

Methane Formation by Flame-Generated Hydrogen Atoms in the Flame Ionization Detector

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The precombustion degradation of organic compounds in the flame ionization detector has been studied (1) by heating the additives in hydrogen in a quartz capillary and analyzing the reaction products by GC and (2) by following the degradation of the additives in a hydrogen flame, by means of a thin fused silica probe inserted from the bottom of the flame and connected to the ion source of a mass spectrometer. The results show that the thermic hydrogenolysis of hydrocarbons at flame temperatures produces mixtures of methane, ethene, and ethyne. In the flame, however, ethyne, benzene, isobutane, and conceivably all hydrocarbons are quantitatively converted into methane at temperatures below 600 °C, that is, before the proper combustion has started. The splitting of the C–C bonds is preceded by hydrogenation of double and triple bonds and aromatic rings. The reactions, no doubt, are caused by hydrogen atoms, which are formed in the burning hydrogen and which diffuse into the inner core of the flame. The quantitative formation of methane appears to explain the “equal per carbon” rule for the detector response of hydrocarbons, since all carbons are “exchanged” for methane molecules.

The flame ionization detector (FID) for gas chromatography, which depends on ion production when additives are burned in a hydrogen flame, has been used for about 40 years, but the chemical and physical processes by which it operates are still not known in detail.^{1–4} In particular, there is no definitive explanation of the rule of “equal per carbon response”, according to which the molar response of a hydrocarbon is directly proportional to its number of carbon atoms.

Because of the equal per carbon rule and because the response of the FID is linearly correlated to concentration over a wide range, it has normally been assumed that molecules are cracked in the flame into the same one-carbon fragments before ionization takes place. Thus, Sternberg et al.¹ suggested an equilibrium mixture of several one-carbon fragments from all additives. Blades^{2,3} assumed that the methyl radical was the universal one-carbon fragment, while Nicholson,⁴ on the basis of a kinetic analysis, suggested that the common one-carbon fragment for alkanes was methane but declared that “ethene and ethyne are exceptions, which do not degrade to methane in the FID.”

Additives with functional groups have smaller ratios of molar response (RMRs) than the number of carbons would indicate, the effective carbon number (ECN) being diminished.^{1,5,6} The chemical basis for this is expected to be related to the cracking process.

In a hydrogen diffusion flame such as that used in the FID, the fuel (hydrogen + additive), after leaving the jet, forms an inner cone of reducing gas, which is heated by the surrounding flame and reaches temperatures up to ~1400 °C, before it is attacked by the diffusing oxygen in the reaction zone. According to Nicholson, this temperature is sustained for 100 μ s. It has been thought that the additives in the anaerobic zone are cracked and hydrogenated to small molecules and/or radicals, which are then attacked by oxygen and oxygen-containing radicals.

Using rate data from the literature, Nicholson predicted the outcome of this cracking process for simple alkanes; for example, ethane, propane, and butane would be transformed almost quantitatively to methane.

Nicholson, however, was unable to predict the fate of more complex molecules, and it was therefore thought to be of interest to take a closer look at the anaerobic phase of the combustion by suitable procedures and to study the decomposition patterns for various additives by experiment.

The possibility that the precombustion degradation is caused by the high temperature, which is reached before the combustion, was tested by leading the additives in a large excess of hydrogen through a thin quartz capillary heated to about 1400 °C in a hydrogen flame. The gases from the outlet were collected over water and studied by GC and IR.

The importance of the surrounding burning hydrogen for the degradation process was studied by burning hydrogen with additives in air as in a normal FID. A fine (0.11 mm i.d.) movable fused silica capillary was introduced from the bottom of the burner through the orifice into the lower parts of the flame. The other end of the capillary was connected directly to the vacuum of the ionization chamber of a mass spectrometer so that the composition of the hot gases in the cracking zone could be monitored.

EXPERIMENTAL SECTION

Gases were of commercial quality. No impurities were found by GC and MS except for a 1.2% content of acetone in the ethyne.

Instrumentation. The gas chromatograph was a Hewlett-Packard 5890 Series II instrument equipped with a standard injector and FI detector. A 100 m \times 0.2 mm \times 0.33 μ m HP-5 capillary column was used. The mass spectrometer was a VG Trio-2 quadrupole instrument.

