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Combustion and Pyrolysis Reactions of Alkylated Polycyclic Aromatic Compounds: The Decomposition of ^{13}C Methylarenes in relation to Diesel Engine Emissions.

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Abstract

The thermal decomposition of methylarenes labelled with ^{13}C in the methyl group was investigated. This was conducted using both a direct injection diesel engine and a pyrolysis flow cell connected to a GC-MS. 2- ^{13}C methyl-naphthalene and 9- ^{13}C methyl-phenanthrene were synthesized by means of the Corey-House coupling reaction and their identity and purity confirmed by mass spectrometry and NMR. GC-MS analysis of the aromatic fraction separated from the extract of the exhaust particulate collected from the engine operated with n-hexadecane doped with the labelled methyl-naphthalene showed that the ^{13}C was not redistributed among the methyl groups of higher PAH. However, with 9- ^{13}C methyl-phenanthrene in the fuel a significant amount was retained in the particulate, even though the principal in-cylinder reaction was dealkylation. Pyrolytic reactions of the ^{13}C -labelled methyl arenes were studied in a micro-pyrolysis-GC-MS-apparatus and confirmed dealkylation as the predominant reaction. The detailed chemical mechanism of the pyrolysis was explained by a scheme involving two alternative radical transfer reactions.

Keywords: PAH, pyrolysis, demethylation, ^{13}C Carbon labelled.

1. Introduction

Alkylated, especially methylated, polycyclic aromatic hydrocarbons (PAH), also known as methylarenes, are important constituents of petroleum-derived transport fuels such as diesel fuel [1] and are also products of coal pyrolysis [2,3]. Methylated PAH are also found in the products of pyrolysis and combustion of pure hydrocarbon liquid fuels [4] and biofuels [5,6]. In spite of considerable recent improvement in the level of PAH emissions from diesel engines [7], there is still concern as to their presence in particulates and consequent health hazards [8]. PAH are also thought to be pre-cursors [9] of emission-originating black carbon which is second only to carbon dioxide as a source of climate forcing [10]. It has been shown that the 'survivability' of PAH during diesel combustion is an important factor in determining the composition of emissions [11,12]. A number of geochemical indicators for petroleum exploration involve ratios of methylphenanthrene concentrations [13]. Studies have been made of the behaviour of these compounds using labelling techniques, eg by the ^{14}C method [14,15], and other analytical and labelling methods [14,16,17]. The advantage of using ^{13}C is that it is not a radioactive tracer so does not carry the same environmental risks on release to the atmosphere.

An important reaction influencing overall polycyclic aromatic compounds (PAC) survival is demethylation of alkyl PAH [18,19] involving cleavage of the strong aryl-alkyl C-C bond, probably by displacement of CH_3 by H [20]. The demethylation reaction can be followed by use of ^{14}C labelled substrates, but the attendant health and safety issues led us to explore the possibility of ^{13}C labelling with product analysis by gas chromatography-mass spectrometry (GC-MS). ^{13}C methyl PAH are conveniently prepared in high yield via the Corey-House

coupling reaction [21-23] with [^{13}C]methyl iodide. There have only been a few studies undertaken using ^{13}C labelling and these are summarised in a recent publication [24].

In the present study measurements were made using both engine as well as laboratory flow tube pyrolysis experiments [4,25]. The products of pyrolysis of 2- [^{13}C] methylnaphthalene and 9- [^{13}C] methylphenanthrene were studied with a flow cell reactor [24] with on-line analysis by GC-MS.

2. Experimental Methods

2.1 Synthesis

The syntheses of 2- [^{13}C] methylnaphthalene and 9- [^{13}C] methylphenanthrene were carried out by a procedure adapted from that of Langstrom and Sjöberg [21] for the rapid synthesis of aromatic hydrocarbons containing methyl groups labelled with ^{13}C . The hydrocarbons were prepared respectively from 2-bromonaphthalene and 9-bromophenanthrene via the Corey-House coupling reaction [22, 23] between [^{13}C]methyl iodide and either lithium di-(2-naphthalenyl)cuprate or lithium di-(9-phenanthryl)cuprate. The structure of these species is given in Fig. 1

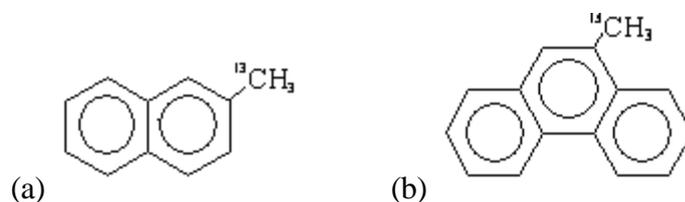


Figure 1. Structure of (a) 2- [^{13}C]methylnaphthalene, and (a) 9- [^{13}C]methylphenanthrene

