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METAL COORDINATION CHEMISTRY: REMOVAL AND RECOVERY OF METAL COMPOUNDS FROM HEAVY CRUDE AND SHALE OILS WITH MULTIDENTATE LIGANDS. QUARTERLY PROGRESS REPORT

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Publication Date
1982-06-01
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Metal Coordination Chemistry:
Removal and Recovery of Metal Compounds from Heavy
Crude and Shale Oils with Multidentate Ligands

Quarterly Progress Report for Period
April 1 - July 1, 1982

Prepared for the Bartlesville Energy Technology Center

Pr.No. 19-81BC009799003
B&R Code AC 05515
BETC PTPA No. 210
Acct. No. 210D

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June 1982

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This work was supported by the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.
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i
Introduction

In previous publications,\textsuperscript{1,2} we identified methyl and phenylarsonic acid as well as arsenate in oil shale products; namely, shale oil and oil shale retort waters. We believe that the biogeochemical origin of these compounds would be important to elucidate. The reasons being that either these compounds have a biogeochemical origin in oil shale kerogen or that they are formed during the pyrolysis of oil shale kerogen. Additionally, it is desirable from a process standpoint and for environmental reasons that the origin of these compounds be established.

In this report, we show data that identifies methyl and phenylarsonic acid that was isolated from Green River oil shale kerogen.

In a previous report,\textsuperscript{3} we demonstrated the usefulness of HPLC-GFAA analysis for fingerprinting heavy crude oils and utilizing these histograms in defining the molecular weights of various vanadyl compounds found in these oils. In this report, we examined the asphaltenes of several crude oils via HPLC-GFAA analysis and provide a comparison to the data obtained on the whole heavy crude oils.

Identification of Methyl and Phenylarsonic Acid Found in Green River Oil Shale Kerogen

In earlier experiments, we used the total methanol extracts of a Green River oil shale kerogen sample to identify by HPLC-GFAA and GC-EIMS analysis phenylarsonic acid and, tentatively by HPLC-GFAA, arsenate. We now describe similar experiments with HPLC purified fractions of the methanol extract in which we have derivatized both phenylarsonic acid and the hithertofoe unidentified methylarsonic acid with 3-
methylcatechol followed by GC-EIMS analysis. The known compounds from the reaction of 3-methylcatechol and either phenyl or methylarsinic acid, i.e., the five coordinate organoarsenic catecholates (eq. 1) were chromatographed on a 30 m fused silica capillary column interfaced to an electron impact mass spectrometer (GC-EIMS) and gave the following mass spectra and reconstructed ion chromatographs (Figures 1-4).

A similar analysis, as stated above, with the HPLC purified factors provided unequivocal evidence for the identification of methylarsinic acid as well as reconfirmation of the previously indentified phenylarsinic acid (Figures 5-9).

These exciting discoveries open a new field which we have called organometallic geochemistry and which further enhances our original goals of providing polymeric ligands to remove inorganic and organoarsenic compounds from shale oil.

Analysis of Asphaltenes of Cerro Negro, Boscan, Wilmington and Prudhoe Bay Heavy Crude Oils for Vanadyl Porphyrin and Non-Porphyrin Compounds by HPLC-GFAA

In the previous report, we analyzed the heavy crude oils, extracted oils and extracts on size exclusion HPLC columns, which showed the molecular weight distribution for vanadyl compounds in four heavy crude oils. Recently, we have extended this study to the asphaltenes of Cerro Negro, Boscan, Wilmington and Prudhoe Bay isolated via pentane precipitation. Analysis of the vanadium content in the asphaltenes by x-ray fluorescence provided a comparison to the whole heavy crude oils previously studied (Table 1).
As shown in Table 1, the asphaltene fraction, as has previously been understood, has a high concentration of the vanadium present. More importantly, we have examined these asphaltene fractions by SEC-HPLC-GFAA analysis and determined the vanadium distribution with $mw > 900$; $< 900$, $> 400$; $< 400$. Table 2 states our results and shows conclusively that vanadyl compounds incorporated into molecules with $> 900$ mw are present in the asphaltenes in very high concentrations as is the porphyrin and non-porphyrin vanadyl compounds. These latter results need to be examined along with an analysis of the maltene fraction (oil remaining after pentane precipitation of asphaltenes) and extracts of the asphaltenes.

The fingerprints of the asphaltenes for the heavy crude oils studied are presented in Figures 10-13 and the calibration curve in Figure 14.

We believe these preliminary results on the fingerprinting of asphaltenes for vanadyl compounds will help in future speciation studies for identification of these compounds in the heavy crude oils and components of the oil.

**Future Work**

We hope to start on the synthesis of polymer-bond catechol derivatives to determine their reactivity with methyl and phenylarsonic acid. In addition, reactions of shale oil with 3-methylcatechol will be performed to see if we can react the coordinated methyl and phenylarsonic acids with this catechol and form the five-coordinate organoarsenic catecholates. This experiment will allow a preliminary view of the
feasibility of catechols in competing with the large molecules associated with iron that coordinate the organoarsenic compounds.

The heavy crude oils have been reanalyzed on a combination of 50-100 Å SEC columns and better separations have been offered. More interestingly, the maltenes and extracts of asphaltenes are analyzed by HPLC-GFAA and should provide some interesting comparisons with the heavy crude oils.