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Hydrogenolysis in a Capillary. Quartz capillaries of 0.3–0.4 mm o.d. and 0.15–0.20 mm i.d. were fitted with polyethylene capillary tubing. The capillaries were heated either in a thermostated 2.5 cm × 2.5 cm brass cylinder with a 1 mm perforation or in a hydrogen flame. The heating zone was from 8 to 40 mm. The ends of the capillary were supported, since the flame temperature was close to the softening point of quartz. Mixtures of pure hydrogen, to which were added 0.5% by volume amounts of additives, were led through the capillary (2–3 mL/min) from a 20 mL disposable syringe, and the effluent was collected over water in a test tube. The gas was analyzed in the GC at –50 °C and in IR using a 100 mm gas-tight cuvette. Carbon monoxide adsorbed at 2150 cm^{–1}. Hydrocyanic acid was detected by adsorption of the capillary outlet in sodium hydroxide and transforming the cyanide into Prussian Blue [iron(III)–hexacyanoferrate(II)].

Sample Preparation. The mixtures of hydrogen and additive for flame experiments and FID response measurements were prepared in a 10 L hydrogen cylinder. After evacuation of the cylinder, the additive was introduced through a rubber septum using gas-tight syringes, and the cylinder was filled with hydrogen to 8.0 bar.

Hydrogenolysis in the Flame. A flame of hydrogen and additive was lit at the end of a stainless steel tube of 1.34 mm i.d. The bottom of the tube had a narrow guiding tube, through which the probe capillary was inserted. This was a 6 m × 0.11 mm i.d. deactivated fused silica tube (SGE) connected to the mass spectrometer. The calculated flow rate of hydrogen was 0.2 mL/min. The probe was centered in the burner tube by means of a coil of thin constantan wire, and its position was controlled by the use of a pair of compasses. For the measurement of temperature, the probe was exchanged with a calibrated iron–constantan thermocouple with 0.05 mm leads.

Mass Spectrometry. The ion source of the mass spectrometer was operated at 200 °C in the positive ion electron impact mode. To reduce to a very low level the background peaks at *m/z* 14 and 16 from doubly charged N₂ and O₂, respectively, an electron energy of 21 V was selected. Individual mass peaks were measured on the tune editor screen of the Lab-Base software (VG). In the case of cyclohexane from reduction of benzene, a mass spectrum was recorded showing the base peak at *m/z* 56.

The relative responses of additives versus methane and, in the case of benzene, cyclohexane were determined with the use of standard mixtures in hydrogen at 1.0 bar in a 5.3 L flask. The standards were fed to the mass spectrometer through the same 6 m long capillary which was used as the probe in the flame experiments.

FID Response Measurements. The FID of the HP gas chromatograph was operated in a normal way at 250 °C and with an air flow of 400 mL/min, except the usual supply of hydrogen at about 30 mL/min was replaced with 28 mL/min of hydrogen with additive, fed directly from the 8 bar reservoir through a 2 m × 0.11 mm i.d. fused silica capillary connected at the column entrance. Stable picoampere readings on the display were obtained after 10–15 min.

RESULTS AND DISCUSSION

Hydrogenolysis at 1400 °C. From the free energy of formation data for hydrocarbons,¹³ it is calculated that, at tem-

Table 1. Relative Molar Distributions (GC) of Hydrocarbons Obtained by Heating Vapors of Volatile Compounds to 1400 °C in an Excess of Hydrogen

additive	methane	ethene	ethyne	non-hydrocarbons ^a
methane	100			
butane	100			
cyclohexane	100			
ethene	37	16	47	
ethyne	21	16	63	
isobutene	80	8	12	
benzene	45	13	42	
naphthalene	90	3	7	
methanol	100			CO
ethanol	82	7	11	CO
ethylamine	74	12	14	HCN
ethyl bromide	29	8	63	HBr
dichloromethane	100			HCl
acetone	100			CO

^a Non-hydrocarbons were determined qualitatively.

peratures up to 1400 °C, equilibrium mixtures of hydrocarbons at a total partial pressure of 10^{–4} bar (100 ppm) in hydrogen at 1 bar contain 99% (molar) or more methane, the remainder being ethyne and a small proportion of ethene. Even at 1500 °C, the equilibrium contains 94% methane. At higher pressures of hydrocarbons, and at temperatures above 1200 °C, the equilibrium shifts toward formation of ethyne. Thus, hydrocarbons at concentrations relevant to gas chromatography would be expected to be converted to methane in the hot precombustion zone in the hydrogen flame of the FID, on the assumption that there is sufficient time for attaining equilibrium.