Under positive nitrogen pressure, a slight excess of either 2-bromonaphthalene (8.28g) or 9-bromophenanthrene (10.27g) was added to finely cubed lithium (0.595g) in 100mL still-dried ether in a flame-dried flask. After stirring and reflux until the lithium dissolved, the aryl lithium solution was syringed into a second dried flask cooled in dry ice and containing 7.60g desiccator-dried cuprous iodide and 100mL of still-dried ether. The red/brown reaction mixture was further cooled in dry ice and 5.00g [^{13}C] methyl iodide added. The cooling bath was replaced by a water bath at 30°C and the mixture refluxed. The product hydrocarbon solution was purified by washing with dilute hydrochloric acid, separation of the organic layer, repeat washing and extraction with water, before washing with saturated sodium bicarbonate solution and then water; after drying over magnesium sulphate, the solvent was removed by rotary evaporation.

The identity of the products was confirmed by direct-inlet mass spectrometer as shown in Fig. 2.

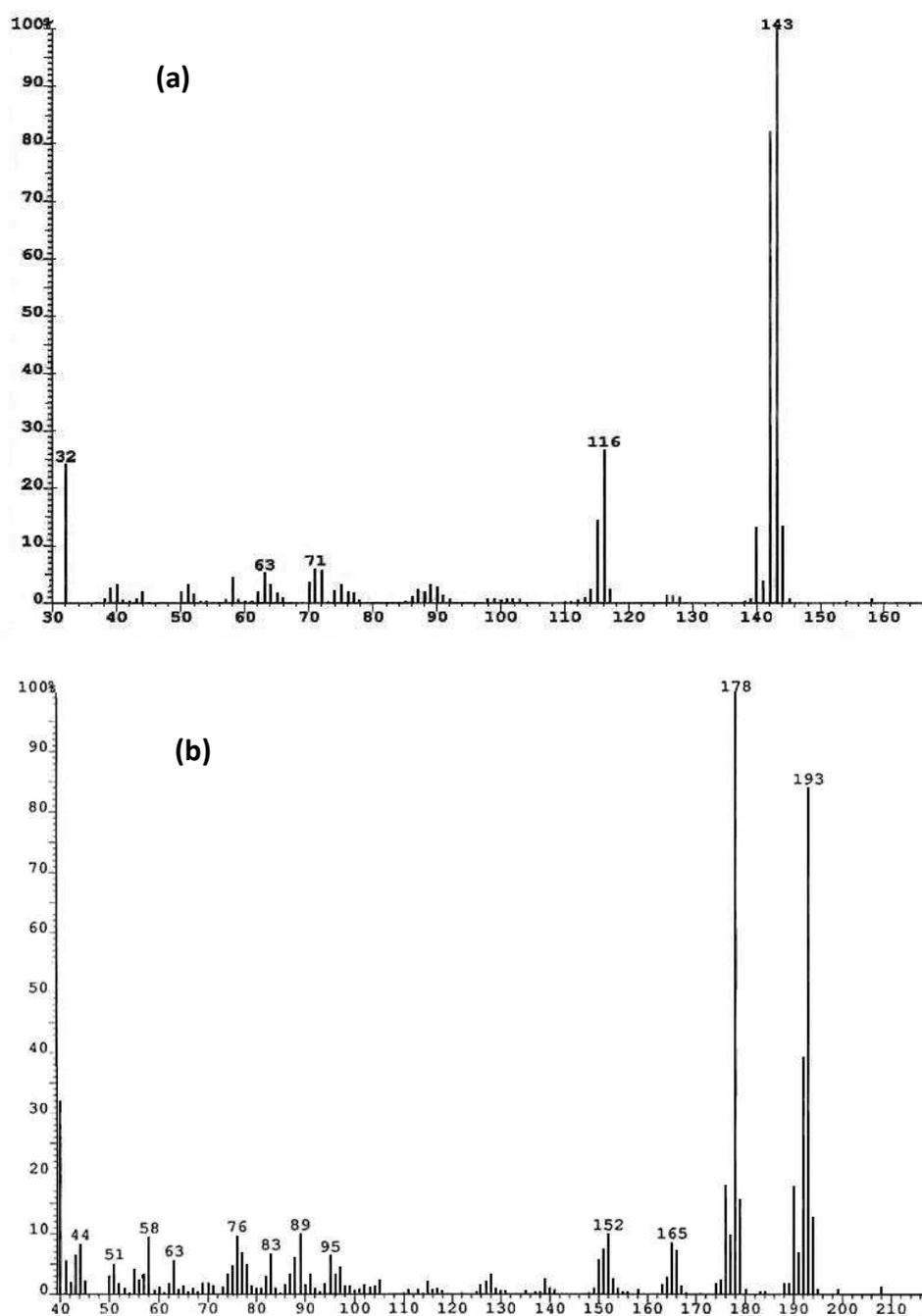


Figure 2. Direct inlet mass spectrum of (A) 2-[¹³C]methyl naphthalene, and (B) 9-[¹³C]methyl phenanthrene. The peaks at m/z 143 and 193 corresponds to the molecular ion.

