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Mechanism of the flame ionization detector II. Isotope effects and heteroatom effects

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Abstract

The relative molar flame ionization detection (FID) response (RMR) for a hydrocarbon does not change when deuterium is substituted for hydrogen. The exception is methane for which an inverse deuterium isotope effect of 3.5% is observed for tetradeuteromethane. [¹³C]Methane shows an inverse isotope effect of 2%. The reason for the small or non-existent isotope effects is that H/²H exchange takes place in the pre-combustion hydrogenolysis in the flame. This was shown by taking samples from the lower part of the flame by means of a fused-silica capillary probe. By the same technique the hydrogenolytic reactions in the hydrogen flame of compounds added to the hydrogen gas in low concentrations were followed. Alcohols, ethers, ketones, and esters all produced methane and carbon monoxide, while amines produced methane and hydrogen cyanide, halogen compounds methane and hydrogen halide, etc. The FID response of an organic compound is the sum of the responses from the products formed in the hydrogenolysis. © 1997 Elsevier Science B.V.

Keywords: Flame ionization detection; Detection, GC; Isotope effects; Heteroatom effects

1. Introduction

The response obtained with flame ionization detection (FID) varies in proportion to the number of carbon atoms in the molecule [1]. This was for many years unexplained [1–4], but recently it was found that carbon atoms in a hydrocarbon are quantitatively converted to methane molecules in the lower part of the flame where a flux of the mobile hydrogen atoms is formed by diffusion inward from the combustion zone [5]. The atomic hydrogen first adds to multiple bonds and, for example, converts benzene quantitatively to cyclohexane. At slightly higher temperatures carbon–carbon bonds are broken, and eventually all carbons are completely hydrogenated to methane. These processes are extremely fast and come to completion in the flame at 600–650°C, that

is at temperatures well below the temperatures found in the combustion zone. Methane molecules are therefore the common denominator for all types of hydrocarbons and FID is basically methane detection.

Carbon atoms bonded to heteroatoms are known to contribute less to the FID response, meaning that they are not, at least not quantitatively, transformed to methane molecules. The technique of taking samples from the various zones in the flame by means of a quartz capillary has now been used to investigate this problem and also to study the effect on the FID response of isotopic substitution of various additives.

The decomposition patterns obtained by hydrogenolysis in the flame were compared with patterns found by hydrogenolysis over a platinum catalyst

and with high-temperature hydrogenolysis in a quartz capillary.

2. Experimental

2.1. Materials

High-purity hydrogen gas (99.9997%) was used. Deuteriated materials were from Cambridge Isotopes. Other additives were standard-grade laboratory chemicals.

2.2. Instrumentation

A Hewlett-Packard 5890 Series II gas chromatograph was used equipped with a standard split injector and a FI detector. A 100 m × 0.2 mm, 0.33- μ m HP-5 capillary column was used. The mass spectrometer was a Shimadzu GCMS-QP5000. A 6 m × 0.11 mm I.D. deactivated fused-silica tube (SGE) was connected to the mass spectrometer and to the hydrogen burner (Fig. 1), as described [5] or

to a platinum catalyst. This was made from 40 cm of 0.05-mm platinum wire which was compressed in a 0.35-mm I.D. quartz capillary to occupy 15 mm in the tube; platinum surface area ca. 0.6 cm². The capillary was placed in a tubular electric heater, I.D. 4 mm, and length 30 mm. The temperature was measured with a thermocouple. Well-defined mixtures of hydrogen with additives were prepared by adjusting the stream of hydrogen to 16 ml s⁻¹ using a Porter Instruments flow regulator and feeding the additive to the hydrogen from a 5- μ l Hamilton syringe using an adjustable motorburette from Harvard Instruments. The concentrations of additive were normally 50–100 ppm (v/v).

2.3. Hydrogenolysis over Pt

For investigations of platinum-catalysed hydrogenolysis the platinum catalyst was connected to the inlet capillary of the mass spectrometer, and to a 10-cm piece of capillary which was placed in a stream of additive/hydrogen inside a 1.6-mm I.D. stainless steel tube.

