

MECHANISMS OF HYDROCARBON FORMATION DURING FLASH PYROLYSIS OF KEROGEN

Walter A. Hartgers, Jaap S. Sinninghe Damsté and Jan W. de Leeuw

Organic Geochemistry Unit, Faculty of Chemical Technology and
Materials Science, Delft University of Technology, De Vries van
Heystplantsoen 2, 2628 RZ Delft, The Netherlands.

Keywords: alkylbenzenes, fatty acids, sodium salts, aromatic carotenoids

INTRODUCTION

Geomacromolecules, which account for by far the greatest part of organic matter in sediments, are, due to their physical properties and complex structures, not easily accessible for common spectroscopic methods to elucidate their structure. Therefore, thermal and chemical degradation techniques are often applied to obtain structural information on these substances. Flash pyrolysis (Py) in combination with gas chromatography (GC) and mass spectrometry (MS) has proven to be a useful method of characterizing geomacromolecules (e.g. kerogen) at a molecular level.^{1,2} Upon flash pyrolysis of kerogen mixtures of *n*-alkanes, *n*-alk-1-enes, saturated and aromatic (poly)cyclic hydrocarbons are commonly generated.

However, the mechanisms by which these compounds are formed are not completely known. This is surprising since a full understanding of the thermal degradation processes is essential for interpretation of the compound distributions with respect to the macromolecular structure. Therefore, we have flash pyrolysed silicon-bound hydrocarbons, which serve as model compounds for hydrocarbon moieties in kerogen.³ Although these experiments gave some insight into the thermal degradation of hydrocarbon moieties, the major pyrolysis products were formed by processes involving the O-Si and Si-C bonds and are thus not really representative of hydrocarbon moieties in kerogen.

In this paper we report the C₀-C₄ alkylbenzene distributions in flash pyrolysates of two kerogens and flash pyrolysis experiments with new model compounds (sodium salts of fatty acids) aimed at the interpretation of the alkylbenzene distributions of the kerogen pyrolysates.

EXPERIMENTAL

Sediment samples were extracted and decarbonated (Paris Basin shale, G6-2-2⁴) or isolated (Womble shale⁵) and subsequently re-extracted with organic solvents.

Hexadecanoic acid and 12-hydroxy-octadecanoic acid are commercially available (Aldrich) and were converted to their corresponding sodium salts by adding a NaOH solution followed by evaporation of the water. 16-(4'-methylphenyl)hexadecanoic acid was synthesized by a Grignard reaction of 16-oxo-hexadecanoic acid, prepared by oxidation of 16-hydroxydecanoic acid (Aldrich), with 4-bromomagnesium-toluene and subsequent hydrogenolysis⁶ of the formed alcohol using triethylsilane and BF₃·etherate.

The samples were pressed onto ferromagnetic wires. These wires were inductively heated in 0.15 s to their Curie-temperature (610° or 770°C) at which they were held for 10 s. On line gas chromatography (GC) was performed using a Hewlett Packard HP-5890 gas chromatograph equipped with a cryogenic unit and programmed from 0°C (5 min) to 320°C (10 min) at a rate of 3°C/min. The pyrolysate was separated on a 25 m fused silica capillary column coated with chemically bound CP Sil-5 (0.32 mm I.D.; film thickness 0.45 μm).

Py-GC-MS was performed using the same pyrolysis and GC-conditions as mentioned above with a Hewlett Packard HP-5890 gas chromatograph directly coupled to the EI ion source of a VG-70s double focussing mass-spectrometer (mass range *m/z* 40-800; cycle time 1.8 s; ionisation energy 70 eV). C₀-C₄ alkylbenzenes were identified by comparison of relative retention time and mass spectral data with those of authentic standards.

RESULTS AND DISCUSSION

Alkylbenzenes in flash pyrolysates of kerogen

Alkylbenzenes are often important pyrolysis products of immature kerogens and coals. They are assumed to be formed via β -cleavage of alkylaromatic moieties in the kerogen structure.¹ The origin of these alkylaromatic units in kerogen is far from understood. Therefore, the C₀-C₄ alkylbenzene distributions of ca. 30 pyrolysates of immature kerogens from different geographical locations and of different types were examined to see whether these are biologically controlled.