This possibility was tested by simulation of the flame conditions with respect to temperature and reaction time by heating a stream of additives in hydrogen in a quartz capillary to about 1400 °C. The results from experiments with various compounds using an 8 mm heating zone with a reaction time of about 0.2 ms are presented in Table 1. The concentration of additives was typically 0.5%. The molar equilibrium composition at 1400 °C is calculated to be about 71% methane, 28% ethyne, and 1% ethene. The compositions of the effluents, Table 1, are not equilibrium values but apparently result from kinetically controlled reactions and reflect the initial pyrolytic and hydrogenolytic steps, which are characteristic for the individual molecules. The initial reactions are very dependent on the types of bonding present. From the results shown in Table 1, one may state as rules of thumb that single bonds between carbon atoms under these conditions (1400 °C and 0.2 ms) are broken and methane is formed; that double and especially triple bonds are “stable”, so that addition of hydrogen and subsequent C–C bond splitting is slow; and that hydrogen may be eliminated from ethene. Carbon–oxygen bonds either break or stabilize to triply bonded carbon monoxide by elimination of neighboring groups or atoms. Compounds having a carbon–nitrogen bond in an analogous way form triply bonded hydrocyanic acid. Halogen compounds eliminate hydrogen halide. If the heating zone was 40 mm, corresponding to 1 ms reaction time, the concentrations of methane obtained from ethyne were much closer to equilibrium values, showing that the reaction time available in the flame (0.1 ms) is far too short for equilibration.

From the experiments described, one would conclude that the chemical entities which in a hydrogen atmosphere survive cracking at 1400 °C and enter the reaction zone in the flame would

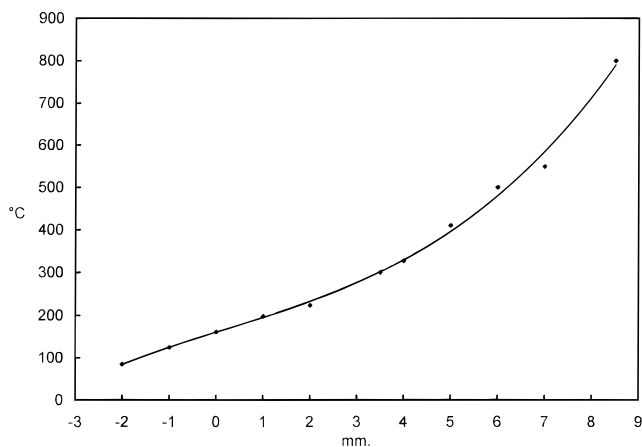


Figure 1. Temperature in a standard hydrogen flame (see text) at the indicated positions above the orifice of the burner, as measured using a calibrated iron—constantan thermocouple with 0.05 mm leads.

be the hydrocarbons methane, ethyne, and ethene, accompanied by carbon monoxide, hydrocyanic acid, or hydrogen halide if oxygen, nitrogen, or halogen were present in the additive. The equal per carbon response is, however, difficult to understand on this basis, and, as described below, the real situation in the FID is very poorly simulated if the heating is performed without direct contact with the burning hydrogen.

Hydrogenolysis in a Flame. Our studies of the processes taking place in the burning hydrogen flame were based on the possibility of introducing a probe into the interior of the flame from the bottom, where the entering fuel has not yet been heated by the hot surroundings. The chemical changes could be followed by moving the probe up and down. The temperatures at the various probe positions were measured by inserting a thermocouple with very thin leads, again from the bottom of the flame. The values found at a given distance from the orifice were very dependent on the rate of the hydrogen flow, which was measured with a flowmeter. For convenience, a rather large standard flow, 16 mL/s, was adopted. The reactions in the flame were no different in a small flame, but since all distances were smaller, the positioning of the capillary was more difficult. The use of a large flame also meant that the presence of the probe and the removal of sample gas (0.2 mL/min, ~0.02%) did not disturb the flame processes. The temperatures read on the thermocouple (Figure 1) probably represent an upper limit for the true temperatures, since the metal may be heated by surface reactions like recombinations of hydrogen radicals.

The analysis of the composition of the gases in the lower part of the hydrogen flame gave very surprising results, especially when compared with the hydrogenolysis in the capillary.