2.4. Hydrogenolysis in the flame

For investigations of precombustion hydrogenolysis in the hydrogen flame the procedure described in Ref. [5] was used. A hydrogen flame burning in oxygen–argon (20:80) was arranged by placing the burner in a pyrex tube 18 × 360 mm. The 1.36-mm I.D. stainless steel burner tube was surrounded with a plug of glass wool just above the inlet tube for argon–oxygen (Fig. 1). The hydrogen flow was adjusted to 16 ml s⁻¹ and the flow of Ar–O₂ to 100 ml s⁻¹.

2.5. Isotope effects on FID response

Isotope effects for hydrocarbons were measured by isotopic separation on the GC column of a precision-weighted 1:1 mixture of a deuteriated and a non-deuteriated compound. Response ratios were determined by integration of the baseline separated ²H peak and ¹H peak. Isotope effects for methanes and ethane were measured by preparing precision-weighted 1:1 mixtures of alkyl iodides and per-deuteroalkyl iodide and quantitatively reducing them

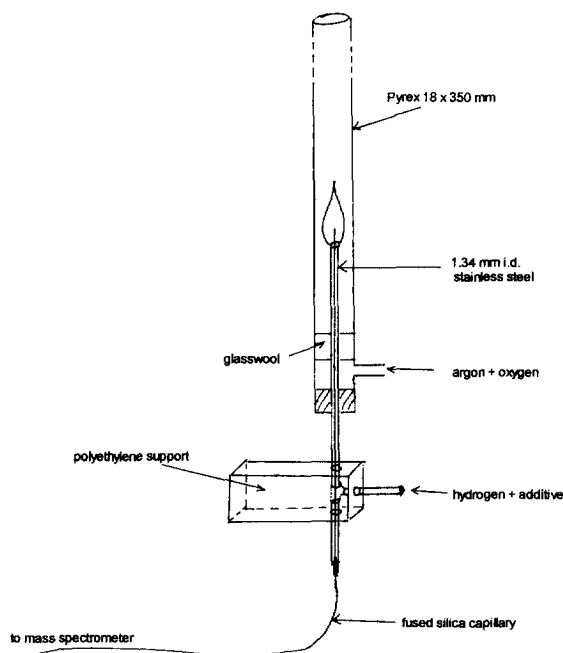


Fig. 1. Hydrogen flame assembly with the fused-silica probe entering the flame from the bottom. Mounted with a pyrex mantle for use in an argon–oxygen atmosphere.

to alkanes with hydrogen iodide in ampoules at 250°C, as described previously [6]. Response ratios were obtained as above using suitable GC columns [6].

A 1:1 mixture of $^{13}\text{CH}_3^2\text{H}$ and C^2H_4 was prepared by reducing a 1:1 mixture of [^{13}C]methyl iodide and [$^2\text{H}_3$]methyl iodide with deuterium iodide. Knowledge of the RMR for $^{13}\text{CH}_3^2\text{H}$ and C^2H_4 and for the different sets of isotopically substituted methanes shown in Table 1 allowed an estimate of the RMR of C^2H_4 versus CH_4 .

3. Results and discussion

3.1. Deuterium isotope effects

A deuterium-substituted hydrocarbon would a priori be expected to degrade in the flame to deuterium-substituted methanes, and it seemed possible that there would be an isotope effect on the molar FID response (RMR) of the various deuterated methanes. Blades actually reported very significant effects (10–40%) of substituting deuterium for hydrogen in ethane and methane [3]. The RMRs for various hydrocarbons were therefore compared with the RMRs for their fully deuterated analogs. It was found (Table 1) that the RMR for four multicarbon compounds did not, within the experimental uncer-

tainty, change by deuteration. RMRs for deuterated methanes, however, showed small but significant isotope effects (Table 1). It is seen that three deuterium atoms in methane increase the response by 2.0% and the same increase is seen for the introduction of ^{13}C . If all four hydrogens in methane are exchanged with deuterium the response is estimated to increase by 3.5%.

Experiments showed that using two sets of conditions, multicarbon compounds containing deuterium were degraded to methane with simultaneous quantitative exchange of deuterium with hydrogen. The conditions were precombustion degradation in the hydrogen flame at 600°C and platinum catalysed degradation at 700°C. Uncatalysed degradation in a quartz capillary at 1300°C produced hydrogen/deuterium exchanged mixtures of methane, ethene, and ethyne [5]. Up to a certain concentration, the conversions are assumed to be quantitative for all hydrocarbons although exact measurements were carried out only for benzene, cyclohexane, ethyne, and isobutene [5]. The exchange of deuterium with hydrogen is likewise assumed to be quantitative, although the presence of water with large peaks at m/z 17, 18, and 19 compromised the observation of signals from deuteromethanes. The fact that multicarbon compounds show isotope effects for their RMRs smaller than 0.5–1%, however, seem unexplainable except by a combination of a quantitative degradation with a quantitative $\text{H}/^2\text{H}$ exchange.

