0/\sqrt{R}.$$

The maximum permissible accelerating voltage of the ions into the quadrupole field is given by

$$4{\cdot}2\times10^2(v^2L^2A/R),$$

where L is the length of the rods in metres. The potentials U and V must be stabilized to a factor better than $1/2R$, as must also ω and r_0. The theory which led to the above figures was based on rods of rectangular-hyperbolic cross-section, but these may reasonably be approximated by circular rods of radius $1{\cdot}16r_0$. Solid stainless steel rods, of diameter 0·496 in. (1·26 cm) and length 13·562 in. (0·3445 m), were used. They were machined by R.P.E. Westcott (Ministry of Aviation), and had diameters and straightness better than ± 0·001 in. Adequate length is needed in order to allow the ions to settle into stable motion, which requires several r.f. cycles. This cannot be done by increasing v indefinitely, because of the dependence of power on v^5; similarly, r_0 cannot be increased indefinitely. Values of $v = 2{\cdot}8$ Mc/s and $r_0 = 0{\cdot}214$ in. were used. The working requirements for various masses are summarized in Table 1, on the basis of $C = 40$ pF and $Q = 40$. The largest allowed accelerating potential for input of ions to give $R = A$ is 400 V. The system is designed to have R up to 100 over a mass range of 1 to 140 for singly charged ions.

TABLE 1. CHARACTERISTICS OF QUADRUPOLE MASS ANALYSER

mass	V (volts)	U (volts)	power (watts)
130	2180	365	164
100	1675	281	97
50	835	140	24
20	334	56	4
10	167	28	1

This kind of instrument has a number of advantages over magnetic deflexion types for the present work. The mass scale is insensitive to the energy of incoming ions, and their energy distribution. The instrument may be operated at residual pressures up to 10^{-5} torr since ion path lengths are short and because mass selection is not affected by collision in which there is no mass exchange. It can be used with the same characteristics for negative and positive ions merely by reversing the accelerating potential. Transmission is high because of the absence of grids or narrow slits.

(*b*) *General arrangement*

A lateral cross-section of the general arrangement is shown in figure 1. The flame burns against a small hole (A), so that the sampled gases expand rapidly into the first vacuum chamber (B), which is maintained at $\leqslant 10^{-3}$ torr by a 6 in. Edwards silicone oil pump. For analysis of positive ions, the hollow conical first electrode (C) is maintained at about -80 V with respect to the earthed outer enclosure. This electrode rejects negative ions and selectively filters positive ions from neutral species. A roughly formed beam of positive ions consequently impinges on the entrance hole (diam. 1·0 mm) of the quadrupole housing (D). The pressure inside this housing and in the second chamber (E) is held at $< 10^{-5}$ torr by a 2 in. diffusion pump. Additional pumping is provided in both chambers by cold traps maintained at liquid nitrogen temperature. For the observation of positive ions the housing is at -200 V with respect to the frame. After entering this region the beam undergoes further expansion and the majority of the neutral species leave the stream of ions. These latter are both focused and shifted by the immersion lens (F) so as to pass through the aperture (G) (diameter, 0·015 to 0·040 in.), into the quadrupole field, the potential of this input hole being the same as that of the housing.

The ions are consequently separated from the neutral particles and are accelerated into the quadrupole field. The quadrupole rods are bored at the ends to accommodate boron nitride bushes, which also fit into holes jig-bored in brass mounting plates. The rods are thus mounted symmetrically and are insulated from each other and their supports. Opposite rods are connected by brass strips and the whole structure is given rigidity by four outer brass rods between the end plates. The housing, which is constructed from non-magnetic stainless steel and brass, alines the rod assembly with respect to the entrance hole system. Electrical connexions are made directly to terminals on the rods. The end plates, which have large holes in them to increase pumping speeds, are gold plated.