^1H NMR spectroscopy was used to confirm the isotopic purity as >99% from a comparison of the intensities of the methyl resonances of the ^{12}C and ^{13}C containing- isomers, as shown in Fig. 3.

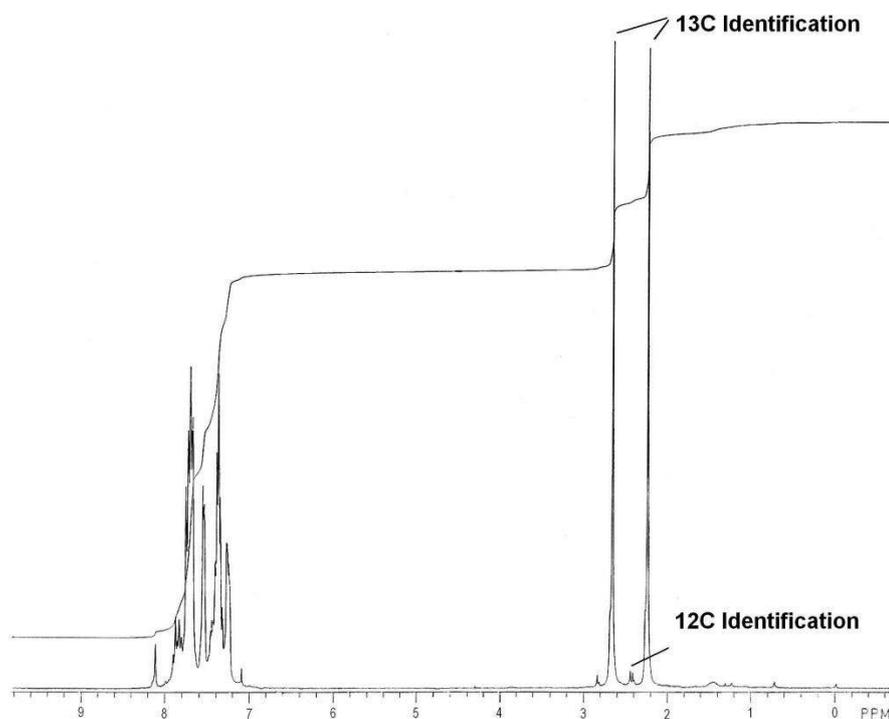


Figure 3. 100 MHz ^1H NMR spectrum of 9- ^{13}C methylphenanthrene showing the methyl proton resonance split by spin-spin coupling to ^{13}C , and signal from residual $^{12}\text{CH}_3$.

2.2 Diesel Engine Tests

The fuels used in the engine tests were: (i) n-hexadecane plus 2000 ppm 2- ^{13}C methyl-naphthalene and (ii) n-hexadecane plus 2000 ppm 9- ^{13}C methyl-phenanthrene. The engine was run on pure n-hexadecane before the tests in order to clean the fuel system and engine.

The engine used was a direct injection Perkins 4.236 modified to single-cylinder format and fitted with a low-emission squish-lip piston and a VCO injector nozzle operated at 1500 rpm

and 52 Nm torque. The test bed had external lubricating oil and water circulation pumps. Prior to testing, a fresh fuel filter was fitted and fresh lubricating oil was used to prevent contamination from previous tests. The engine was run on standard diesel fuel for an hour to ensure a steady-state temperatures had been reached. Then the lubricating oil was replaced with fresh, pre-warmed oil prior to then running the engine with pure n-hexadecane for another hour in order to purge the engine. The oil change was to minimise effects of PAH adsorbed into the oil contributing to the particulate. It should also be noted that the engine modification to single cylinder resulted in increased lubricating oil capacity per cylinder, so PAH contamination via the lubricating oil would be avoided. To prevent PAH contamination via the fuel transfer system, the fuel filter was also replaced with a fresh one between running on diesel fuel and on n-hexadecane. The engine was again purged between the 13C labelled fuels by running on pure n-hexadecane fuel for an hour before sampling commenced.

Particulate samples were taken 3m downstream of the exhaust valve and inside the exhaust manifold where the temperature was approximately 280°C. The equipment for the determination of the SAE smoke number was modified with a heater around the filter. A sample of 25L exhaust gases at 5L/min was cooled to 50°C in an oven and the particulates collected in a 25mm diameter spot on Whatman GF/F 55mm diameter glass-fibre filter paper in a filter holder also maintained at 50°C. The filters were Soxhlet extracted with a 4:1 vol/vol mixture of methanol with toluene with 10 refluxes /hr over 8 hr and protected from light [26]. Blank GF/F filter papers were also extracted. The diesel fuel was analysed for PAH content by GC-MS and found to contain naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene and pyrene. A range of substituted two ring PAH including methylnaphthalenes and C₂-naphthalenes were detected at concentrations of <2μg/g.

