

THE FLAME IONIZATION DETECTOR A THEORETICAL APPROACH

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The flame ionization detector of McWILLIAM AND DEWAR^{1,2} still lacks a comprehensive explanation of the various electrical and chemical phenomena observed. An attempt is made in the present paper to provide at least partial explanations of some of these phenomena by specific mechanisms.

The detector is, in general, sensitive to organic gases and vapours, and insensitive to the common inorganic gases and vapours. It can now be regarded as fairly certain that the response to organics is specifically associated with the carbon atoms. Although the process of ion formation is chemically very inefficient (perhaps 1 in 10^5) the ion collection efficiency can apparently be 100% efficient and the ion currents obtainable are more than adequate for most practical purposes of detection.

It is proposed to discuss the mechanisms of the detector under three headings:

1. Site of ion formation and charge separation.
2. Electric field effects in ion collection.
3. Mechanism of ion formation.

SITE OF ION FORMATION AND CHARGE SEPARATION

The flame burns either pure hydrogen or a mixture of an inert gas and hydrogen, usually in air, and is regarded as comprising three zones of conceptual importance, *viz.*, a gap between the jet and the base of the flame, where no combustion takes place; an ionization and charge separation zone probably corresponding to the inner cone; and the main volume of hot gases above the inner cone. The metal jet serves as one electrode, and a collecting electrode above the flame as the other.

Several considerations lead to the idea that the site of ion formation is a thin layer at the base of the flame. The insensitivity of the detector to carbon monoxide and dioxide suggests that the upper part of the flame will contribute nothing to ion formation from organic molecules, because the latter can hardly be supposed to survive as such for any distance at a temperature in the vicinity of 2000° , and surrounded by an atmosphere rich in oxygen and water vapour.

At the inner cone, however, the temperature is suddenly raised from ambient to well over 1000° , and in this very restricted region it is supposed that the rare event of ion formation takes place.

If an electric field is now applied between the jet and the collector, charge separation takes place at the site of ion formation. Ions of one polarity then cross the cold gap and reach the jet, those of the opposite polarity remain in the flame initially, and eventually may be collected (possibly after chemical re-arrangement or exchange in the flame).

These concepts, if true, lead to several interesting consequences. Let us suppose, for convenience, that the jet is positive and that the field applied is sufficient to cause complete separation at the site of formation of all ions formed. Positive ions now inhabit the upper part of the flame without corresponding negative ions (electrons) with which to recombine, and consequently their residence time before collection does not affect the total ion current. They do, however, constitute a space charge which will modify the electric field in proportion to their concentration. In high concentrations they will also, by mutual repulsion, tend to fan outwards and some may miss the upper electrode altogether if it does not subtend a large enough angle at the jet tip. Finally, if charge separation is to take place at the base of the flame, then this is the place where the electric field should, if possible, be concentrated for the best effect.

The hypothesis that formation of ions takes place in a thin zone at the inner cone of the flame is supported by the work of KINBARA AND NAKAMURA, as quoted by ONGKIEHONG³, on hydrocarbon flames.

The results of changing the shape of the collector electrode in such a way that the electric field is concentrated around the jet tip, as discussed below, are regarded as supporting the idea that the base of the flame is the site of ion formation and charge separation.

ELECTRIC FIELD EFFECTS

A considerable variety of collector electrode shapes have been used by various workers—rods, wires, rings and gauzes, for example. At adequate voltages these give sensitive and sometimes linear responses to small amounts of organics. McWILLIAM⁴ has shown, however, that the geometry of the upper electrode is very much concerned with extending linear response into the high concentration region. In his work he used a gauze square and found that if this was placed sufficiently close (5 mm) to the jet the linear range could be extended to concentrations of ethylene at least of several per cent, whereas if the electrode was raised much above 5 mm the response fell off progressively from linear as the concentration increased, indicating a complete loss of some of the ions available.

These effects can be explained by the mutual repulsion of the ions as discussed above. At the author's suggestion, McWILLIAM tried the effect of a cylindrical hat-shaped gauze electrode. Although placed so that the crown of the hat was much more than 5 mm above the flame, this gave results as good as those obtained with the close flat electrode, the sides of the hat preventing the escape of mutually repelling ions. The lower edge of the cylinder was approximately level with the tip of the jet. As a rough guide, it seems that the upper electrode periphery should subtend an angle

of at least 90° at the tip of the jet in order to get linear response over the whole range of concentrations up to at least 5% of a light gas. Still higher concentrations can be tolerated with an upper electrode of optimum design, as discussed below. The voltage required for linear response with a suitable electrode increases with sample concentration, but no practicable increase of voltage will compensate for an electrode design which is inherently inadequate for high concentrations.