Benzene may be taken as an example. A mixture of 49 ppm (v/v) of benzene in hydrogen was burned at a flow of 16 mL/s to form a 30 mm flame. The tip of the capillary probe was positioned just below the orifice, and the intensity of the m/z 78 peak of benzene was recorded. At a position of the probe 4.5 mm above the orifice, the signal for benzene was very weak and the m/z 84 peak of cyclohexane showed up, with an intensity corresponding to nearly quantitative conversion. A small percentage of cyclohexene was also detected at m/z 82. When the probe was raised a further 2 mm, the cyclohexane signals disappeared, while the m/z 16 and 15 peaks of methane were observed. The conversion of benzene to methane was quantitative. As the probe was raised

in the inner core of the flame, increasing amounts of nitrogen and water were detected, whereas the oxygen concentration was lower than that of the sample mixture, as measured below the orifice. The recorded level very likely reflects the background of the mass spectrometer itself, meaning that the concentration of oxygen in the lower part of the flame is close to zero.

The quantitative conversion of benzene to methane, i.e., 6 mol of methane from 1 mol of benzene, was also observed when the concentration was doubled to 98 ppm, but a well-defined zone containing only cyclohexane was not present. At a concentration of 1000 ppm, the yield of methane was about 25%. Only very small amounts of cyclohexane and cyclohexene were detected. This points to a limit for full conversion to methane of about 200 ppm.

The flame investigations were performed also with ethyne and isobutane. With ethyne, quantitative conversion to methane, i.e., 2 mol of methane from 1 mol of ethyne, was observed at concentrations of 313 and 625 ppm. The latter value appears to be close to the limit for full conversion, since doubling of the ethyne concentration gave the same amount of methane. Very likely, ethyne is reduced to ethane, followed by hydrogenolysis of the C—C bond, but ethane was not detected at any position of the probe.

The aliphatic hydrocarbon isobutane was tested at a concentration of 48 ppm, where full conversion to methane was observed.

Thus, hydrogenolysis of C—C bonds, which requires heating to above 1000 °C in the capillary, now takes place below 600 °C, while hydrogenation of benzene to cyclohexane (not observed in the capillary) occurs at 400 °C. The results must be due to the presence of rather large concentrations of hydrogen atoms produced in the flame.

Combustion of hydrogen produces hydrogen radicals, together with oxygen-containing radicals. Because of their relatively much higher mobility, the hydrogen radicals penetrate deeper into the inner cone of the flame than do the oxygen-containing radicals. In this way, the combustion, although it is an oxidation process, produce a zone in which extremely vigorous hydrogenations take place.

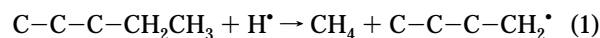
Since the hydrogen flow of 16 mL/s corresponds to a flow rate of 11.3 m/s in the 1.34 mm i.d. tube, an estimate may be made of the reaction time for the observed reactions. After leaving the orifice, the hydrogen continues upward in a laminar stream, while the beam is expanding because of diffusion and heating. The time needed to reach 4.5 mm is of the order of 500 μ s, and 6.5 mm is reached in ~750 μ s. The temperature was found to be ~400 °C at 4.5 mm and ~600 °C at 6.5 mm (Figure 1). That the additives are converted to methane at an early stage means that injected methane and "flame-produced" methane will have the same fate in the oxidizing part of the flame and therefore will produce the same number of ions (see below). If the flame was smaller (lower flow of hydrogen), the temperature increase per millimeter was increased correspondingly, and the chemical conversions were completed as before.

Since the reactions observed take place at low temperatures, they probably require stoichiometric amounts of hydrogen atoms both for the saturation of the multiple bonds and for the subsequent fission of the C—C bonds of the saturated hydrocarbons.

Reactions of hydrogen atoms have been studied both in the gas phase and in solution.⁷⁻⁹ The generation of the atoms has been by electrical discharge in hydrogen at room temperature or by heating of hydrogen to extreme temperatures.

Hydrogen atom reduction of benzene at low temperature was studied by Knutti and Bühler¹⁰ and by Kim et al.¹¹ The products were cyclohexane (30%), methane (60%), and ethane (10%).¹¹ They found benzene to be 100 times less reactive than cyclohexadiene and cyclohexene. In accordance with this, only minor amounts of cyclohexene and cyclohexadiene could be detected in the flame.

It is known¹² that attack of hydrogen on a paraffinic carbon atom may lead to fission of C-C:

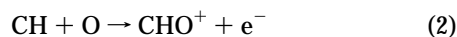


A strong C-H bond is formed at the cost of the weaker C-C bond. It is a reasonable assumption that the radical formed takes up hydrogen and that repetition of the steps finally results in the complete conversion of the hydrocarbon into methane. Methane has the strongest C-H bonds of all paraffinic hydrocarbons and is the logical end product when they react with an excess of hydrogen atoms. This mechanism seems attractive but needs verification.