The particulate extracts were analysed as follows. The solvent was removed from the extracts by rotary evaporation and then gentle evaporation under a stream of oxygen-free nitrogen. Extracts were separated into aliphatic, aromatic and polar fractions on a 10 cm long 1cm diameter column containing 40µm chromatographic silica by sequential elution with n-pentane, benzene or toluene, and methanol. The solvent was removed from the fractions by gentle evaporation as for the particulate extract. The fractions were weighed and taken up in 250µL toluene from which 1µL aliquots were analysed in a Carlo Erba Mega HRGC 5300 capillary gas chromatograph attached via a heated line to a Finnegan MAT 705B ion trap detector. The mass range was set at 50 – 350Da with a scan speed of 0.3s. Both total ion current (TIC) and selective ion monitoring (SIM) chromatograms were recorded. Quantification of the analysis was achieved by use of external standards.

2.3 Flow Reactor Studies.

Pyrolysis of 2-[¹³C] methylnaphthalene and 9-[¹³C] methylphenanthrene was undertaken in a flow system with direct sampling and analysed by GC-MS as previously described [4,24]. This was carried out on a modified CDS 5200 Series pyrolyser in trap mode with an SGE Pyrojector set at the required temperature and fitted into the probe injector. The maximum operating temperature possible was 900°C. Liquid samples were injected by syringe. The flow cell reactor was a 6mm o.d. 4.5mm i.d. stainless steel tube, total length 250 mm, with a laminar flow of 10 – 100mL/min helium carrier gas. The sample was injected into the 50mm long first section heated to approximately 200°C, and then passed into the 60mm long reactor zone section heated as required to 600 – 900°C; from here the products passed into a 100mm long quenching region held at 200°C, from this section into the CDS 5200 interface and adsorbent Tenax TA trap at 40°C and then into the GC column for analysis. The trapping and

trap desorption system allowed the analysis of C4 – C20 hydrocarbons but the gaseous products H₂, CO, CO₂, CH₄ were not trapped and were vented.

After the reactor, the resulting products were desorbed from the trap at 300°C in a helium flow onto the GC column of a Shimadzu 2010 GC-MS system. The products were separated on a 60m long Rtx 1701 0.25 mm i.d. 0.25 µm film thickness column with a 40 – 250°C temperature programme.

The reaction zone was assumed to be given by the length of the heated reactor. Reaction times were calculated on that basis and a detailed mathematical analysis of the heating-up time and of the reaction time has been made [25]. The liquid samples (0.5 µl) were injected directly into the flow cell using a syringe over a period of 0.5 s. With helium as the carrier gas it was calculated using the method outlined before [25] that for example, with a reactor wall temperature of 800°C the inlet helium carrier gas heats to 799.4°C after 1mm. If nitrogen had been used it would only heat up to 764°C in the first 1mm. At the exit of the reactor the gases enter a section with a temperature of 200°C. With helium the temperature of the exit gases had dropped to 762°C after 1mm and to 514°C after 10mm [2].

3. Results and Discussion

3.1 ¹³C Compounds in the Study of Diesel Engine In-Cylinder Reactions.

Analysis of the mixtures of PAH in diesel fuel and diesel engine emissions, which are dominated by alkyl-substituted aromatics, was undertaken by GC-MS as described above.

For example, Figure 4 shows the SIM traces corresponding to the monomethyl-(m/z 192), C₂ (m/z 206), and C₃ -substituted (m/z 220) phenanthrenes for the GC-MS analysis of the

aromatic fraction of a diesel particulate extract. Literature retention indices [27] were used to identify the chromatographic peak of 9-methylphenanthrene (Figs 4-6).