The shape and position of the upper electrode also affects the relations between current and voltage at voltages below that required for maximum current, and these relations are not the same when the polarity is reversed, as shown by DESTY *et al.*⁵ at low sample concentrations and by McWILLIAM⁴ at high ones. DESTY has suggested that the polarity differences are related to the relative mobilities of the positive ions and electrons and the consequent differences in space charge effects. This is undoubtedly true, but DESTY found a curious kink in the curves when the jet is positive which is not explained, although he has speculated that it may be caused by two different species of positive ion.

In the author's view the kink and other features of the voltage-response curves can be explained entirely by the effects of space charge on the distribution of the electric field. As mentioned above, the efficiency of charge separation is regarded as a function of the field intensity immediately above the jet. Now with a jet consisting of a thin tube there is, in the absence of space charge, a concentration of field just above the tip, as shown schematically in Fig. 1a. The effect of a space charge formed in the main body of the flame will be a tendency to lift the equipotential lines away from the tip and to distribute them more evenly in the space between the two electrodes. The first incidence of space charge as the voltage is increased from zero thus affects the field at the crucial point rather sensitively. When the space charge has built up to the point where the field is more or less uniform between the electrodes, further increase of voltage causes an approximately linear increase in the field and the response rises again to saturation. The kink is not observed when the jet is negative because the much higher mobility of the electrons reduces the space charge in the body of the flame, although as DESTY's curves show, there is a small effect from the electron space charge which is shown up by changing the geometry of the upper electrode. If the upper electrode is optimally designed the saturation voltage with positive jet is always less than with negative jet, as will be shown, and this is believed to be explained by the difficulty of moving the massive positive ions counter-current to the gas stream flowing at about 5 m/sec at the jet exit.

Experimentally, the concept of field distortion by the geometry of the electrodes has been supported by the author's experiments with collector electrodes designed to exaggerate the distortion up to a practical limit. These electrodes consisted of gauze cylinders of various diameters, closed at the top, and placed so that the jet, in the extreme case of the narrowest cylinder, was well up inside the cylinder. It was reasoned that the equipotential lines should be distributed in the manner shown schematically in Fig. 1b. Using a steady sample concentration from *n*-hexane at dry ice temperature, a carrier gas of 50/50 N_2/H_2 mixture and a 23 gauge hypodermic

needle tube for the jet, the minimum positive jet voltage required for saturation current decreased from 70 for a flat disc 1 cm above the jet to 10 for the narrowest cylinder, and the kink, which was very evident with the flat disc electrode, only showed as a slight decrease in slope.

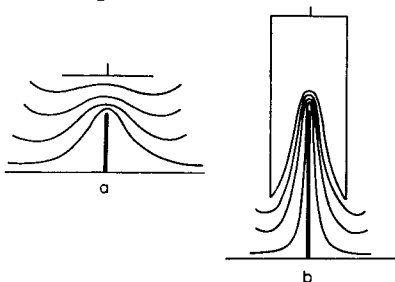


Fig. 1. Schematic representation of equipotential lines for two electrode shapes.

If the ions formed in the reaction zone are regarded as randomly distributed in velocity and direction then those with high velocities in the right direction should be easily extracted and those with high velocities in the wrong direction should be difficult to extract. The overall effect on response, as voltage is increased from zero, and in the absence of space charge effects, should correspond to the integral of the Gaussian function. In Fig. 2, a plot of this integral from tabulated values, and adjusted to fit at zero and at saturation, is shown superimposed on the response curve using the long narrow cylinder electrode. The fit is exact up to half saturation, and the deviation above this point is taken to be a measure of the residual space charge effect. At lower concentrations, the fit is better still.