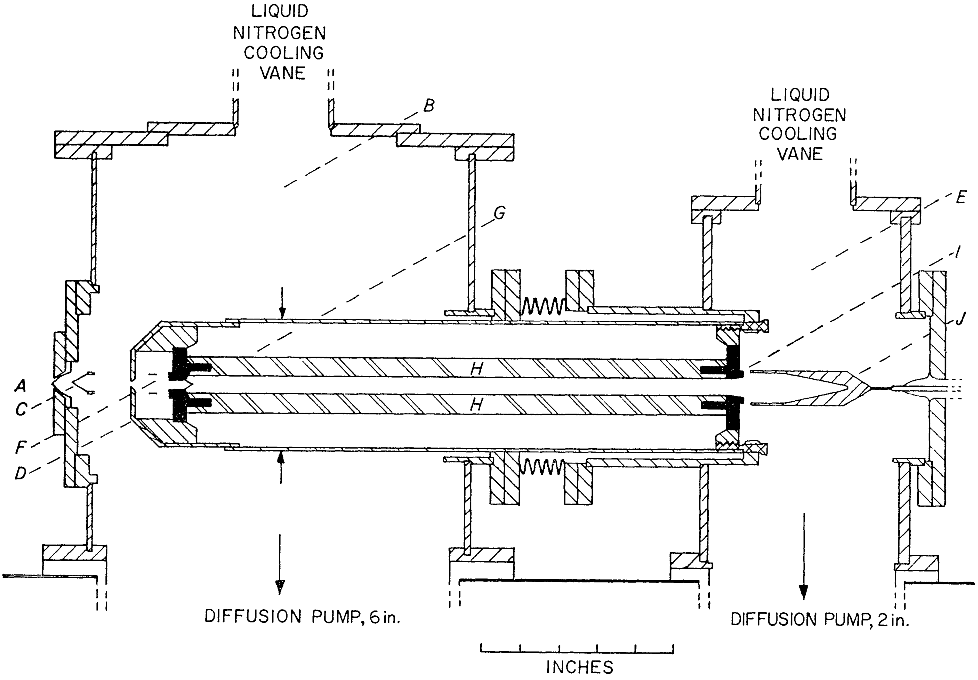

FIGURE 1. Sampling system and quadrupole mass-spectrometric analyser (diagrammatic).

The r.f. quadrupole supply is derived from a T 1190 A (Naval surplus) transmitter with a maximum output of 450 W, crystal stabilized at a frequency of 2·8 Mc/s. U and V are both constant to better than 1 %. A special r.f. stabilizer system was built for the transmitter, as well as a unit for controlling both U and V. The d.c. component is derived by rectification of the r.f. signal, and potential dividers are used to obtain the appropriate U/V for the required resolving power. The potential along the symmetry axis of the rod assembly is arranged to be equal to that of the housing. The mass spectrum is scanned manually by changing the output from the transmitter with the ratio U/V fixed. For resolving powers of 70 or less flat-topped peaks are obtained. Most measurements were made in this region. The line shape is almost triangular at higher resolving powers.

The problem of sampling is concerned principally with the situation at the primary entrance hole at A (figure 1). This orifice is at the apex of a thin 60° angle cone of electroformed nickel and has sharp edges, so as to minimize disturbance of the flame. Various cones had holes with diameters in the range 0·002 to 0·006 in. The holes were characterized by flow rates of air of 0·5 to 2·4 cm^3/s measured at atmospheric pressure and room temperature. The larger holes were big enough effectively to give a true sample of the ionized flame gases with only small contributions from boundary-layer gases. This is in line with previous experience (Bascombe, Green & Sugden 1962) that holes with flow rates greater than 1·3 cm^3/s gave little falsification of the sample. The nickel cones are mounted in a heavy brass plate with efficient water cooling via internal channels.

Despite the efforts made to give maximum pumping speed immediately behind this first sampling hole, ions are likely to undergo a few collisions with neutral molecules in the first chamber. This is not expected to be a serious disadvantage from the flame standpoint, since it constitutes a negligible extension of reactions already occurring in the flame gases at much greater rates. It does, however, result in a scattering of many ions, so that some do not enter the quadrupole housing and are thus lost to detection. Rough tests show that about 1 in 50 ions entering the first hole actually reach the detector.

This latter consists of a Faraday cup (J) kept at a potential of -50 V and directly connected to a vibrating reed electrometer (Electronic Instruments Ltd, mass spectrometer amplifier). The mass scale was calibrated by using flames with alkali metal additives, which give known positive ionic masses. Negative ions, which can be observed by reversal of the signs of all the potentials associated with the spectrometer, had an identical mass scale with that of the positive ions. The potentials quoted above correspond with good working conditions; they can all be varied over substantial ranges. Sensitivities of detection for positive and negative ions were almost the same. The spectrometer is capable of detecting ionic concentrations down to 10^5 cm^{-3} in the flame.

The principal operating difficulty is that of fouling of the electrodes by the flame gases, whereby surface layers and associated potentials build up. This can be combated successfully by frequent cleaning of the first electrode and the entrance hole to the second chamber. Gold plating of all vacuum parts close to the ion beam, except the stainless steel quadrupole rods, also helps to reduce the fouling tendencies.