Partial hydrogen/deuterium exchange in an intact molecule was observed in [$^2\text{H}_6$]benzene either in the lower part of the hydrogen flame (ca. 400°C), while quantitative exchange occurred easily by platinum-catalysed hydrogenolysis at 300°C. The mechanism for such exchange may well be a series of additions and/or eliminations of hydrogen, since elimination was found to be extremely fast from 1,3-cyclohexadiene at 300°C. Platinum catalysis and 500°C was required to obtain hydrogen/deuterium exchange in pentane mixed with deuterium gas and the exchange was accompanied by eliminations and rearrangements.

Much more extensive hydrogen isotope exchange is possible during the total hydrogenolysis of the carbon-carbon bonds in a molecule, which occurs at 600°C in the flame and at 700°C on the platinum

Table 1
Relative molar response (RMR) in the flame ionization detector of isotopically labelled compounds

Type of labelling	RMR
$\text{CH}_4/\text{C}^2\text{H}_3\text{H}$	0.981 ± 0.005 (8)
$^{13}\text{CH}_4/\text{C}^2\text{H}_3\text{H}$	1.002 ± 0.007 (8)
$\text{CH}_4/^{13}\text{C}^2\text{H}_3\text{H}$	0.949 ± 0.009 (2)
$^{13}\text{CH}_4/^{13}\text{C}^2\text{H}_3\text{H}$	0.980 ± 0.006 (2)
$^{13}\text{CH}_3\text{D}/\text{C}^2\text{H}_4$	0.985 (1)
$\text{CH}_4/\text{C}^2\text{H}_4$	0.966^a
$\text{C}_2\text{H}_6/\text{C}_2^2\text{H}_5\text{H}$	0.997 ± 0.008 (2)
$\text{C}_6\text{H}_6/\text{C}_6^2\text{H}_6$ (benzene)	0.995 ± 0.008 (4)
$\text{C}_6\text{H}_{12}/\text{C}_6^2\text{H}_{12}$ (cyclo-hexane)	0.997 ± 0.009 (4)
$\text{C}_{12}\text{H}_{10}\text{CO}/\text{C}_{12}^2\text{H}_{10}\text{CO}$ (Ph_2CO)	0.995 ± 0.007 (2)

Standard deviations are given, and in parentheses the number of determinations. For double experiments the deviation from mean is shown.

^aEstimated.

surface. This reaction involves free radical chain processes in a high flux of hydrogen atoms. All C–C bonds break and exchange reactions take place in the fragments by known and unknown reaction mechanisms.

Methane itself is a unique hydrocarbon. Elimination in methane is possible only at very high temperatures, and hydrogen abstraction is more difficult with methane than with any other hydrocarbon. Undiluted methane is stable at 500°C but decomposes at 700°C with the formation of polycyclic aromatic hydrocarbons and hydrogen. At very high dilution in hydrogen, methane is stable up to 1000–1100°C. Because of this high thermal stability, isotopically labelled methane may be assumed to pass through the precombustion zone in the flame partly unchanged. The observed deuterium isotope effects on the FID response (Table 1) should probably be explained in this way. When feeding tetra-deuteriomethane (1000 ppm in hydrogen) to the flame it was possible to find concentrations of CH₄ corresponding to 25–35% conversion, but for the reasons mentioned the concentrations of partly exchanged methanes could not be determined.

Only a speculative explanation may be given for why a deuterated methane gives increased response. The ion-producing reaction in the flame is [7–9] the reaction of methylidyne with oxygen:



In the formation of the methine radical from the methane molecule three hydrogens must be stripped off. The yield of ions is only 1 per 10⁶ methane molecules meaning that the largest part of carbon-containing fragments including CH react via alternative schemes. The concentration of CH is a steady state determined by its rate of formation relative to its rate of disappearance. The stripping of hydrogen atoms is slowed down in deuterated or ¹³C-labelled methane and these effects are primary isotope effects. The slower degradation seems to increase the steady-state concentration of CH. This is concluded since the same isotopic substitutions slow down reaction (Eq. (1)) and for this reason should diminish the rate of ion production. It is interesting that the increase in RMR from C²H₃H to C²H₄ is almost equal to the increase from CH₄ to C²H₃H (Table 1).