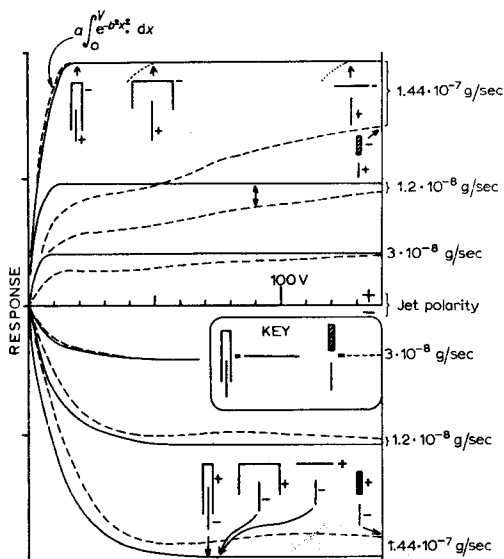


Fig. 2. Response vs. voltage for narrow cylindrical gauze electrode (solid lines) and vertical rod (broken lines) for three concentrations. Saturation voltages required for other electrodes also indicated, and relation to Gaussian function shown for one curve.

An interesting question arises with hollow cylindrical electrodes, namely the fate of ions which have passed through the equipotential line corresponding to the upper electrode potential itself, and have thus entered the Faraday cage region. It might be thought that a large dead volume in the Faraday cage would cause a lag in response time, but actually an ion which has entered the cage is already effectively collected as far as the electrical circuit is concerned, and its physical contact with the metal can take place at leisure.

It follows from this reasoning that the narrow hollow cylindrical electrode should indeed have the fastest response time because the upper electrode (represented in effect by its equipotential line) is very close to the jet and hence very close to the reaction zone. The response time in terms of the resolution of a series of spike pulses of sample will depend on the time required to clear the field of the ions formed at each pulse. The clearance function should be Gaussian and theory would indicate that resolution should improve as voltage is increased, even above that required for saturation. In practice, the resolution is usually governed not by the ion collection rate but by the time constant of the electrical circuit, which is quite appreciable with multi-megohm resistors and unavoidable stray capacitance. The residence time in the reaction zone of organic molecules entering with the carrier gas stream is quite short. Thus, if the inner cross section of the jet is 0.1 mm^2 and the gas rate is 30 c.c./min, the issuing velocity is 5 m/sec. If the reaction zone is say 1 mm deep, (it may be much less) the residence time is thus about 0.2 msec, during which a sample molecule must either form an ion pair or be destroyed without yield.

In Fig. 2 a comparison is made of the response *vs.* voltage curves, at three moderately low concentrations in the range $3 \cdot 10^{-8}$ to 10^{-7} g/sec, for electrodes of two extreme types, *viz.* a flat-ended vertical rod and a narrow gauze cylinder, each for positive and negative jet polarities. It will be seen from the traces that although the rod is as good as the cylinder for low concentrations (with negative jet), its performance falls away remarkably at high concentrations and it requires much higher voltages to achieve the true saturation current. With positive jet the rod produces kinks on the ascending portion of the response curve, as observed by DESTY. With negative jet, kinks are also produced at voltages higher than those which at first sight produce the saturation current and the current actually decreases with increasing voltage over a certain voltage range. This is a genuine and reproducible effect only observed with the rod and is perhaps explained as follows:

At low to moderate voltages the vertical surfaces of the rod, for some distance above the base plane, collect electrons which miss the base plane. As the voltage rises still further, the collection area moves downwards towards the base plane and a "mushroom" of space charge is formed about the latter. Some of the outer fringe of electrons are thus deflected outwards still further and are too far removed from the vertical surfaces for collection: they thus escape altogether.

At higher sample concentrations, the narrow gauze cylinder with positive jet is far better than all other shapes tried, both with respect to the lower voltages required for saturation current and the extension of linear response to very high

concentrations. For capillary column work, 20 V would suffice in most cases, for samples up to a few micrograms. In the range above 1% sample concentration at the detector, response appeared sensibly linear up to 17% ethylene, the highest concentration tried, at a voltage of 320. Few, if any, katharometers give linear response in these high ranges. No other electrode system tried showed any possibility of reaching saturation current in the highest range, at least without extremely high voltages. The precision of the linear relationship has not been measured over the complete range of concentrations, taken as a whole, from the lowest to the highest. To check this would require accurate chemical and electrical calibrations at the extreme ends of the concentration scale on the same instrument. Although perhaps few people would expect to extrapolate over a range of 10,000 to 1, the utility of being able to do so is considerable, since the major components can be used to calibrate the minor ones.