(c) *Burner and flames*

The burner was a simple Pyrex capillary tube of internal diameter 2 mm, which when fed with premixed gases gave a single reaction cone about 1 cm in height, followed by a burnt gas zone some 10 cm long tapering to a point, because of entrainment of air, from a maximum diameter of almost 1 cm. The flame was burnt horizontally with its axis along the axis of symmetry of the quadrupole system, thus playing directly on the first sampling hole. The burner could be moved along this axis, for sampling at different points along the length of the flame.

Provision was made for atomization of small quantities of aqueous salt solutions into the flame gas supplies, as well as for saturation of a known part of the supply with vapours of organic halogen derivatives. The main gases used were ordinary cylinder supplies of hydrogen, oxygen and nitrogen, with facilities for addition of a small amount of an additional gas, such as acetylene.

Two basic flames were used in this work, their essential properties being given in table 2. The burnt gas temperatures derive from sodium *D*-line reversal measurements. The burnt gas compositions for equilibrium at these temperatures were

TABLE 2. FLAME GAS COMPOSITIONS AND TEMPERATURES

unburnt composition			temperature	equilibrium partial pressures (atm) in burnt gas					flow velocity of burnt gas
H_2 :	O_2 :	N_2 by vol.	(°K)	$[H_2O]$	$[H_2]$	[H]	[OH]	$[N_2]$	(cm/s)
4·0	1·0	4·0	2005	0·250	0·249	$8{\cdot}08 \times 10^{-4}$	$8{\cdot}02 \times 10^{-5}$	0·500	$1{\cdot}8 \times 10^{3}$
3·5	1·0	3·0	2270	0·302	0·226	$3{\cdot}96 \times 10^{-3}$	$8{\cdot}05 \times 10^{-4}$	0·454	$2{\cdot}6 \times 10^{3}$

calculated by using the data and methods given by Gaydon & Wolfhard (1960). It is known, however, that the actual values of [H] and [OH] considerably exceed the equilibrium ones given in the table, particularly for the cooler flame (Bulewicz, James & Sugden 1956). A difficulty with these simple unshielded flames is that entrainment of air modifies the burnt gases. This effect becomes serious along the axis further than 2 cm from the reaction zone. The burnt gas flow velocities of table 2 apply just downstream of the reaction zone.

3. RESULTS AND DISCUSSION FOR NEGATIVE IONS

No negative ions were detected when flames were burnt without additives. When aqueous M/100 potassium chloride was sprayed into the supply a large variety of negative ions were found in the cool sheath around the burnt gas. The results were very similar to those of Knewstubb & Sugden (1962), who did a similar experiment, and to those of Fite & Rutherford (1964) on afterglows in atmospheric gases. They will not be discussed in detail here, since they are not relevant to the properties of the hot flame gases and the reaction zone.

The only negative ions found in the hotter parts of the flames were OH^- and Cl^- (from the potassium chloride), and their concentrations at various points along the axis of the cooler flame are shown in figure 2, together with the values for K^+ ions—the predominant positively charged species. Because of charge balance the concentration of free electrons can be taken to be equal to that of K^+ ions within the first 3 cm from the reaction zone.

It is of interest to consider the mechanism by which negative ions are formed, at least in the first 2 cm or so downstream from the reaction zone before entrainment has had very severe effects on the flame gas composition. Two types of reaction may be considered, in the first place as balanced reversible processes—i.e. processes which are sufficiently fast for the concentrations to be related to the equilibrium constant in the normal way. They are:

(i) three-body recombination

$$Cl + e^- + M \rightleftharpoons Cl^- + M, \quad OH + e^- + M \rightleftharpoons OH^- + M;$$

and

(ii) dissociative attachment

$$HCl + e^- \rightleftharpoons Cl^- + H,$$
$$H_2O + e^- \rightleftharpoons OH^- + H.$$

They will lead to different balances because in general $[H] > [H]_e$. In the flame of figure 2 we have $[H] = 7[H]_e$ at 1 cm from the reaction zone. The chlorine is apportioned between HCl and Cl in the flame by the balanced reaction (Bulewicz, Phillips & Sugden 1961).