This indicates that the first attack on intact methane is slow relative to the following H-stripping reactions, and that it may be the prolonged lifetime of the intact, labelled methane molecules that causes the higher yield of ions.

A slightly prolonged survival in the flame must likewise be the reason for the increase in RMR for ¹³C-labelled methane.

That the deuterium isotope effects measured are small is because only a small fraction of methane molecules escape isotopic exchange. The 'true' isotope effects may be found only after determining in detail the extent of the H/²H exchange prior to the combustion.

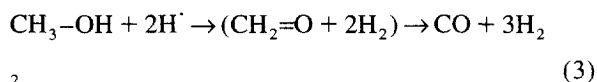
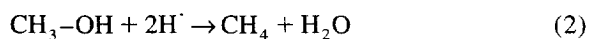
3.2. Heteroatom effects

The 'equal per carbon' rule for the FID response is valid only for hydrocarbons. A carbon atom which is associated with a heteroatom often gives a less than normal contribution to the response. Empirical rules have been formulated for the 'effective carbon numbers' (ECNs) for the various types of functional groups [1,10,11]. A study of the processes in the interior of the hydrogen flame should reveal a chemical explanation. From the earlier work [5] it was known that hydrogenolysis at flame temperature (1300°C) of, for example, alcohols, ketones and esters, produces methane, ethene, and ethyne and carbon monoxide. Amines produced the three hydrocarbons plus hydrocyanic acid, and halogen compounds produced hydrocarbons plus hydrogen halides. Hydrogenolysis in the flame converted the hydrocarbons quantitatively to methane at temperatures below 700°C. A carbon bonded to a heteroatom may or may not be converted to a methane molecule by flame hydrogenolysis. Since carbon monoxide gives zero response in the FID and hydrocyanic acid gives a low response, a diminished ECN should be expected for substituted compounds if hydrogenolysis in the flame also produces CO and HCN. If a quantitative analysis was possible, a correlation could be made between the observed RMR and the sum of the responses of the flame-produced entities.

In the present investigation the probe-sampling of the hydrogen flame was used with various types of organic compounds added to the hydrogen, mass spectrometry being used for the identification of the

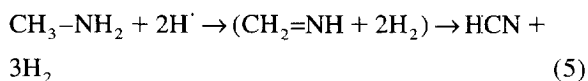
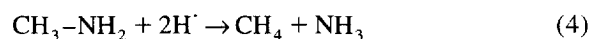
decomposition products. A serious problem was that the most interesting peaks (for CO and HCN) had m/z 28 and 27, which in low-resolution MS are indistinguishable from signals from the unavoidable atmospheric nitrogen. The obstacle was overcome by using a hydrogen flame burning in argon–oxygen (80:20). Since the properties of the flame burning in argon may be assumed to deviate from the flame burning in air the observations should be considered to be only qualitative or semi-quantitative. The temperatures measured in the ‘argon’ flame were not significantly different from the temperatures measured in the normal hydrogen flame [5].

Hydrogenolysis at 6–800°C in a hydrogen flame, or at 700–800°C over a platinum catalyst, are more complete than hydrogenolysis at 1400°C in a quartz capillary since methane is formed from all carbons, which are not hetero-substituted. In any of the three cases the fate of the hetero-substituted carbon is, however, the same. Compounds containing oxygen produce CO, amines produce HCN and halogen compounds produce HX. That the RMRs for alcohols vary with the alkyl is a consequence of the competition between hydrogenation of the C–O bond and hydrogen abstraction with the formation of carbon monoxide. For methanol:



Methanol molecules which react according to Eq. (3) do not contribute to the detector response. An effective carbon number for methanol of 0.75 therefore means that Eq. (2) is three times faster than Eq. (3). With multicarbon alcohols, thermally induced elimination of water followed by alkene reduction gives no loss in ECN, but C–C fractionation at the α -position and fission of C–H with the production of carbon monoxide compete and cause a loss in ECN. That the ECN for ethanol is 1.70 shows that elimination is fairly important while only 30% of the oxygen-carrying carbons are converted to CO.