Figure 1 shows the alkylbenzene distributions of the flash pyrolysates of two kerogens from the Toarcian Paris Basin and the Ordovician Womble Shale which both contain type II kerogens. Significant differences between the distribution patterns are observed. For example, the abundance of 1,2,3,4-tetramethylbenzene (compound 36, Table 1) in the Womble flash pyrolysate relative to that in the Paris Basin pyrolysate is noteworthy. The substitution pattern of this compound suggests that it is generated by β -cleavage of macromolecularly bound aromatic carotenoid structures. Five major aromatic carotenoids occurring in nature are: renieratene, isorenieratene, isorenierapurpurin, chlorobactene and okenone (figure 2).⁷ They all possess 1-alkyl-2,3,4-trimethyl- and 2-alkyl-1,3,4-trimethylbenzene moieties, which are likely to generate 1,2,3,4-tetramethylbenzene upon flash pyrolysis.

Since these aromatic carotenoids are mainly biosynthesized by photosynthetic sulphur bacteria, it is suggested that these bacteria were important contributors to the organic matter of the Ordovician Womble shale. Because of the natural habitat of photosynthetic sulphur bacteria this, in turn, suggests that a part of the photic zone of the water column or sediment was anoxic.

This example shows that alkylbenzenes (and possibly other flash pyrolysis products) contain palaeoenvironmental information. However, to decode this information the mechanisms involved in the formation of these pyrolysis products (*e.g.* β -cleavage in case of alkylaromatic units) need to be known. The study of model compounds is, therefore, a prerequisite to fully understanding kerogen pyrolysis product distributions.

Flash pyrolysates of model compounds

The sodium salt of 16-(4'-methylphenyl)hexadecanoic acid was selected for study because unlike free fatty acids it will not evaporate off the wire without degradation and is, thus, a simple model compound for aromatic moieties in kerogen. It yields upon flash pyrolysis (figure 3A) a homologous series of 4-alkyltoluenes and 4-alkenyltoluenes with a chain length of up to 15 carbon atoms. The series of 4-alkenyltoluenes probably have their double bond in the ω -position. These compounds are supposed to be formed by simple homolytic C-C bond cleavage. 1,4-Dimethylbenzene which would be the favoured pyrolysis product resulting from β -cleavage of the aromatic moiety is also a major compound (figure 3A).

However, the presence of 4-methylstyrene as a major pyrolysis product is puzzling. ¹H NMR and TLC of the synthesized product indicated that it is not completely pure and contains a non-GC amenable impurity, which may be responsible for the formation of 4-methylstyrene upon pyrolysis. Alternatively, an uncommon rearrangement reaction of 16-(4'-methylphenyl)hexadecanoic acid sodium salt may also lead to the generation of this compound. Furthermore, the abundance of toluene and benzene in the pyrolysate is remarkable since the formation of these products requires the cleavage of a C-C bond α to the aromatic ring. Since this degradation pathway is deemed unlikely due to the relatively high bond strength, cyclisation and aromatization of the alkyl chain may be an alternative route to generate these products during flash pyrolysis.

To investigate this phenomenon in more detail, the sodium salts of hexadecanoic acid and 12-hydroxy-octadecanoic acid were also flash pyrolysed (figures 3B and 3C). Flash pyrolysis of hexadecanoic acid generates a series of *n*-alkanes and *n*-alk-1-enes up to C₁₅ (figure 3B). The lack of hydrocarbons with more than 15 carbon atoms shows that recombination of two radicals is not an important process. The peaks eluting after heptadecane are identified as hexadecanal and hexadecanoic acid, which evaporate from the wire during flash pyrolysis. The results of this experiment are comparable to the flash pyrolysate of Silicon bound *n*-octadecane.³ Benzene, toluene and other alkylbenzenes were not generated in detectable amounts,

indicating that cyclisation and aromatisation of the *n*-alkyl chain is not occurring during flash pyrolysis.

Surprisingly, flash pyrolysis of the sodium salt of 12-hydroxy-octadecanoic acid generates a homologous series of alkan-7-ones and alken-7-ones with the unsaturation in the ω -position as the major products. However, more important from our point of view, benzene, toluene and, to a lesser extent, other alkylbenzenes (*i.e.* 1-phenylalkanes, 2-alkyltoluenes) which can be formed by cyclisation and aromatisation of a linear chain are also important pyrolysis products. This indicates that if an alkyl moiety contains at least one functional group alkylbenzenes can be formed *via* cyclisation and aromatisation reactions during flash pyrolysis.

CONCLUSION

Alkylbenzene distributions in kerogen pyrolysates have a potential to give information on biological contributions and palaeoenvironmental conditions. However, much more work aimed at the understanding of the thermal processes responsible for their formation has to be performed before we can fully decode the information contained in pyrolysis product distributions. Experiments with model compounds are essential in this respect but our preliminary investigations are rather confusing and warrant further investigation.

