BEHAVIOUR OF MODEL SUBSTRATES IN CATALYTIC HYDROPYROLYSIS TO INVESTIGATE PRESERVATION OF BIOMARKERS RELEASED FROM KEROGENS AND ASPHALTENES

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Introduction

The use of hydropyrolysis (commonly abbreviated to hypy), which refers to pyrolysis assisted by high hydrogen gas pressures (>10 MPa) in the presence of a dispersed catalyst, as an analytical pyrolysis method for liberating covalently-bound biomarker hydrocarbons from kerogen was first reported by Love et al.\textsuperscript{(3)} This and other subsequent studies have demonstrated the unique capability of the fixed-bed catalytic hydropyrolysis procedure to release much higher yields of aliphatic biomarker hydrocarbons (including \(n\)-hydrocarbons, hopanes and steranes) from immature kerogens compared to mild catalytic hydrogenation and traditional pyrolysis methods.\textsuperscript{(1-5)} A combination of slow heating (<20°C min\(^{-1}\)), high hydrogen pressure (15 MPa) and use of a dispersed sulphided molybdenum catalyst represents the most effective regime for achieving high conversions to DCM-soluble products whilst minimising the structural rearrangement of biomarker species.\textsuperscript{(6)} Kerogen-bound hopanes and steranes undergo the same epimerization reaction pathways as their free counterparts in the bitumen, but they are generally considerably less mature in terms of isomerisation at both ring and side-chain chiral centres. As a consequence, the biomarker profiles can be used to assess the maturity of source rocks with greater precision than using the free hydrocarbons and the successful application of hydropyrolysis to a contaminated core has been demonstrated.\textsuperscript{(5)} Further, hydropyrolysis tests on asphaltenes isolated from a biodegraded oil seep have shown that biomarker structures sequestered in heavy oil fractions are generally quite similar and, therefore, single stage hydropyrolysis is perfectly satisfactory for giving representative distributions of bound biomarkers. To investigate the extent of cracking and isomerisation undergone by \(n\)-alkanes and steranes upon formation from specific functionalities, a series of hydropyrolysis tests have been conducted on stearic acid, oleic acid and 5-\(\beta\) cholic acid, together with cholesterol bound to a phenolic group via an ether link.

Experimental

Stearic acid, oleic acid and 5-\(\beta\) cholic acid were purchased from Aldrich. 4-hydroxybenzyl cholosteryl ether was synthesized from sodium cholesterolate and \(\text{C}_7\text{H}_4\text{COOC}_6\text{H}_4\text{CH}_2\text{Br}\) (1:1 mole ratio) and also via the general synthetic route depicted in appendix 1 for preparing both ether and sulphide linked sterane moieties. Attempts were made to incorporate 4-hydroxybenzyl cholosteryl ether into a phenolic resole by reacting it with phenol and formaldehyde (total phenol to formaldehyde mole ratio of 2.5:1, mole ratio of phenol to 4-hydroxybenzyl cholosteryl ether of 3:1) to place the cholosteryl moiety in a macromolecular structure. Single stage hydropyrolysis tests were conducted at 520°C and 15 MPa as described previously\textsuperscript{(1-5)} on the carboxylic acids and the resin by adsorbing the former on either silica or an active carbon and mixing the latter with sand before adding the dispersed Mo catalyst in the usual manner (3% /w/w Mo loading). Samples were heated resistively from 50°C to 250°C at 300°C min\(^{-1}\), and then from 250°C to 500°C at 8°C min\(^{-1}\), under a hydrogen pressure of 15 MPa. A

Figure 1. Hopane distribution (m/z 191 single ion chromatogram) showing the hopanes released from a high S sediment (from Framvaren Fjord, Norway) via hydropyrolysis.\textsuperscript{(8)}

As well as providing excellent biomarker profiles for kerogens, it has been established that hydropyrolysis oils have similar bulk carbon skeletal parameters as the parent kerogens, again as a result of the high oil yields and minimal structural alteration for the hydrocarbon moieties.\textsuperscript{(9)} In view of the potential of hydropyrolysis for a number of applications in oil exploration and as a general characterisation technique for geomacromolecules, there is a need to consider both the extent of heteroatom (C-O and C-S) bond cleavage in hydropyrolysis and the impact this might have in terms of isomerisation and cracking on the resultant biomarker distributions.

Two-stage hydropyrolysis in which the primary oil vapors pass through a bed of hydrotreating catalyst can result in the release of significantly higher concentrations of alkane biomarkers than its single stage counterpart due to a greater extent of C-O and C-S bond cleavage occurring\textsuperscript{(10)} However, the aliphatic biomarker profiles are generally quite similar and, therefore, single stage hydropyrolysis is perfectly satisfactory for giving representative distributions of bound biomarkers. To investigate the extent of cracking and isomerisation undergone by \(n\)-alkanes and steranes upon formation from specific functionalities, a series of hydropyrolysis tests have been conducted on stearic acid, oleic acid and 5-\(\beta\) cholic acid, together with cholesterol bound to a phenolic group via an ether link. A
hydrogen sweep gas flow of 10 dm$^3$ min$^{-1}$, measured at ambient temperature and pressure ensured that the products were quickly removed from the reactor vessel. Products were trapped on silica as previously described and then analysed by GC-MS.