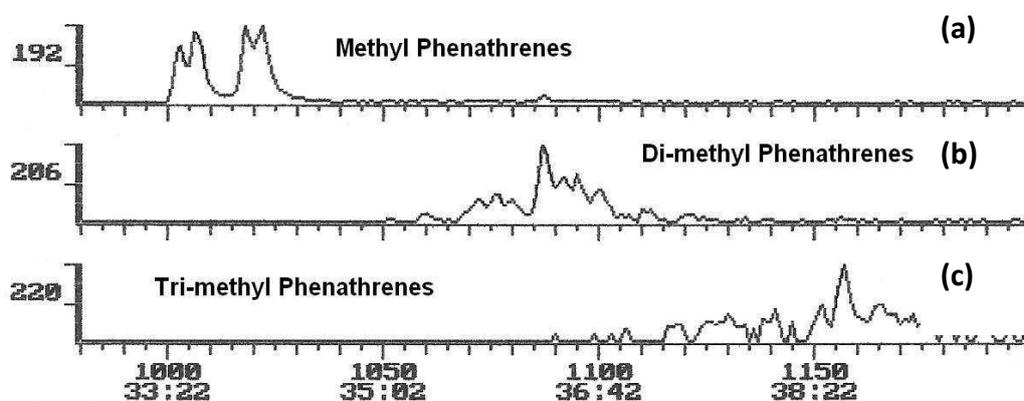


Figure 4. Alkylated phenanthrene region of GC-MS chromatogram of diesel engine exhaust particulate extract with selective ion monitoring at: (a) m/z 192 (monomethylphenanthrenes), and (b) C_2 -phenanthrenes; and (c) C_3 -phenanthrenes. For GC conditions, see text.

GC-MS analysis with SIM at m/z greater by one unit allows detection of ^{13}C containing species; thus m/z 193 is selective for [^{13}C] methylphenanthrenes, if present. Fig.5 compares the GC-MS traces in the methylphenanthrene region with SIM at m/z 192 and 193 and is consistent with the presence of ^{13}C -labelled compounds only at natural abundance levels. When operating the diesel engine with n-hexadecane fuel doped with 2000 ppm 2- [^{13}C] methylnaphthalene, the PAH mass spectra results were similar to those typically seen for unlabelled PAH; for example, SIM at m/z 192 and 193 indicates that the ^{13}C had not been redistributed among the methyl groups of the alkylated three-ring and higher PAH for the 2- [^{13}C] methylnaphthalene runs.

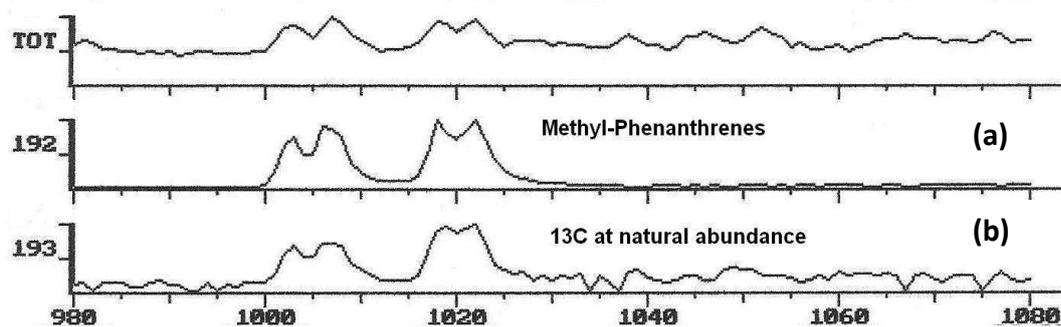


Figure 5. Methylphenanthrene region of GC-MS chromatogram of diesel engine exhaust particulate extract, monitoring: (a) SIM at m/z 192 [^{12}C]methylphenanthrenes); and (b) SIM at m/z 193 (methylphenanthrenes containing ^{13}C at natural abundance).

A n-hexadecane fuel doped with 2000 ppm 9- ^{13}C] methylphenanthrene produced, however, a particulate containing a measurable amount of the unburned additive; the intensity of the peak in the m/z 193 SIM chromatogram (Fig. 6) in the retention time region where 9- ^{13}C] and [^{12}C] methylphenanthrenes coelute approaches that of the peak recorded at m/z 192. This is confirmed by the relative intensities of the peaks at m/z 192 and 193 in the mass spectra shown in Fig. 7 of the 9-methylphenanthrene chromatographic peak. An estimate of the concentration of 9- ^{13}C] methylphenanthrene was made by comparison of the observed and library mass spectra. It was observed that the principal reaction of 9- ^{13}C]methylphenanthrene occurring in the diesel engine is de-alkylation, without significant involvement of the methyl group in rearrangement reactions to form new PAH species.

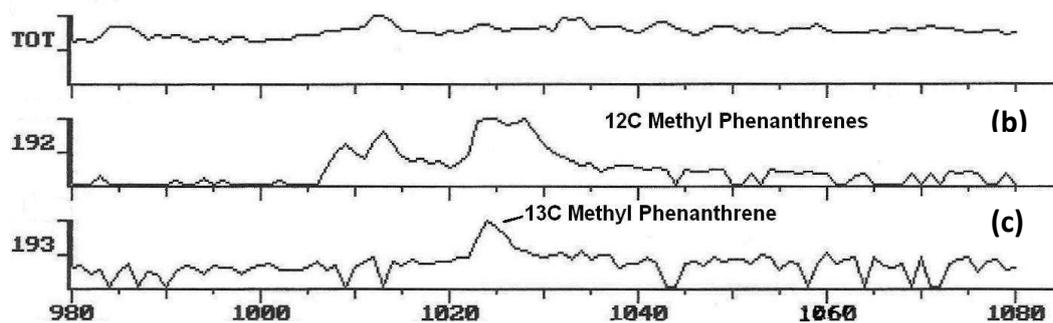


Figure 6. Methylphenanthrene region of GC-MS chromatogram of extract of exhaust particulate from diesel engine fuelled with 2000 ppm 9- ^{13}C methylphenanthrene in n-hexadecane, monitoring: (a) total ion current; (b) SIM at m/z 192 (9- ^{12}C methylphenanthrenes); and (c) SIM at m/z 193 (methylphenanthrenes containing ^{13}C).