$$HCl + H \rightleftharpoons H_2 + Cl$$

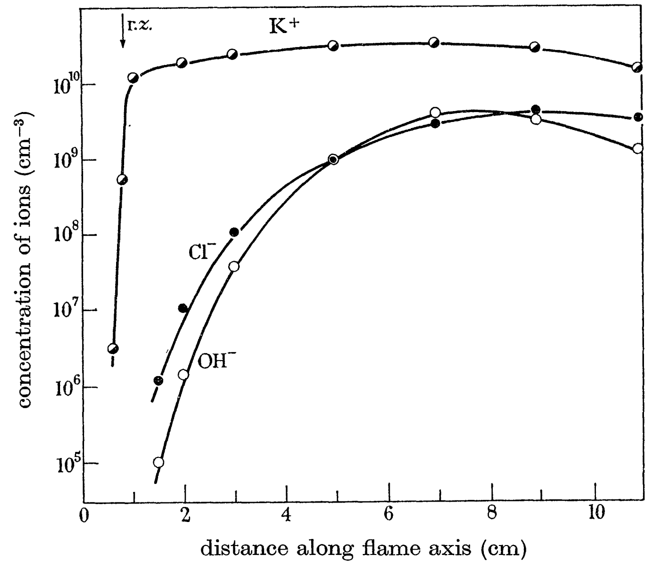

FIGURE 2. Positive and negative ions produced by addition of potassium chloride to a hydrogen flame at 2005 °K.

TABLE 3. OBSERVED AND CALCULATED (NEGATIVE ION/ELECTRON) RATIOS

The data relate to a distance of 1 cm downstream from the reaction zone in a flame with $H_2/O_2/N_2 = 4{\cdot}0/1{\cdot}0/4{\cdot}0$ at 2005 °K containing 2·3 parts in 10^7 of added potassium (chloride).

	observed value	equilibrium value	balance of three-body recombination	balance of dissociative attachment
$[Cl^-]/[e^-]$	3×10^{-4}	$1{\cdot}3 \times 10^{-3}$	$9{\cdot}1 \times 10^{-3}$	$1{\cdot}9 \times 10^{-4}$
$[OH^-]/[e^-]$	4×10^{-5}	$3{\cdot}4 \times 10^{-3}$	$2{\cdot}4 \times 10^{-2}$	$4{\cdot}8 \times 10^{-4}$

and calculations show that at 1 cm in the 2005 °K flame $[HCl]/[Cl] = 50/1$, giving $[Cl] = 1{\cdot}7 \times 10^{10}$ atoms/cm³ for M/100 KCl which supplies $8{\cdot}4 \times 10^{11}$ molecules/cm³ to the flame gases. The equilibrium value, $[Cl]_e$, is $2{\cdot}3 \times 10^9$ cm⁻³.

The values of $[Cl^-]/[e^-]$ and $[OH^-]/[e^-]$ at 1 cm from the reaction zone of the flame of figure 2 have been calculated on the basis of total equilibrium ($[H] = [H]_e$), balance of three-body recombination and balance of dissociative attachment respectively and are compared with observations in table 3.

Electron affinities of 83·3 kcal/mole (Berry & Reimann 1963) and 41 kcal/mole (Branscomb & Smith 1955) were taken for Cl and OH respectively. The latter value is rather uncertain. It will be seen that agreement between observation and calculation is good for dissociative attachment to form Cl^-. This is in agreement with very convincing arguments of a totally different nature advanced by Padley, Page & Sugden (1961). It also agrees with the observation from figure 2 that $[Cl^-]/[e^-]$ increases away from the reaction zone which, since [H] is decreasing in the same sense, is consistent with the changing balance of dissociative attachment but not with that of balance of three-body recombination.

The agreement with dissociative attachment balance for OH^- is less good, although much better than with the other predictions. Much better agreement would be obtained with an electron affinity of OH about 10 kcal/mole lower (30 kcal/mole). This kind of mechanism for OH^- is supported by the increase of $[OH^-]/[e^-]$ away from the reaction zone.

The prediction of rates of negative ion formation is hampered by lack of attachment rate constant data. If one takes the only available figure for 3-body attachment of about 10^{-30} cm^6/s, which is for the reaction $O_2 + e^- + O_2 \rightarrow O_2^- + O_2$ (Chanin, Phelps & Biondi 1962) as applying to Cl and OH in flames then the rates of formation of Cl^- and OH^- at 1 cm from the reaction zone are respectively about 10^9 cm^{-3}/s and 10^{14} cm^{-3}/s. In calculating these quantities it has been taken that $[Cl] = 2 \times 10^{10}$, $[OH] = 2 \times 10^{15}$, $[e^-] = 10^{10}$ and $[M] = 4 \times 10^{18}$ cm^{-3}. The reverse rates for collisional dissociation of negative ions, obtained via the equilibrium constants of the reaction are respectively 3×10^7 and 7×10^{10} s^{-1}. This suggests that this kind of reaction will not be balanced in the flame gases.