For amines a very analogous series of reactions is taking place:



For multicarbon amines thermal elimination, C–C bond-splitting and HCN formation via Eq. (5) will compete. Unlike CO, HCN has a positive ECN and the FID response from an amine results from the formation of both formylium ions from methane molecules and nitrosonium ions from HCN molecules [3].

Compounds containing a single halogen atom may undergo elimination or hydrogenation in the flame. In both cases the hydrocarbons would be transferred into methane molecules with no loss in ECN. An analysis of the degradation products of 1-chlorobutane in the hydrogen flame showed butylene, ethylene, methane, and hydrogen chloride. The RMR found relative to cyclohexane was 4:6 within 0.2%. Obviously the ions producing the FID signal result from combustion of four molecules of methane formed by flame hydrogenolysis of the molecule.

RMR for aromatic halogen compounds and for compounds with several halogens at one carbon are more complicated. Methyl chloride, dichloromethane, chloroform, and tetrachloromethane give less and less response with RMRs decreasing from almost 1.0 to about 0.5 [1]. Methane and hydrogen chloride were found in the flame, but no other compounds.

Tetrachloromethane showed emission of light when added to the burning hydrogen. Light emission by reaction of hydrogen atoms with CCl_4 has been reported by Gaydon and Wolfhard [12]. In the hydrogen flame a pale yellow-white cone was seen from the burner opening and 5–10 mm up using the standard flame. The phenomenon is not unlike the luminous cone in a bunsen burner. The cone became larger when higher concentrations were used, because the flux of hydrogen atoms has a limited capacity for reaction with CCl_4 . The low response for CCl_4 (RMR=0.5) shows that reduction to methane is not quantitative. Of the added tetrachloromethane 50% is not hydrogenated, but converted in the flame to unknown compounds (radicals?) which in the oxidizing zone produce carbon dioxide and chlorine (?) without ion production. In the present work it was not possible to identify the fragments formed from highly halogenated com-

pounds during the pre-combustion degradation. Most likely the fragments are shortlived radicals, such as for example CCl_2 , which will not pass through the capillary to the mass spectrometer. A more direct connection will be needed in order to investigate this further.

Tetrachloroethene has an ECN of 2.25 which is more than expected if the reduction to two molecules of methane plus four molecules of hydrogen chloride is quantitative. Apparently a small fraction of this compound reacts in an alternative way and produces other positive ions. The ion-producing side reaction(s) must amount only to a few percent, since even though many halogen compounds have RMRs above 1.0 per carbon the deviations are never above 10–20% [1]. It is highly unlikely that an ion-forming reaction, which bears no chemical resemblance to Eq. (1) would give almost the same yield of ions.

The RMRs for a series of perfluorohydrocarbons have been reported [13]. For tetrafluoromethane and hexafluoroethane the RMR was near zero. But for higher perfluoroalkanes the RMRs were increasing, and the higher alkanes had RMRs not far from what is obtained with the corresponding hydrocarbons. A possible explanation is that hydrogen atoms are incapable of breaking the C–F bond in an intact molecule, but C–C bonds in the larger molecules may break with the formation of radical fragments and then the complete conversion into methane molecules is possible.

The RMR for hexafluorobenzene was in the present work found to be 0.65 showing that formation of methane is not quantitative. No probe experiments were performed since it seemed improbable that the halogen-containing fragment formed has the necessary stability.

4. Conclusions

Organic molecules containing deuterium normally show no change in RMR in the FID when deuterium is exchanged with hydrogen. This is because the pre-combustion degradation under the influence of the high flux of hydrogen atoms causes the pro-

duction of non-deuteriated methane in the anaerobic sector of the flame. The only exception to the rule is methane itself, in which carbon–deuterium bonds survive to a certain degree. A small inverse isotope effect is observed for this compound amounting to 3.5% for tetradeuteriomethane.

^{13}C Methane also shows an inverse isotope effect on the FID response of the order of 2%.

Carbon atoms with bonds to heteroatoms may diminish the ECN. In the pre-combustion degradation oxygen compounds produce FID-inactive carbon monoxide as well as methane, and the ECN can be identified with the number of methane molecules. Nitrogen compounds produce hydrogen cyanide which gives a low contribution to the response, and the ECN is the sum of a contribution from methane and a contribution from HCN. Halogens give variable effects depending on their type, number, and position.

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