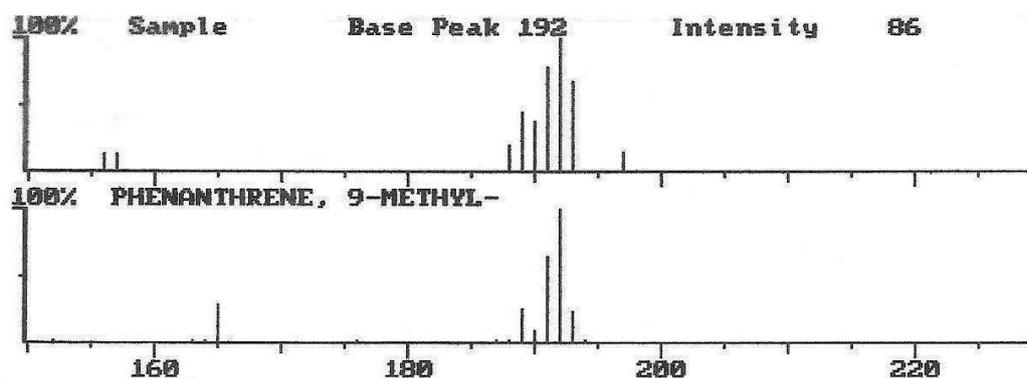


Figure 7. Mass spectra of the 9-methylphenanthrene co-eluting peaks in Figure 5.

Confirmation of in-cylinder de-alkylation of 9- ^{13}C methylphenanthrene is provided by the increased concentration of the parent compound phenanthrene in the particulate: 0.87 mg/kg fuel, as compared with 0.27 mg/kg when the fuel was n-hexadecane alone. This result indicates that the ^{13}C -containing additive has been de-alkylated leaving the phenanthrene

nucleus, and is similar to that of Rhead and colleagues [20, 28] who demonstrated in-cylinder de-alkylation of methyl naphthalene using a ^{14}C labelled compound.

3.2 ^{13}C in the Study of PAH Pyrolysis Reactions.

Pyrolytic reactions of ^{13}C labelled compounds were investigated in the pyrolysis-GC-MS apparatus (Py-GC-MS) at temperatures of 800 and 900°C. The maximum temperature possible was 900°C but it was also operated at 800°C to show the variation of products with temperature. The Py-GC-MS total ion current chromatogram of the pyrolysis products of 9- ^{13}C methylphenanthrene at these temperatures are given in Fig. 8. This shows that the major product is the parent PAH phenanthrene containing ^{13}C only at the natural abundance level, thus confirming demethylation as the predominant pyrolytic reaction. Also detected beyond 9- ^{13}C methyl phenanthrene in the TIC of the pyrolysis products were a number of small peaks which retention indices and mass spectra (molecular ion with m/z 208, fragment ion with m/z 192 from loss of one $^{13}\text{CH}_3$) were di- ^{13}C methylphenanthrenes. GC-MS showed in addition that 1- ^{13}C and 2- ^{13}C methyl naphthalenes were generated, shown from their mass spectra (loss of $^{13}\text{CH}_3$) to contain the isotopic label in the methyl group; the presumably resulting naphthalene did not contain ^{13}C ; an alternative synthetic route to naphthalene is that from cyclopentadiene, which would also account for the formation of indene [9]. Other PAH formed in small amounts by the pyrolysis of 9- ^{13}C methylphenanthrene included (see Fig. 8) biphenyl and fluorene and the monocycles benzene, toluene and styrene, but GC-MS showed that none of these contained significant quantities of ^{13}C .