There are no data for the dissociative attachment reactions but it does not seem unreasonable to take a pre-exponential factor of 10^{-8} cm^3/s, which gives rate constants at 2005 °K of 10^{-10} and 10^{-16} cm^3/s for the reactions of electrons with HCl and H_2O molecules respectively, the activation energy being taken to be the same as the endothermicity. The rates of production of Cl^- and OH^- at 1 cm from the reaction zone then become 10^{12} cm^{-3}/s in both cases, and the rates of the reverse processes 10^{12} and 5×10^{10} cm^{-3}/s respectively.

These figures strongly support the dissociative attachment mechanism

$$HCl + e^- \rightleftharpoons Cl^- + H$$

as a near-balanced, dominant reaction for Cl^- production. The rates of the 3-body reaction are smaller by four orders of magnitude. The time available (order of 10^{-4} s) for near-equilibration of the observed population of Cl^- is ample.

The position is not so clear for OH^-, which the figures suggest is predominantly formed by three-body attachment, without equilibration. This is only explicable if the rate constant of $OH + e^- + M \rightarrow OH^- + M$ has been overestimated by at least two orders of magnitude, since it is found that more Cl^- than OH^- ions are formed. In that case, however, the dissociative mechanism would be becoming important. It would seem that, because of the nature of the situation ($[Cl] \ll [OH]$ but (electron affinity of Cl) $\gg$ (electron affinity of OH)), the rough estimates of rate constants are sufficient to give a clear prediction for Cl^- but not for OH^-.

4. Results for positive ions

Flames without additives showed a small number of positive ion peaks, all with maxima in the reaction zone. They are assignable to NH_4^+ (18), H_3O^+ (19), the first and second hydrates of H_3O^+ (37 and 55) and trace impurities of Na^+ (23) and K^+(39). H_3O^+ was dominant, with a peak concentration of about 10^8 ions/cm³. This ion is known to be a genuine flame ion (i.e. not to arise because of interactions with the sampling system) and to occur as a result of trace impurities of hydrocarbons in the gas supply (Green & Sugden 1963): about 50 parts in a million of such impurities would give rise to the observed amount. The other ions derive from H_3O^+; in particular the NH_4^+ ion is produced by proton exchange of H_3O^+ ions with NH_3 molecules formed by catalytic reaction on the sampling orifice. The very small amounts of NH_4^+ ion (10^6 ions/cm³) support the view that adequately large sampling holes were being used to give a good sample of genuine flame ions with little interference from boundary layer phenomena at the sampling hole (Bascombe *et al.* 1962).

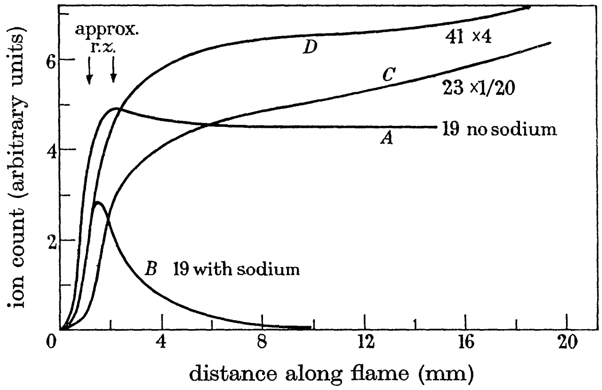

FIGURE 3. Positive ion concentrations for H_3O^+, Na^+ and $Na^+.H_2O$ in a hydrogen flame at 2005 °K.

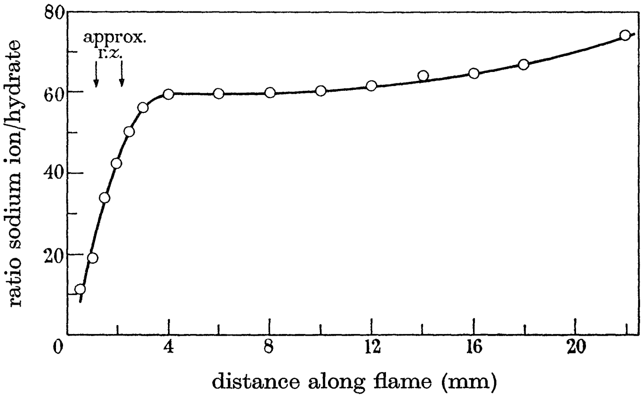

FIGURE 4. The ratio $[Na^+]/[Na^+.H_2O]$ as a function of distance along flame axis.

Addition of alkali elements A (as sprays of aqueous chlorides) gave the ions A^+ and, in smaller quantity, $A^+.H_2O$. The succeeding further two hydrates were found in very much smaller amounts. Figure 3 shows the results for sodium. The following features are noteworthy:

(i) The slow fall of H_3O^+ without added alkali and its rapid fall downstream from the reaction zone with alkali.

