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Stability and hydrogenation of polycyclic aromatic hydrocarbons during hydropyrolysis (HyPy) – Relevance for high maturity organic matter

Hendrik Grotheer [a,*], Aileen M. Robert [a,b], Paul F. Greenwood [a,b], Kliti Grice [a]

[a] Western Australian Organic and Isotope Geochemistry Centre, Department of Chemistry, The Institute for Geoscience Research, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

[b] Centre for Exploration Targeting, University of Western Australia, Crawley, WA 6009, Australia

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ABSTRACT

A series of hydropyrolysis (HyPy) experiments have been conducted on a small suite of authentic polycyclic aromatic hydrocarbons (PAHs: coronene, pyrene and perylene) to investigate the HyPy behaviour of these PAHs. This information may help in the interpretation of the structural significance of aromatic HyPy products, often detected in high abundance, from high maturity kerogens. The PAHs were separately treated by HyPy and were all susceptible to some extent of hydrogenation. Perylene also decomposed into low molecular weight aromatics (e.g. methylbiphenyls). Structurally, perylene is much less stable than the more condensed PAHs coronene and pyrene. The total product concentrations (wt% of starting PAH) from all HyPy experiments were consistently less than 100 wt%, probably due to either the condensation of semi-volatile products on walls of the transfer line prior to reaching the HyPy trap or the inefficient cold trapping of highly volatile products. Hydrogenation of PAHs was prevalent and was found to be significantly influenced by the addition of a Mo-S based catalyst and potentially the C/Mo ratio, but largely independent of the two final temperatures used (520 °C and 550 °C). The fully aromatised and hydrogenated products for any stable ring system may provide a general indication of the size distribution of aromatic units within the kerogen structure.

1. Introduction

Hydropyrolysis (HyPy), an analytical process conducted at high temperature (up to 550 °C) and hydrogen pressure (150 bar) in the presence of a dispersed sulfided molybdenum catalyst, has been widely used to characterise coals and oil shales (Snape et al., 1989, 1994). An important attribute of catalytically assisted HyPy cracking is the release of macromolecularly bound hydrocarbons with minimal isomeric alteration (Love et al., 1995, 1997). In addition to structural characterisation, HyPy has proven to be a useful tool for a broad range of organic geochemical applications, including authentication of the organic composition of geological materials compromised by oil or migrated bitumen or extreme levels of biodegradation (Murray et al., 1998; Russell et al., 2004); evaluation of organic matter (OM) composition of meteorites (Sephton et al., 2004); the detection of indigenous hydrocarbons in Archean rocks with implications for the evolution of early life (Brocks et al., 2003; Marshall et al., 2007; French et al., 2015); and to investigate the role of sulfur in contemporary toxic oozes (Lockhart et al., 2013).

Most HyPy studies have focused on aliphatic products, yet polycyclic aromatic hydrocarbons (PAHs) have also been detected following HyPy treatment of a range of high thermal maturity samples. PAHs were the major products from the HyPy treatment of the black carbon fraction of soils (Meredith et al., 2013), charcoals (Ascough et al., 2010) and Archean rocks (Brocks et al., 2003; Marshall et al., 2007; French et al., 2015). We also recently observed a relatively high abundance of parent and hydrogenated PAHs from the HyPy treatment of high maturity organic sediments host to a large orogenic gold deposit (Robert et al., 2014). The products of the Au-associated organic matter (OM) were dominated by pyrene which had previously been reported to be a major HyPy product released from charcoals (Ascough et al., 2010).

Here we describe a series of HyPy experiments with three pure PAH compounds: pyrene [**I**], perylene [**VII**] and coronene [**XV**]. The extent of their thermal degradation and the type and abundance of products from these experiments may prove helpful in the interpretation of the aromatic-rich HyPy profiles typical of high maturity kerogens.

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* Corresponding author. Tel.: +61 8 92663894.
E-mail address: h.grotheer@curtin.edu.au (H. Grotheer).

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Systematic investigation of the isolated behaviour of different compounds is a fundamental step in establishing their behaviour and reactivity under new analytical conditions, and the results from such basic but essential experiments often help to interpret the analysis of more complex materials (i.e., organic sediments). Indeed, model compounds have often been analysed to improve our understanding of pyrolysis reaction mechanisms (Smith et al., 1989; Mukherjee et al., 1994; Abbott et al., 1995; Rushdi et al., 2003; Nkansah et al., 2011) or to monitor their behaviour under simulated hydrothermal petroleum conditions (McCollom et al., 1999). The HyPy behaviour of PAHs, however, has not previously been studied. Model compound-based HyPy studies have so far been largely limited to functionalised compounds like carboxylic acids, stearic and oleic acids as well as saturated and unsaturated C_{27} sterols (Meredith et al., 2006).

2. Materials and methods

Three model PAHs were used to investigate the effect of HyPy treatment at selected temperatures and catalyst loads. Individual stock solutions of pyrene (~70 ppm; $C_{16}H_{10}$, 99%, Sigma Aldrich [**I**]), perylene (~130 ppm; $C_{20}H_{12}$, ⩾99.5%, Sigma Aldrich [**VII**]) and coronene (~130 ppm; $C_{24}H_{12}$, 97%, Sigma Aldrich [**XV**]) were produced and stored in a freezer at −20 °C. Roman numbers refer to the chemical structures shown in the Appendix, where [**I**–**IV**] represent pyrene-, [**VII**–**XI**] perylene- and [**XV**–**XX**] coronene-related structures. Structures [**XII**–**XXI**] show additional PAHs. Silica gel (high purity, 40 Å, 35–70 mesh, Sigma Aldrich) was annealed at 550 °C for 16 h and stored at 160 °C prior to preparation of the following beds: (a) pure silica gel; and (b) silica gel loaded with 5 wt% sulfided molybdenum catalyst ($(NH_4)MoO_2S_2$) as previously described by Love et al. (1995). Sub aliquots (0.5 mL) of the respective PAH solutions were separately adsorbed onto the catalyst and non-catalyst loaded silica beds (0.5 g).