Fig. 3 shows the voltages required for saturation current for the rod and narrow cylinder electrodes over the concentration range from 10^{-8} to 10^{-4} g/sec for positive and negative jet potentials. Wide cylinders, and discs, with positive jet potential, give curves intermediate between the extremes of the rod and narrow cylinder but

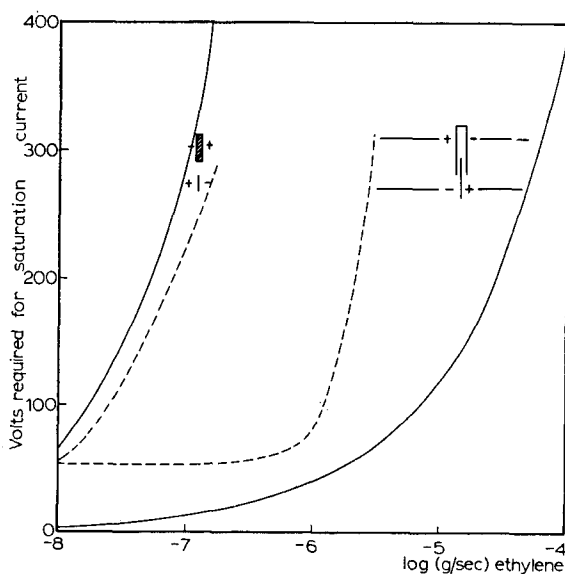


Fig. 3. Sample rate vs. voltage required for saturation current.

with negative polarity they give initially almost identical flat portions (at 40 V) up to about 10^{-7} g/sec, which then turn sharply upwards in the same manner as the narrow cylinder curve, but at a concentration about a factor of 2 lower. The flat initial portion of these curves, showing independence of concentration, represents the counter-current effect mentioned above. The sharp turn upwards must represent the onset of space charge effects. The sharpness of the upturn, as compared with the more gradual rise when the jet is positive, may possibly be accounted for by

the fact that although electron diffusion is not much hindered by the presence of gas, electron motion upwards is also not much assisted by the upward flow of the gas. The opposite holds for the positive ions, which are assisted in their upward passage by the gas stream. Total gas velocity should thus affect the shape of the curves, including effects due to the velocity of the ventilation air.

MECHANISM OF ION FORMATION

It is evident from MÜLLER's work⁷ that the electric field itself cannot produce ions in the flame detector from any ordinary molecule with an ionization potential of the order of 10 eV, since this would require a field of the order of 100 MV/cm, while the available field in the flame is usually only a few hundred volts per cm.

The problem then is to find a thermal or thermochemical mechanism which is specific for carbon atoms which are initially in particular environments (organic molecules). The hydrogen possibly contributes nothing but a high temperature. Hydrocarbons alone burning in air give large ion yields. On the other hand, carbon monoxide has been shown in this laboratory to be useless as the combustion gas and to give a very low background current, while in a hydrogen flame it is said by ONGKIEHONG³ to give a weak signal.

The very wide range of linearity observed with the hydrogen flame ionization detector seems in the author's view to exclude on the grounds of reaction kinetics any mechanism requiring the collision or co-operation of even two carbon atoms per ionization event, let alone the formation of a large assembly. It might be possible to concede a two-carbon reaction if methane and other single-carbon molecules behaved differently from those containing two or more carbons, but this is not observed, and methane is as sensitively detected at low concentrations as are the higher hydrocarbons.

We are driven to suppose then that all or most of the carbon atoms in organic molecules have each a certain though low probability of reacting to form an ion pair, and that the reaction must take place, if it takes place at all, during a residence time between about a tenth and one millisecond at a temperature between ambient and about 2000°.

There are few clues regarding the nature of the ion formation process. We know that simple inorganic gases and vapours do not yield ions, that organic substances in general do give responses, including carbon tetrachloride and dichlorodifluoromethane, and that organic molecules containing carbon linked to oxygen show some relative reduction in ion yield. Thus ONGKIEHONG³ suggests a rule for discounting such carbons in calculating ion yields.

There are two exceptions, recently discovered in this laboratory, to the general rules regarding inorganic and organic responses. MCWILLIAM⁴ has found, contrary to the usually accepted finding, that carbon disulphide does give a response at very low concentrations, although of a very peculiar kind limited by a unique self-suppressing effect at higher concentrations. Also, the author has found that formic

acid gives no measurable response even from the saturated vapour at room temperature (about 2%). (These two liquids, together with water, thus offer three convenient solvents for introducing trace samples without interference to the record).