(ii) The very rapid rise of Na^+ (and its hydrate) in and near the reaction zone, followed by a much smaller, nearly linear increase with distance.

Figure 4 shows the variation of the ratio of the counts of Na^+ and $Na^+.H_2O$ with distance. This ratio is almost constant in the 1 cm immediately downstream of the reaction zone, i.e. in the region where the temperature is nearly constant and entrainment is negligible. Similar results were obtained for the other alkali elements. Figure 5 shows the result of adding small amounts of acetylene to the flame gas supply. It is evident that the ion concentration is greatly boosted in the reaction zone to a level from which it decays towards equilibrium.

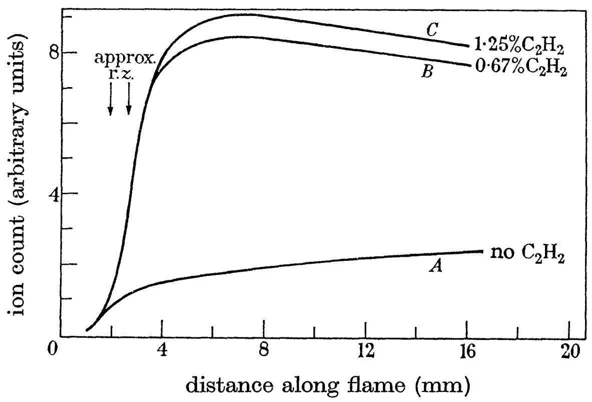

FIGURE 5. The effect of addition of acetylene to a hydrogen flame on the of Na^+ ions from added sodium.

5. HEATS OF FORMATION OF MONOHYDRATED ALKALI IONS

The constancy of the ratio $[A^+]/[A^+.H_2O]$ with distance over a restricted range of distance near the reaction zone in which temperature is nearly constant and entrainment negligible suggests that the equilibrium

$$A^+.H_2O \rightleftharpoons A^+ + H_2O$$

is being maintained. On this assumption equilibrium constants K have been derived for two temperatures and are shown in table 4. Application of the Second Law method based on two temperatures only gives ΔH values of 54, 27 and 40 kcal/mole for $A \equiv$ Li, Na, K respectively, but all with errors in the region of ± 20 kcal/mole.

A Third Law calculation has been attempted, which has, therefore, required an estimate of the rotational and vibrational parameters of the hydrated ions in order to estimate the entropy change in the reaction. The hydrates have been taken to have planar C_{2v} structures, with the O atom directed towards the A^+ ion, and separated from it by the ion-water molecule distances given by Moelwyn-Hughes (1957). Of the six vibration frequencies, three have been taken to be the same as those of the H_2O molecule, the others being essentially an A^+–O stretch ν_4, an A^+–(OH_2) bending frequency ν_5 and an out-of-plane vibration ν^9. These have been estimated very roughly by analogy with the large amount of data given by Herzberg (1960) for a wide variety of molecules. The parameters used are shown in table 5.

TABLE 4. EQUILIBRIUM CONSTANTS OF $A^+.H_2O \rightleftharpoons A^+ + H_2O$ AND HEATS OF REACTION

A	$[A^+]/[A^+.H_2O]$	Kp (molecule cm^{-3})	ΔE_0°	ΔH^0_{298} (total hydration)
(i) 2005 °K				
Li	2·4	$2{\cdot}2 \times 10^{18}$	45	118
Na	62	$5{\cdot}7 \times 10^{19}$	29	94·5
K	260	$2{\cdot}4 \times 10^{20}$	19	75
(ii) 2270 °K				
Li	12	$1{\cdot}2 \times 10^{19}$	43	118
Na	140	$1{\cdot}4 \times 10^{20}$	28	94·5
K	800	$7{\cdot}8 \times 10^{20}$	16	75

TABLE 5. ESTIMATED PARAMETERS OF $A^+.H_2O$ (C_{2v} SYMMETRY) O–H DISTANCE, HOH ANGLE AND ν_1, ν_2, ν_3 AS IN H_2O

A	A^+–O distance (Å)	ν_4 (cm^{-1})	ν_5 (cm^{-1})	ν_6 (cm^{-1})
Li	2·0	620	415	405
Na	2·3	450	375	365
K	3·0	400	345	335

The mean values of ΔE_0^0, the heat of reaction at 0 °K, obtained for these calculations are given in the penultimate column of table 4. The probable error is about ± 5 kcal/mole and derives mainly from the assumptions about the structure. The results from the two flames agree to within 3 kcal/mole, with mean values of 44, 28·5 and 17·5 kcal/mole for $A \equiv$ Li, Na, K respectively.