REFERENCES

1. Larter, S.R. and Horsfield, B. (1991), In: "Organic Geochemistry", M.H. Engel and S.A. Macko (eds), Plenum Press, New York. In press.
2. Rullkötter, J. and Michaelis, W. (1990), *Org. Geochem.*, **16**: 829-852.
3. Hartgers, W.A., Sinnighe Damsté, J.S. and de Leeuw, J.W. (1991), *J. Anal. Appl. Pyrol.* In press.
4. Mackenzie, A.S., Patience, R.L., Maxwell, J.R., Vandenbroucke, M. and Durand, B. (1981), *Geochim. Cosmochim. Acta*, **45**: 1709-1721.
5. Fowler, M.G. and Douglas, A.G. (1984), *Org. Geochem.*, **6**: 105-114.
6. Parnes, Z.N., Boelestova, G.I. and Kursanov, D.N. (1977), *J. Org. Chem. USSR*, **13**: 434-436.
7. Liaaen-Jensen, S. (1978), In: "Photosynthetic Bacteria", R.K. Clayton and W.R. Sistrom (eds), Plenum Press, New York. pp 233-248.

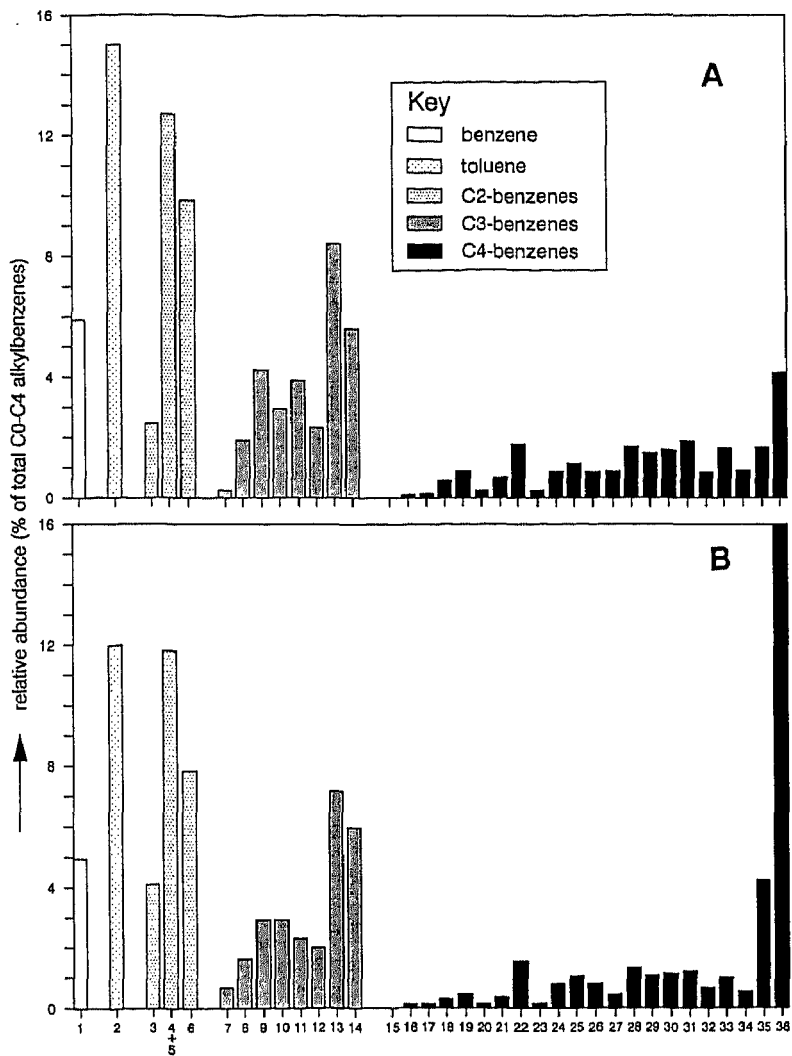


Figure 1. Bar plots showing the distribution of the C₀-C₄ alkylbenzenes in the flash pyrolysates of the kerogen of (A) Paris Basin G6-2-2 and (B) Womble shale. Numbers refer to compounds listed in Table 1.

Table 1: Alkylbenzenes identified in kerogen pyrolysates.