Non-Hydrocarbons. Although more investigations are required, the results obtained by heating additives with hydrogen with and without a flame give many hints to the understanding of the various RMRs for compounds with functional groups. The loss in the response obtained for oxygen-containing compounds is related to the extent of formation of carbon monoxide, which has RMR = 0. In the same way, the loss of response for nitrogen compounds depends on the extent of formation of hydrocyanic acid, with RMR = 0.3, etc. The response obtained from alkyl halides results from a more or less complete flame reduction to methane. Though it has not been proved, it must be assumed that all nonsubstituted carbons are converted into methane.

An investigation of this and related problems concerning the fate of nonsubstituted hydrocarbons in the hydrogen flame using the probe technique is being planned. A single non-hydrocarbon additive, diethyl ether, was tested. Approximately 3 mol of methane was produced per mole of ether. Other degradation products were not detected. Carbon monoxide, which is probably formed, could not be analyzed because considerable amounts of nitrogen diffuse into the precombustion zone.

Ion Formation. It is known^{14,15} that the most important route to ion formation in the combustion process is the reaction of methylidyne with oxygen:



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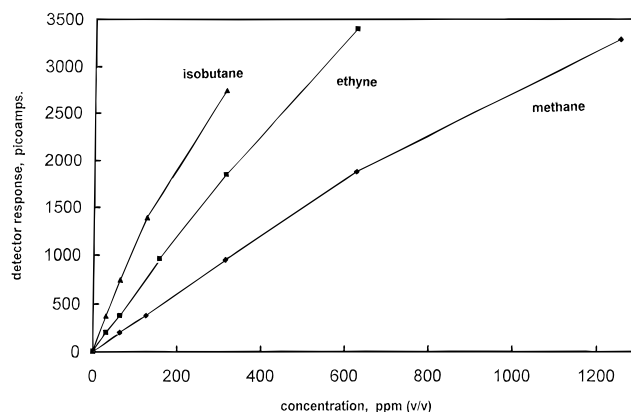


Figure 2. Detector response in picoamperes of mixtures of additives at various concentrations using a HP 5890 gas chromatograph. Flow, 28 mL/min.

The key fragment CH is needed for ion production according to eq 2. The rule of equal per carbon response requires that all carbon atoms in a molecule have an equal chance of producing an ion in the detector, which means that they should have an equal chance of producing CH. The actual yield of ions is about 1 per 10⁶ C atoms.

RMR for Ethyne. The RMR for ethyne in the FID has been reported to be 30% higher per carbon than that found for other hydrocarbons.^{1,3} This generally accepted RMR value for ethyne has been the basis for many mechanistic suggestions for the production of ions from ethyne. It would, however, be incompatible with the present observations if the ratio of the RMRs for ethyne and methane were different from 2:1. Measurements of detector response versus concentration were therefore made for three hydrocarbons using the detector of the HP 5890 gas chromatograph. From the plots obtained (Figure 2), it is seen that, for the linear parts, the values of the slopes (3.006, 6.095, and 11.68) relate very closely to the numbers of carbons in methane, ethyne, and isobutane (1:2:4).

At higher concentrations, the response is lower than expected. There are, in theory, two ways in which the response may be limited: either the degradation to methane becomes incomplete, or the relative yield of ions becomes lower. For ethyne, it seems obvious that the ionization is limiting, since the ethyne response per carbon is equal to that of methane at the concentrations used. Consistent with this, the formation of methane from ethyne in the flame is quantitative in the whole range. For isobutane, however, degradation sets the limit, since the plot for this gas deviates from linearity at a lower relative carbon content.

The measurements of the FID response versus concentration described above have removed a serious obstacle from understanding the mechanism of the FID, in showing that the RMR for ethyne is very close to 2.00. This result means that there are no significant exceptions from the "equal per carbon" rule for hydrocarbons.

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CONCLUSION

Observation of a quantitative conversion of alkanes, benzene, and ethyne to methane in the hydrogen flame constitutes the finding of a "missing link" in the understanding of the mechanism of the FID. This detector's "equal per carbon response" is due to its ability to convert all carbon atoms of a hydrocarbon to a common denominator: methane molecules.

The simple and convenient generation of hydrogen atoms by means of a flame should be useful for mechanistic purposes.

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