The final column of table 3 gives the total heats of hydration for infinite dilution in water, as quoted by Moelwyn-Hughes (1957). They are 3 to 4 times larger, as would be expected from a hydration shell of at least four molecules of water, but are in the same order. Finally, the general reasonableness of the figures is confirmed by a simple calculation which gives 30 kcal/mole for the energy of interaction of a point dipole of 1·82 debye (H_2O) with a single electronic charge situated 3 Å away on its axis.

6. THE INTERACTION OF H_3O^+ IONS WITH SODIUM

The recombination of H_3O^+ ions with electrons has been shown to be rapid, as would be consistent with a dissociative mechanism

$$H_3O^+ + e^- \rightarrow H_2O + H; \quad k_r.$$

Various workers have found k_r to be about $2 \times 10^{-7}\,\mathrm{cm^3/s}$ (King 1957; Calcote 1962; Green & Sugden 1963). Where both H_3O^+ and electrons are produced in equal amounts by traces of hydrocarbon impurity, and amount to a maximum of $10^8\,\mathrm{cm^{-3}}$ each in concentration, the rate of recombination will be very low, as shown in figure 2. The addition of sodium or other ionizable alkali raises other possibilities, however, by means of which the disappearance might become much faster. Figure 6 shows that the fall of $[H_3O^+]$ is first order in the ion itself. Two mechanisms are consistent with this:

$$\text{(i)}\quad H_3O^+ + e^- \rightarrow H_2O + H;\ k_r,$$

the electrons deriving from ionization of sodium by an independent method, and amounting to about $2 \times 10^9\,\mathrm{cm^{-3}}$ in the case of figure 3. Alternative products (not distinguishable in the circumstances) are $OH + H_2$.

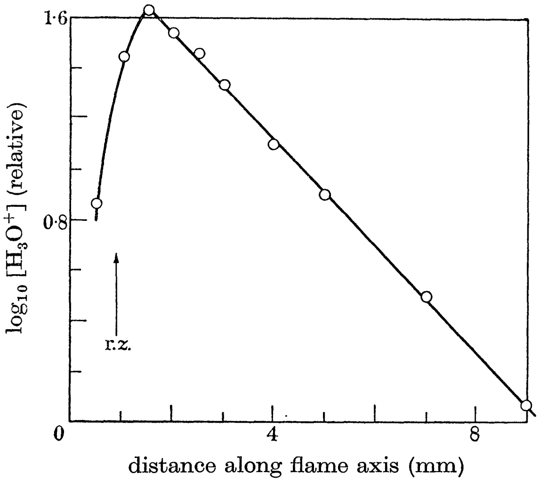

FIGURE 6. The first order disappearance of H_3O^+ in the burnt gas of a hydrogen flame with added sodium.

This yields $k_r = 4{\cdot}7 \times 10^{-6}\,\mathrm{cm^3\,s^{-1}}$, which is larger by a factor of 20 than the accepted value.

$$\text{(ii)}\quad H_3O^+ + Na \rightarrow H_2O + H + Na^+;\quad k_m$$

which with $[Na] = 8{\cdot}4 \times 10^{11}\,\mathrm{cm^{-3}}$ gives $k_m = 1{\cdot}1 \times 10^{-8}\,\mathrm{cm^3/s}$. Although there is no direct figure with which to compare this, it is of reasonable order of magnitude for an ion-molecule reaction of this simple type. It would not be possible to distinguish this reaction from

$$H_3O^+ + Na \rightarrow H + Na^+.H_2O$$

in the present system.

The exchange reaction would therefore seem to be preferred to the recombination reaction.

7. THE PRODUCTION OF SODIUM IONS IN THE REACTION ZONE

It is evident from figure 5 that addition of hydrocarbons gives a strong impetus to production of sodium ions in and near the reaction zone, which is quite evident in that figure and also in figure 3 for 'pure' hydrogen, which contains the order of

50 p/M of hydrocarbon impurity. Beyond the reaction zone the alkali ions are considered to arise from a process

$$A+M \rightarrow A^{+}+e^{-}+M,$$

possibly with intervention of a hydrate, which is associated with a very large collisional cross section, given an energy of activation equal to the ionization potential. It is evident that the boost in the reaction zone must come from an even faster reaction which is in some way linked with the ionization associated with the hydrocarbon (added or impurity) itself. One such process is that considered in § 6:

$$\mathrm{Na}+\mathrm{H_3O^+} \rightarrow \mathrm{Na^+}+\mathrm{H_2O}+\mathrm{H}; \quad k_m.$$

The most widely held current view of the formation of the H_3O^+ ions themselves is that they derive from CH radicals, possibly electronically excited, by the following mechanism (Green & Sugden 1963; Calcote 1962)

$$\mathrm{CH^{(*)}}+\mathrm{O} \rightarrow \mathrm{CHO^+}+e^-,$$

$$\mathrm{CHO^+}+\mathrm{H_2O} \rightarrow \mathrm{H_3O^+}+\mathrm{CO}.$$

The CH radicals appear in the reaction zone and do not persist beyond it.