1	benzene	20	1-isopropyl-2-methylbenzene
2	toluene	21	1,3-diethylbenzene
3	ethylbenzene	22	1-propyl-3-methylbenzene
4+5	1,3-/1,4-dimethylbenzene	23	1,4-diethylbenzene
6	1,2-dimethylbenzene	24	1-propyl-4-methylbenzene
7	iso-propylbenzene	25	n-butylbenzene
8	n-propylbenzene	26	1-ethyl-3,5-dimethylbenzene
9	1-ethyl-3-methylbenzene	27	1,2-diethylbenzene
10	1-ethyl-4-methylbenzene	28	1-propyl-2-methylbenzene
11	1-ethyl-2-methylbenzene	29	1-ethyl-2,5-dimethylbenzene
12	1,3,5-trimethylbenzene	30	1-ethyl-2,4-dimethylbenzene
13	1,2,4-trimethylbenzene	31	1-ethyl-3,4-dimethylbenzene
14	1,2,3-trimethylbenzene	32	1-ethyl-2,6-dimethylbenzene
15	t-butylbenzene	33	1-ethyl-2,3-dimethylbenzene
16	iso-butylbenzene	34	1,2,4,5-tetramethylbenzene
17	sec-butylbenzene	35	1,2,3,5-tetramethylbenzene
18	1-isopropyl-3-methylbenzene	36	1,2,3,4-tetramethylbenzene
19	1-isopropyl-4-methylbenzene		

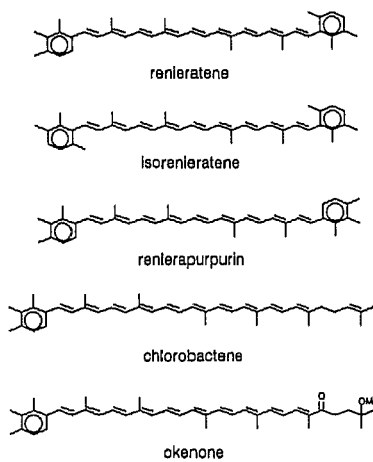


Figure 2. Chemical structures of some aromatic carotenoids.

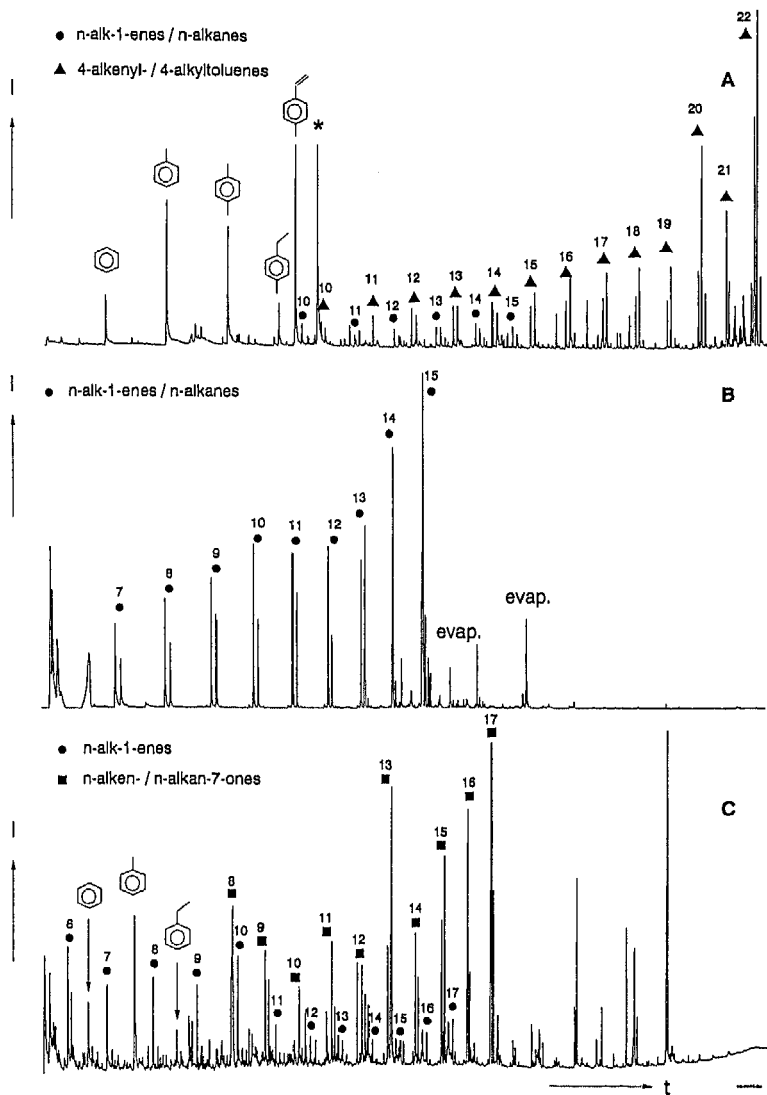


Figure 3. TIC (A, C) and GC (B) traces of the flash pyrolysates (770°C) of the sodium salts of (A) 16-(4'-methylphenyl)hexadecanoic acid, (B) hexadecanoic acid and (C) 12-hydroxy-octadecanoic acid. Numbers indicate total numbers of carbon atoms of compounds identified.