The discovery of the lack of response to formic acid followed from a theoretical speculation that formic acid might be the species responsible for the primary ion-forming reaction, by chemical dissociation into formate-ion and a proton aided by the high exothermic reaction of the proton with a water molecule to form H_3O^+ . If this hypothesis were true, the response to formic acid vapour should have shown a considerable enhancement. The complete lack of response, taken in conjunction with observations regarding the reduced response of other partly oxidised molecules, suggests that the energy of oxidation of the carbon atoms is in some way connected with the ionization phenomenon. In formic acid, the carbon is as highly oxidised as it can be, short of forming carbon dioxide.

If we consider the changes in bond energies involved in forming carbon dioxide from carbon atoms, disregarding completely the bond energies of any links broken in the process of oxidation, we have—from values listed by COTTRELL⁶, the following rough picture:

Hydrocarbon C:	Full bond energy of $CO_2 = 2 \times 192 = 384$ kcal/mol
Alcohol C:	$384 - 85.5 = 298.5$ kcal/mol
Ketone C:	$384 - 179 = 205$ kcal/mol
Carboxyl C:	$384 - 85.5 - 179 = 119.5$ kcal/mol

We know from the formic acid experiment that carboxyl carbons contribute nothing, in one case at least. We also have the observations of ONGKIEHONG and others that ketone carbons must be either partly or wholly discounted. Carbon monoxide should be in a similar category on the above theory, and in fact gives only a weak response, according to ONGKIEHONG. Methanol gives a sensitive response, probably less, however, than methane on a molar basis. Carbon tetrachloride on this hypothesis should give the same molar response as methane, whereas in fact it gives probably about half this: the rule can thus not be applied in any strict quantitative sense, but it may be an approximation to the truth and indicate the order of energy required in the ion formation. The reasons for neglecting the energy of other bonds broken in the oxidation process are firstly that in the present state of knowledge the available quantitative data are not adequate for more than rough qualitative speculation and secondly that DESTY's results for benzene and cyclohexane, which gave almost identical molar responses, suggest that bonds (other than to oxygen) can vary considerably without a very marked effect. The quite sensitive response of carbon tetrachloride indicates lack of necessity for any special kind of pre-existing bond, *e.g.* C—H or C—C. It may be that carbon atoms destined to be involved in ion formation are already stripped of one or more of their attachments by thermal cracking. The essential step in ion formation may be an electronic transition of low probability in an excited CO_2 molecule, the energy of excitation being provided by the oxidation process.

If complete oxidation of carbon atoms in a short time in a restricted space is a pre-requisite to ion formation, the physical accessibility of the carbon atoms to collision by high velocity oxygen molecules, leading to a one-step formation of CO_2 , may be of importance. Thus methyl groups would be more accessible than CH_2 groups, and tertiary and quaternary carbons would be perhaps in effect inaccessible. If the probability of reaction is favoured by greater accessibility to oxygen attack, then one might expect differences in sensitivity due to this factor to be decreased when oxygen is in free supply and to be accentuated under conditions of oxygen starvation. DESTY'S⁵ results for eleven hydrocarbons have been examined to see whether a correlation can be found between physical accessibility and response, with results that appear to be interesting though not conclusive. The series is too short for sufficient independent checks of the quantitative theory, which had to be evolved step by step by working through the list, making "rules" to suit the observed responses. The fit is thus partly or wholly Procrustean in all except one case. Nevertheless, the "rules" seem logically defensible, qualitatively speaking, albeit the arguments may sometimes seem rather fine-spun. This series is the longest available to the author in which the measurements are all expressed in absolute terms and independent of integration errors and of reference to relative values.

Starting the series with the straight chain C_6 , C_7 and C_8 hydrocarbons, it was assumed that the methyl groups would contribute more than the CH_2 's. The calculation can thus be performed in terms of the "apparent CH_3 value" of each carbon, giving this a value unity for CH_3 itself. The observed responses for this series were 0.510, 0.579 and 0.640 coulombs/mole respectively. By trial and error, the apparent CH_3 value of the CH_2 's was found to be approximately 0.5 for a good fit. Thus we have

$$\begin{aligned} n\text{-Hexane: } & 2 + (4 \times 0.5) = 4 \text{ CH}_3: 0.1274 \text{ coulombs/CH}_3 \\ n\text{-Heptane: } & 2 + (5 \times 0.5) = 4.5 \text{ CH}_3: 0.1286 \text{ coulombs/CH}_3 \\ n\text{-Octane: } & 2 + (6 \times 0.5) = 5 \text{ CH}_3: 0.1280 \text{ coulombs/CH}_3 \\ & \text{Average } 0.1280 \text{ coulombs/CH}_3 \end{aligned}$$