Considering figure 3, the rate of production of H_3O^+ ions at the maximum of $[H_3O^+]$, in the absence of sodium, is

$$k_r[\mathrm{H_3O^+}]^2 \sim 2\times10^{-7}\times4\times10^{16} = 8\times10^{9}\,\mathrm{cm^{-3}/s} \quad ([\mathrm{H_3O}]_{\mathrm{max.}} \sim 2\times10^{8}\,\mathrm{cm^{-3}}),$$

whereas the rate of production of $[Na^+]$, which on the exchange (k_m) basis should not exceed this, is $10^{13}\,\mathrm{cm^{-3}/s}$, a very large discrepancy. Similarly, the rate of production of Na^+ ions at the maximum of $[H_3O^+]$ with added sodium should be $k_m[\mathrm{H_3O^+}]/[\mathrm{Na}] \sim 10^{-8}\times10^{8}\times8\times10^{11} \sim 10^{12}\,\mathrm{cm^{-3}}$, while the observed rate is about 6×10^{13}. Finally, the amount of Na^+ produced in the reaction zone exceeds the maximum value of $[H_3O^+]$ by a factor of at least 10. This would appear to rule out the exchange reaction as a major product of sodium ions.

A similar kind of reaction with other ion types produced by the hydrocarbon is ruled out since these have much smaller concentrations than that of H_3O^+, and would require impossibly large rate constants. A possibility which must be considered is that the electrons produced by the hydrocarbon (in the form of CH) are 'hot'—i.e. have a temperature higher than that of the surrounding gases. If the primary electrons are produced by

$$\mathrm{CH^*}(^2\Sigma)+\mathrm{O} \rightarrow \mathrm{CHO^+}+e^-$$

then 74 kcal/mole of energy are released, much of which could appear as translational energy of the electrons. This would dissipate rapidly, but might persist, having acquired a near-Boltzmann distribution, for long enough to influence the rate of ionization of sodium by

$$e^-+\mathrm{Na} \rightarrow 2e^-+\mathrm{Na^+}.$$

Observations on electron temperature are conflicting. Cozens & von Engel (1964), using a crude Langmuir probe system with a turbulent flame, claim values in the region of 10 000 °K, whereas Travers & Williams (1965), who have made more precise experiments with a triple probe system, conclude that the electron temperature is not significantly different from the thermal value. Further work, preferably by another method, is required.

The exchange of electronic energy with molecular vibrational energy is known to be efficient, and Cozens & von Engel (1964) have suggested that this exchange in 'collisions of the second kind' maintains electrons hot by interaction with vibrationally excited products or intermediates of combustion. There is no strong evidence to support the idea of a large degree of vibrational disequilibration in hydrogen flames, however, though it may be admitted that the amount necessary might be small. A process of collisional ionization of sodium ions, with an activation energy equal to the ionization potential (120 kcal/mole) is about 10^{10} times as fast at 10 000 °K as it is at 2000 °K. The factor is still as high as 10^3 with 2500 °K as the electron temperature.

In these terms the ideas of Cozens & von Engel appear viable as an explanation of the rapid rate of ionization of sodium in the reaction zone when hydrocarbon is present. The latter is necessary as the primary source of very hot electrons, where thermal equilibration is delayed by interaction with molecules with a small vibrational disequilibrium (e.g. OH radicals). It should be noted, however, that the sodium *D*-line reversal temperatures in the flame zone did not show anomalously high values, as might perhaps have been expected if this explanation were correct. Quantitative support for this hypothesis about a rather puzzling phenomenon is desirable.

8. Conclusions

The work has provided satisfactory explanation of the mechanism of formation of OH^- and Cl^- ions in flames, has given quantitative evidence about the stability of monohydrated ions such as $Na^+.H_2O$ at flame temperatures and has led to a rate constant for the reaction $Na + H_3O^+ \rightarrow Na^+ + H_2O + H$. It has revealed, but not fully explained, an anomalously high rate of production of alkali ions in the reaction zone.

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