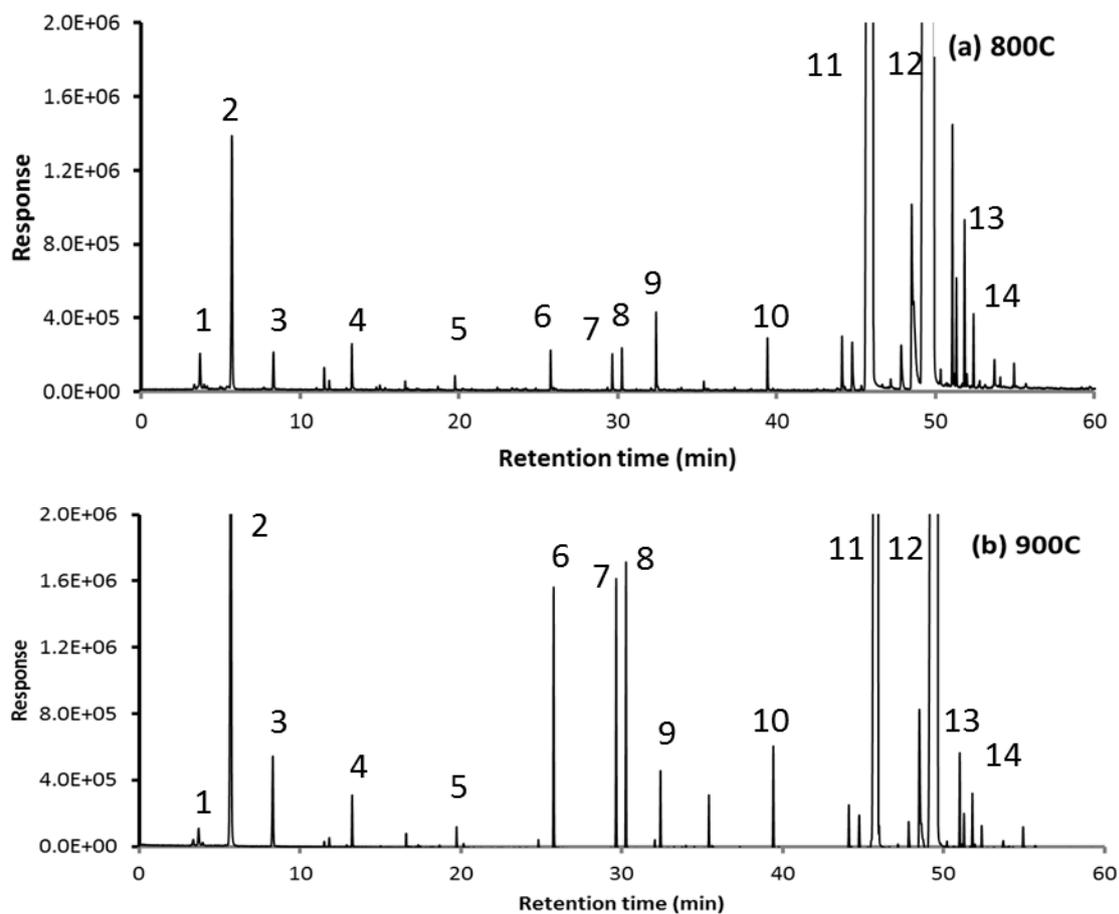


Figure 8. Py-GC-MS total ion current chromatogram for the pyrolysis of 9-[13C]methylphenanthrene: (A) at 800°C, and (B) at 900°C. For conditions, see text.

Selected peak identifications: 1, cyclopentadiene; 2, benzene; 3, toluene; 4, styrene; 5, indene; 6, naphthalene; 7, 2-[13C]methylnaphthalene; 8, 1-[13C]methylnaphthalene; 9, biphenyl; 10, fluorene; 11, phenanthrene; 12, 9-[13C]methylphenanthrene; 13, 14, di-[13C]methylphenanthrenes.

4. Mechanism

A number of authors have postulated processes in demethylation or methylation that have occurred which are consistent with the products obtained from diesel engines [12,16, 20,28].

Thus a plausible mechanism for the formation of methylnaphthalenes containing ¹³C in the side chain is the elimination of aromatic rings. Naphthalene may originate pyrolytically either

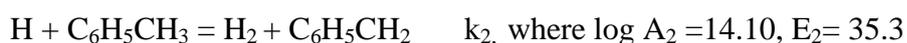
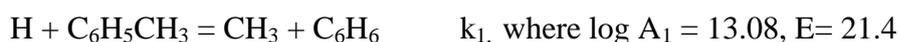
by elimination of an aromatic ring from phenanthrene or by loss of methyl from a methylnaphthalene isomer, or by synthesis from cyclopentadiene.

The definitive early work on the mechanism was by Smith and Savage [18,29] and various reaction paths at reaction temperatures of 350-425°C were postulated and the reactivities were ranked by them on the basis of the Dewar Reactivity Number. An extension to this approach was made by Rhead and Hardy [28] who used values of the LUMO (lowest unoccupied molecular orbital) in the same way, since they are both indirect parameters related to the gas phase reactivity of PAH. But the general conclusions can equally be determined from thermodynamic considerations. Rhead and Hardy [28] found a relationship between the LUMO and the amount surviving of PAH at low engine speeds but not at high speeds and high loads. This might be expected because effectively there are two reaction paths. In the first case, under 'mild' conditions (low engine speed, low torque, low temperature) existing in rich turbulent eddies there is little reaction of the polyaromatic nucleus but with some demethylation of PAH species. Thus some of the PAH present in the initial fuel or formed in the engine would be emitted with little change. Further evidence comes from the flow cell pyrolysis studies made as reported here when undertaken under 'mild' conditions (see Fig. 8). The second reaction path takes place under severe conditions (high speed, high torque, high temperature) where the polyaromatic nucleus undergoes fission reactions. Under these circumstances PAH molecules would partially form, as in the case of dimethylphenanthrenes, or reform during the cooling process in the exhaust cycle. This would lead to products which are largely determined by their thermodynamic stability [30,31] although this depends on the rate of the cooling process in the exhaust system