The samples were pyrolysed using a commercial apparatus (STRATA Technology Ltd) and following traditional operating procedures (Snape et al., 1994; Love et al., 1995; Meredith et al., 2004; Aboglila et al., 2011; Lockhart et al., 2013). Briefly, the samples were pyrolysed with resistive heating from 25 °C to 250 °C at 300 °C/min, and then from 250 °C to the final temperature of either 520 °C or 550 °C at 8 °C/min with the final temperature held for 2 min. A constant pressure (150 bar) and flow rate (5 L/min) of ultra-high purity hydrogen (BOC Group) was maintained throughout thermal treatment. The released compounds were cold trapped on a silica-filled trap, chilled with dry ice. Products adsorbed on the silica trap were eluted with DCM (40 mL) on a large chromatographic column; elemental sulfur was removed with HCl-activated copper turnings.

The reactor and trap were cleaned after each analysis by: (i) 2 × 30 min ultra-sonication in DCM: MeOH 9:1; and (ii) thermal conditioning of the sample-free HyPy reactor at 300 °C/min from 25 °C to 300 °C then 10 °C/min to 550 °C held for 10 min under constant pressure (150 bar) and H_2 flow rate (5 L/min) and confirmed to be contaminant free by HyPy treatment of clean silica gel (loaded with or without catalyst dependent on the next analysis type to be run).

The HyPy released products were analysed by gas chromatography–mass spectrometry (GC–MS). A HP 6890 GC fitted with a ZB-5MS capillary column (30 m × 0.25 mm i.d. × 1 μm film thickness) was used. Ultra high purity helium (BOC) was employed as a carrier gas at constant flow rate (1.3 mL/min), with a GC oven temperature programme of 40 °C (1 min hold) to 330 °C (25 min hold) at 10 °C/min. The mass spectrometer was an Agilent 5975 inert mass selective detector (MSD) with the transfer line temperature maintained at 320 °C. Mass spectra (70 eV) were acquired in full scan mode (30–530 Da) at ~4 scans per second and at a source temperature of 230 °C.

HyPy products were quantified based on external calibration established by analysing the PAHs at several different concentrations. Duplicates were conducted of all HyPy treatments: PAH compounds, catalyst or non-catalyst; 520 °C or 550 °C final temperature. Product yields (wt% reactant) are reported as the average value of duplicate analysis, with their variability expressed as standard variation (SV±).

3. Results

3.1. Hydropyrolysis product yields

In the absence of a catalyst, HyPy product yields were highest from pyrene (68 wt% at 520 °C and 72 wt% at 550 °C), moderate from coronene (47 wt%; 46 wt%) and lowest from perylene (39 wt%; 37 wt%) (Fig. 1; Table 1). The addition of the catalyst significantly reduced the HyPy yield of products from pyrene and perylene, but had little effect on coronene product yields. For example, at 520 °C the yield of pyrene products dropped from 68 wt% without the catalyst to 50 wt% with the catalyst. A similar reduction was evident at 550 °C and the pyrolysis temperature generally had less of an effect compared to the catalyst.

With the exception of the catalyst-free coronene experiments the reproducibility of the total yield was generally reasonable (⩽3 wt%). The duplicate coronene non-catalyst experiments showed relatively larger variabilities of 17 wt% at 520 °C and 7 wt% at 550 °C.

3.2. Pyrene

Total ion chromatograms (TICs) showing distributions of products from the HyPy treatments of pyrene are illustrated in Fig. 2 and product abundances are listed in Table 1. A range of hydrogenated products were detected. The relative abundance differed significantly in the presence or absence of the catalyst, but less so between the final pyrolysis temperatures investigated (Fig. 5). HyPy released products at 550 °C and without the catalyst included pyrene [**I**] (21 wt%), 2H-[**II**] (24 wt%), 4H-[**III**] (21 wt%), 6H-[**IVa,b**] (4 wt%) and 10H-[pyrenes] [**Va,b**] (2 wt%). The corresponding 520 °C pyrolysis showed a similar distribution of products. Whilst the addition of the catalyst reduced overall product yields (by 17 wt% at 550 °C) – particularly of 2H-[pyrene] (reduced by ~half to 9 wt%) and 4H-[pyrene] (by ~three quarters to 5 wt%) – there was an increase in the degree of hydrogenation exemplified by the detection of fully hydrogenated 16H-[pyrene] [**VI**] isomers (13 wt%). No products indicative of the breakdown of the four ringed pyrene structure were detected.

3.3. Perylene

TICs showing the distribution of products from the HyPy treatments of perylene are shown in Fig. 3 and product abundances are listed in Table 1. Catalyst-free 550 °C HyPy products included 14H-[perylene] [**X**] (20 wt%) and 6H-[perylene] [**VIII**] (16 wt%) as well as traces of perylene [**VII**] and 2H-[4H-benz[*de*]anthracene] [**XIV**]. Product yields were lower with the catalyst (by 20 wt% at 550 °C) – particularly 6H- and 14H-[perylene] which had reduced to < 2 wt% – although there was an increase in abundance of the fully hydrogenated 20H-[perylene] [**XI**] (7 wt%) (Fig. 5). No perylene was recovered, but several products were indicative of the breakdown of the perylene ring system and additional rearrangement in some cases. In the presence of the catalyst, perylene breaks down to 2-Me-1,1′-biphenyl [**XII**] (3 wt%), 2H-[4-Me-naphthalene]