We have also initiated, with the help of three summer students and their professor, a synthesis program to obtain needed vanadyl porphyrin and non-porphyrin model compounds for the speciation studies.

Acknowledgements

We wish to thank John Komlenic, Brian Wines, Carl Weiss, Wyman Walker and Raja Tannous for experimental results reported in this quarterly.

References


(3) R.H. Fish, LBID523, Quarterly Report to the Bartlesville Energy Technology Center, Jan. 1, 1982 - April 1, 1982.

Presentations and Publications

\[ \text{EQUATION 1} \]

\[ \text{cis} \quad R \quad \text{trans} \]

\[ \text{OH} + \text{RAs(OH)}_2 \xrightarrow{2-3\text{h}} \text{Me,} \]

\[ + 3\text{H}_2\text{O} \]
FIGURE 1

DATA: FISH247 #1
CALI: CAL #1

SAMPLE: STD: PHENYL ORGANO ARSENATE, DILUTED 109:1
RANGE: G 223.2840 LABEL: H 0.4.0 QUAR: A 0.1.0 BASE: U 20. 3

SCAII: 2.5 TO 20.0
Figure 3. GC-EIMS of the phenylarsenic acid·3-methylcatecholate.
FIGURE 5
SAMPLE: HPLC NAPHTHOL EXTRACT 31-35.5 DT-1-600, DILUTED 10:1
RANGE: 0 250-4000 LABEL: H 0.4.0 QUANT: A 0.1.0 BASE: U 20.3

197.000
0.500

4186.
FIGURE 6

RIG + MASS CHROMATOGRAMS
04/16/02 13:18:00
SAMPLE: HPLC MEON EXTRACT 31-35.5 RT-1-2609
BAUGE: 6 235.4000 LABEL: N 0.4.6 QuE: A 0.1.0 BASE: U 20.3
RGC + MASS CHROMATOGRAMS
DATA: FISH250 q1
CAL: CALIBRATES 61
SAMPLE: HPLC MEAN EXTRACT 31-35.5 ET-1:888, DILUTED 16:1
RANGE: 6 250.4360 LABEL: H 0.4 0.0 QUANTITY: A 0.1.0 BASE: U 20.3

FIGURE 7
SCALES 2050 TO 2100

18.0
197
77.9
274
2035 2039 2047 2058 2078 2099
2041 2022 2056 2073

197.000
187.000
342.
274.

439.
△ ± 0.500
△ ± 0.500
Boscan Asphaltoe

10 mg/20 ml (3:4) dilution CHCl₃
100% THF O.S. t/min

Steric Exclusion 50 Å - 100 Å

Vanadium Specific GFAA
λ = 408 nm

FIGURE 10
FIGURE 11

Cerro Negro Asphaltene
50 mg/10 ml CH\(_2\)Cl\(_2\), all.
100.70 THF 0.5 ml/min.
Steric Exclusion 50A-100A
Vanadium Specific GFAA

λ = 408 nm
Prudhoe Asphaltene

121 mg/20 ml CuCl2 (1:2) dilution
100% THF 0.5 ml/min
Steric Exclusion 50 Å - 100 Å
Vanadium Specific GFAA
λ = 408
<table>
<thead>
<tr>
<th>Location</th>
<th>PPM V in Crude oil</th>
<th>PPM V in Asphaltene</th>
<th>Wt. % of Asphaltene in Crude</th>
<th>% of Total V in Asphaltene</th>
</tr>
</thead>
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<tr>
<td>Boscan</td>
<td>1100</td>
<td>4310</td>
<td>23.3</td>
<td>91.3</td>
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<tr>
<td>Cerro Negro</td>
<td>560</td>
<td>1680</td>
<td>25.7</td>
<td>77.1</td>
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<tr>
<td>Wilmington</td>
<td>49</td>
<td>422</td>
<td>7.05</td>
<td>60.7</td>
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<tr>
<td>Prudhoe Bay</td>
<td>19</td>
<td>327</td>
<td>2.75</td>
<td>47.3</td>
</tr>
</tbody>
</table>
Table 2. Vanadium Distribution in Heavy Crude Oils and Ashphaltenes

<table>
<thead>
<tr>
<th></th>
<th>Boscan</th>
<th>Cerro Negro</th>
<th>Wilmington</th>
<th>Prudhoe Bay</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>&gt;400</td>
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<td>&lt;400</td>
<td>&lt;400</td>
<td>&lt;400</td>
<td>&lt;400</td>
<td>&lt;400</td>
</tr>
</tbody>
</table>

| Heavy Crude Oil  | 527b   | 251         | 315        | 298         |
|                  | 47.9%c | 23.4%       | 28.7%      | 53.2%       |

| Asphaltene       | 2064b  | 777         | 1468       | 739         |
|                  | 47.9%c | 18.0%       | 34.1%      | 44%         |

|                  | 91.2%d | 70.4%       | 109%       | 63.7%       |

a) Molecular Weight 900
b) PPM Vanadium
c) Percent of Total Vanadium in Fraction
d) Normalized to the Heavy Crude Oils
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