The next in the series are cyclohexane, methylcyclohexane, and ethylcyclohexane, which had responses 0.492, 0.537, 0.603 coulombs/mole. If we apply the rule as above (for $6 \times 0.5 = 3 \text{ CH}_3$) to cyclohexane, the coulombs/ CH_3 obtained is much too large, *viz.* $0.492 \div 3 = 0.1640$. Now benzene, with response almost identical at 0.495, would show the same effect, and we are required empirically to add an average of 0.85 CH_3 to the 3 CH_3 for cyclohexane and benzene giving 3.85 CH_3 for each, and yielding coulombs/ CH_3 0.1278 for cyclohexane, 0.1286 for benzene.

The extra CH_3 value is accounted for in the theory by a "bending outward effect", all the ring carbons being less capable of concealment by their neighbours, as compared with the CH_2 's in the straight chain compounds, which in certain foldings are more concealed by their neighbours than are the ring carbons. The value 0.85 is equivalent to 0.142 CH_3 per ring carbon: each ring carbon thus is valued at 0.642 CH_3 groups. Passing now to methylcyclohexane, and only introducing the

new concept that the tertiary carbon is valueless, we have the following:

$$\begin{array}{rcl}
 5 \text{ carbons at } 0.5 \text{ each} & = & 2.5 \\
 5 \text{ carbons at } 0.142 \text{ each} & = & 0.71 \text{ (bending outward effect)} \\
 1 \text{ carbon at } 1 & = & 1.00 \text{ (CH}_3\text{)} \\
 1 \text{ carbon at } 0 & = & 0.0 \text{ (tertiary C)} \\
 \hline
 \text{Total } 4.21 \text{ CH}_3\text{: coulombs/CH}_3 & & 0.1273 \\
 \text{Deviation from } 0.1280 & & -0.55 \%
 \end{array}$$

Similarly for ethylcyclohexane, we have

$$\begin{array}{rcl}
 5 \text{ carbons at } 0.5 & = & 2.5 \text{ (ring)} \\
 5 \text{ carbons at } 0.142 & = & 0.71 \text{ (bending outward effect)} \\
 1 \text{ carbon at } 0.5 & = & 0.5 \text{ (side chain CH}_2\text{)} \\
 1 \text{ carbon at } 1.0 & = & 1.0 \text{ (CH}_3\text{)} \\
 1 \text{ carbon at } 0 & = & 0.0 \text{ (tertiary C)} \\
 \hline
 \text{Total } 4.71 \text{ CH}_3\text{: coulombs/CH}_3 & & 0.1277 \\
 \text{Deviation from } 0.1280 & & -0.23 \%
 \end{array}$$

(This is the only compound in the whole series for which new concepts were not necessary.)

The aromatics were puzzling, with benzene practically indistinguishable from cyclohexane, but toluene and ethylbenzene not showing nearly the increases expected for the side chains. The respective responses were 0.495, 0.508, 0.535 coulombs/mole. On the accessibility hypothesis, it seemed that the aromatic ring was shielding the side chain from collision with oxygen molecules much more than the ring in the cyclohexane series. Assuming that this is so, can one explain the considerable shielding effect on the second carbon in the side chain in ethylbenzene? A model shows that for most of the time this carbon is in fact out of the plane of the ring and is shadowed by it over a considerable solid angle, but why the aromatic ring should do this and not the aliphatic ring is another matter. This might be explained by the greater thermal stability of the aromatic ring, which would enable it to remain intact for a longer time, implying also that the cyclohexane ring is sometimes at least already partly disintegrated at the crucial moment. The effect of 30 % oxygen added to the hydrogen by DESTY, which obliterated the relative reduction in response of toluene compared with *n*-heptane, may thus be explained by the increase in flame temperature, or by the greater chances of a suitable collision in the presence of ample oxygen, so that shielding effects become statistically less rate-determining.