The key reactions involving methylnaphthalene and methylphenanthrene will initially consist of loss of the methyl group by fission, the abstraction of an H atom from the methyl group or

substitution of the methyl group by a hydrogen atom. The choice of a particular route will depend on the time-temperature profile and the other reacting species present. There is only limited data available on these reactions. The kinetics of the substitution reaction of hydrogen atoms with toluene and with methyl naphthalene have been studied as well as the reaction of hydrogen abstraction from the methyl group in toluene, and these reactions are tabulated in the NIST compilation [32].

Taking toluene as a typical methylated species it has been shown [33] that there is competition between the substitution reaction (1) and the abstraction reaction (2). Units of the rate constant k are in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1} \text{kJ}^{-1}$.



A and E are the pre-exponential factor and activation energy respectively. Using these rate expressions it is seen that at about 800 K, k_1 is approximately equal to k_2 . But at higher temperatures k_2 is faster than k_1 ; thus at 1400K k_2 is 5 times faster than k_1 . Consequently substitution reactions will dominate only under mild conditions.

Reaction 2 is followed by the decomposition of benzyl leading initially to the formation of fulvenallene (C_7H_6) [34]; the former can then decompose via a number of routes to form acetylene, cyclopentadiene, diacetylene and vinylacetylene. These products can then reform into aromatic ring compounds under appropriate conditions.

A similar situation holds for the reactions of 1-methylnaphthalene and 9-methylphenanthrene; they have similar enthalpies and the data available suggests that the reaction rates are similar [19,29,35]. The reactions that occur at engine combustion temperatures thus initially lead to H-abstraction and subsequent decomposition of the aromatic ring compounds. During exit

from the engine the products cool and the fragments recombine forming ring compounds, and then depending on the temperature the methylation reactions occur.

This process can be simulated by following the pyrolysis of 1-methylnaphthalene. This can be modelled using Chemkin-Pro [36] which is a chemical mechanism solver coupled with a detailed pyrolysis mechanism, and here the CRECK mechanism was used which is available online [37]. If typical conditions in the initial section of the exhaust pipe are assumed (1350 K, one bar pressure, plug flow and residence time 0.5s) then an initial mixture of 10 mol% methylnaphthalene in nitrogen would result in a consumption of 90% of the methylnaphthalene. A peak concentrations of 15 mol% naphthalene results as well as smaller amount of benzene, toluene and other pyrolysis products. The fact that 1-methylnaphthalene decomposes in this way and the methyl group lost possibly as CH₄ and CO₂ is consistent with the observation that the ¹³C is not distributed among methyl groups of higher PAH.

Insufficient is known about the reaction mechanism of 9- methylphenanthrene to model it in the same way. But the evidence that this is more stable leading to soot formation rather than decomposing to smaller fragments, and this is observed experimentally.

5 Conclusions

1. ¹³C labelled methylarenes can be prepared via Corey-House coupling between the appropriate lithium diaryl cuprate and [¹³C]methyl iodide and the identity and purity of the products, 2-[¹³C]methylnaphthalene and 9-[¹³C]methylphenanthrene, confirmed by direct inlet MS and ¹H NMR.

2. The labelled methyl arenes were doped into n-hexadecane and used as fuel for a DI single cylinder diesel engine and their survival determined by GC-MS analysis of the aromatic hydrocarbon fraction separated from the extract of the exhaust particulate. Experiments with

2-[¹³C] methyl naphthalene showed that ¹³C was not redistributed among the methyl groups of alkylated three-ring and higher PAH.

3. Doping with 9-[¹³C]methylphenanthrene gave particulates containing unburned fuel; the principal in-cylinder reaction was de-alkylation, confirmed by measurements on the product phenanthrene.

4. Complementary pyrolysis of labelled methylarenes in a flow system and direct product analysis by GC-MS again showed that demethylation was the main pyrolytic reaction. Minor amounts of [¹³C]-methyl naphthalenes were also formed in the pyrolysis of 9-[¹³C]methylphenanthrene.

5. The detailed chemical mechanism of the pyrolysis was explained by a scheme involving two alternative radical transfers, methyl substitution and hydrogen abstraction.

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