**Results and Discussion**

**Carboxylic acids** Figures 2 and 3 show the gas chromatograms of the products at different temperatures from stearic and oleic acids adsorbed on active carbon. The yields of recovered hydrocarbons from stearic and oleic acids adsorbed on silica and active carbon are listed in Table 1.

**Table 1. Product yields from stearic and oleic acids adsorbed on silica and carbon determined by GC**

<table>
<thead>
<tr>
<th></th>
<th>Yield, mg/g carbon</th>
<th>Stearic acid</th>
<th>Oleic acid</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
<td>500</td>
<td>550</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>219</td>
<td>554</td>
<td>695</td>
</tr>
</tbody>
</table>

Table 1 indicates that for both adsorbents the yields increase with temperature, but are higher for silica than for the active carbon. Only at 550°C is a significant degree of hydrocracking evident from Figure 2 for stearic acid to give lower boiling $n$-alkanes than $n$-octadecane. At the lower temperatures, the selectivities for hydrogenating stearic acid are $>90\%$. Lower selectivities to $n$-octadecane are observed for oleic acid at 500 and 550°C than at 400°C. A high selectivity ($>90\%$) was also achieved for 5-$\beta$ cholanic acid to 5-$\beta$ cholelale but the yields were slightly lower than for stearic and oleic acids, only reaching 500 mg/g of initial carbon by 550°C. Bearing in mind that 500°C is usually a sufficiently high enough temperature to achieve maximum conversions for relatively immature kerogens, this suggests that surface O complexes are formed as the carboxylic acids are reduced to predominately $C_{18}$ hydrocarbons.

Figure 2. Gas chromatograms of hydropyrolysis products from stearic acid adsorbed on active carbon.

**Figure 3.** Gas chromatograms of hydropyrolysis products from oleic acid adsorbed on active carbon.

It is interesting to note also that, when adsorbed on silica, asphaltenes typically only give conversions of 300–400 mg/g of C compared to over 900 mg/g of C for immature kerogens. Although interactions among relatively large aromatic clusters could contribute to high char yields, complex formation between asphaltenes and surface oxygen functional groups may again be a contributory factor to suppressing yields.

**Onset of ether bond cleavage** A series of experiments at different temperatures were conducted on the 4-hydroxybenzyl cholestanyl ether-containing resin to establish the onset temperature for C-O bond cleavage. The yields are presented in Figure 4, which shows above 350°C the yield increases sharply. Comparable yields of cholestan and cholestanol were obtained indicating the fairly random cleavage of the C-O bond. Thus, this result verifies that any hopanoids released below 350°C from sulfur-rich sediments must be due solely to cleaving sulfide bonds.
Figure 4. Yield of cholestane as a function of hydropyrolysis temperature from the 4-hydroxybenzyl cholestanyl ether co-resol.

Hopanoids – side chain cleavage Figure 1 shows the hopane profile (m/z 191 single ion chromatogram) for the recent high S sediment where the profile is dominated by the biologically-inherited C₃₅ β,β hopane which is a reflection of the hopanoid skeleton being bound into the kerogen predominately via weak sulphided bonds (average of 5 bonds per chain). Indeed, hydropyrolysis at 350°C (see above) of the Framvaren sediment shows that 70%+ of the total hopanes released are still linked by one or more C-O covalent bonds. Since the strengths of C-O (ether) and C-C bonds are comparable, more cracking of the hopane side chain should accompany increasing temperatures (>400°C) of the Framvaren sediment shows that 70%+ of the total hopanes released are still linked by one or more C-O covalent bonds. Since the strengths of C-O (ether) and C-C bonds are comparable, more cracking of the hopane side chain should accompany increasing proportions of C-O bonding for the hopanes. Further, C-C bond cleavage will also result as higher temperatures (>400°C) are experienced by the hopanoid moieties before they exit the reactor. The C₃₂ β,β hopane and lighter hopanes could be diagenetic products and, consequently, the ratio of the C₃₃-C₃₄ β,β hopanes to C₃₅ β,β hopane is probably the best indicator of the proportion of hopanoid side chain (C-C) cracking that occurs in hydropyrolysis. This ratio is ca. 0.6:1.0 for the high S sediment and this is probably a reflection of the fact that one or more C-O bonds still have to be cleaved to released the majority of the hopanes. Although side chain cleavage does occur to an appreciable extent, the ring stereochemistry is not markedly affected with the β,β epimers dominating. As found previously for Göynük oil shale[1], normal pyrolysis results in virtually complete cracking of the hopane side chain with no hopanes beyond C₃₂ being evident.

Conclusions

Selectivities for hydrogenating aliphatic carboxylic acids to the corresponding alkanes are extremely high with >90% being achieved for stearic acid 5-β cholanic acid. No isomerisation was evident for the cholestane-containing resin. Hydrocracking and isomerisation would thus appear to be negligible for single functionalised steranes. However, complex formation with surface oxygen functional groups for both the carboxylic acids and asphaltenees is a contributory factor to not achieving higher conversions until temperatures in excess of 500°C. Ether bonds do not start to cleave until 350°C indicating that biomarkers released at lower temperatures from S-rich kerogens arise from cleaving sulphides only.

Acknowledgement. The authors thank the National Environmental Research Council (NERC) for financial support (Ocean Margins LINK grants, nos. NER/T/S/2000/01366 and 2001/01153).

References


Appendix 1 General synthetic route for ether and sulphide liked steranes