Toluene can be pulled into line by multiplying the value for the side chain carbon by a shielding factor of 0.75. Thus we have

$$\begin{array}{rcl}
 \text{Toluene: } 5 \times 0.642 & = & 3.21 \text{ (ring + bending outward)} \\
 1 \times 0.75 & = & 0.75 \text{ (shielded CH}_3\text{)} \\
 1 \times 0 & = & 0.0 \text{ (tertiary C)} \\
 \hline
 & & 3.96 \text{ CH}_3\text{: coulombs/CH}_3, 0.1280
 \end{array}$$

In the case of ethylbenzene, the shielding factor for the CH_3 is required by the observed response to be greater still, the suggestion being that the ring shadow is greater for an out-of-plane attachment: the factor required is 0.585.

$$\begin{array}{rcl}
 \text{Ethylbenzene: } 5 \times 0.642 & = & 3.21 \\
 1 \times 0.585 & = & 0.585 \text{ (out-of-plane shielded CH}_3\text{)} \\
 0.5 \times 0.75 & = & 0.375 \text{ (in-plane shielded CH}_2\text{)} \\
 1 \times 0 & = & 0.0 \text{ (tertiary C)} \\
 \hline
 4.170 \text{ CH}_3\text{: coulombs/CH}_3\text{, } 0.1280
 \end{array}$$

Turning finally to the two highly branched paraffins, 2,2,3-trimethylbutane and 2,2,4-trimethylpentane, with response factors 0.597 and 0.720 coulombs/mole respectively, we find enhanced response as expected, corresponding to the large number of methyl groups, each having five. The actual response of 2,2,3-trimethylbutane is, however, about 7% lower than expected for five methyl groups (ignoring the quaternary and tertiary carbons). A model shows that the methyl groups are so crowded together that their hydrogen atoms could be imagined to have an appreciable mutual shielding effect on the adjacent methyl carbons. An average reduction of 7% in the value of each methyl group is required to account for the reduction in response.

The response of 2,2,4-trimethylpentane is by contrast 2.3% higher than expected for five methyl groups plus one CH_2 . In this molecule the methyl groups are much less crowded, and also the CH_2 is always "bent outwards". Allowing for the latter, we have

$$\begin{array}{rcl}
 5 \times 1 & = & 5 \text{ (normal CH}_3\text{)} \\
 1 \times 0.642 & = & 0.642 \text{ (bending outward CH}_2\text{)} \\
 2 \times 0 & = & 0 \text{ (tertiary and quaternary C)} \\
 \hline
 5.642 \text{ CH}_3\text{: coulombs/CH}_3\text{, } 0.1280
 \end{array}$$

Whatever the true explanation of response variations may be, it is evident that under the conditions of DESTY's detector the "rules" are likely to be inconveniently complicated for practical use in the precise prediction of response factors. On the other hand, ONGKIEHONG's results seem to fit simpler rules in some cases. DESTY himself found that adding oxygen to the hydrogen decreased the discrepancy between toluene and *n*-heptane. It is not perhaps unreasonable to suppose, on the accessibility hypothesis, that the "rules" may be simpler when oxygen is in very free supply. DESTY's burner consisted of a rather massive platinum tip which would restrict access of air from below the orifice, as compared with a hypodermic needle. Also, he normally used pure hydrogen which has both a very high flame velocity and outward diffusion rate, so that again the flame would cover the jet at the tip over a wide area and render difficult the access of oxygen to the inner cone. It would be interesting to have a comparable and preferably longer series done with a very fine "fish-tail" jet designed for maximum access of air to all parts of the flame at the base, or with a needle jet with Bunsen effect. The improvement in response obtained by the addition of nitrogen when using needle jets may be explained also by greater

accessibility of oxygen at the base of the flame because the lower flame velocity would lift the base of the flame off the jet, as indeed it visibly appears to do when sufficient organic substance is present to make the flame visible.

It is to be hoped that more data, expressed in absolute terms, will become available, especially on the effect of burner design and gas composition on the simplicity or otherwise of sensitivity relationships, and on the effect of oxygen bonds in various environments on absolute responses. The transition in sensitivity in passing from the lower to the higher members of homologous series would also be most useful in the construction of a rational theory.

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SUMMARY

An analysis is presented of the reasons for various changes in the response of the flame ionization detector with respect to electrode geometry and molecular structure of sample species. The electrode geometry affects the distribution of the electric field at the base of the flame, where ionization and charge separation are believed to occur, and also affects the incidence of space charge effects on the electric field. The hypothesis is put forward that one-step oxidation of carbon atoms to CO_2 is essential in ion formation, and that molecular geometry affects the probability of this occurring.

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