Organometallic Geochemistry. Isolation and Identification of Organoarsenic Compounds from Green River Formation Oil Shale

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A Green River Formation oil shale sample was crushed and extracted with refluxing methanol and analysed by high performance liquid chromatography in combination with graphite furnace atomic absorption detection (h.p.l.c.–g.f.a.a.) to provide evidence for the presence of methyl- and phenyl-arsonic acids and the arsenate ion; further evidence for the acids' identification was provided by derivatization with 3-methylcatechol to form the corresponding five-co-ordinate organoarsenic catecholates followed by capillary column gas chromatography–electron impact mass spectrometry (g.c.–e.i.m.s.) analysis.

The molecular characterization of organometallic compounds, which occur as natural products in fossil fuel precursors, is becoming a significant area of research owing to the importance of these compounds in emerging synthetic fuel processes as well as their impact on the environment.[1]

Recently, using a high performance liquid chromatograph coupled to a graphite furnace atomic absorption spectrometer (h.p.l.c.–g.f.a.a.) as an element-selective detector, we identified methyl- and phenyl-arsonic acids as well as the arsenate ion in oil shale retort waters.[2] We have also analysed the shale oils produced by pyrolysis of oil shale and have found that the organoarsonic acids mentioned above also occur, but in association with iron-containing macromolecules with molecular weights in the range of 2000—4000 Daltons.[3]

In order to discern whether these compounds were natural products in the precursor of the shale oil and the retort waters or were formed during pyrolysis, we examined a Green River Formation oil shale which is a fine-grained sedimentary rock containing appreciable quantities of organic material. It consists of three fractions: kerogen, bitumen, and an inert substance. Kerogen and bitumen, which constitute the organic material, are generally regarded as biogeochemical fossil products, emanating largely from lipid fractions of ancient algae and forming the ubiquitous oil source matrix in shales.[4]

The Green River Formation oil shale sample (10 g) was crushed and Soxhlet extracted with 500 ml of methanol for 48 h. This effectively removed about 20% of the total arsenic contained in this oil shale.† Following evaporation (25 ml) and filtration, we analysed the extract by h.p.l.c., using a Dionex anion exchange column with 0.2 M ammonium carbonate in water–methanol (85:15) as the eluting solvent. The arsenic compounds were detected *via* automatic g.f.a.a. analysis at 197.3 nm.[1,2]

The h.p.l.c.–g.f.a.a. arsenic-specific chromatogram of the compounds extracted clearly indicated the presence of methylarsonic acid, phenylarsonic acid, and the arsenate ion, based on retention times of the authentic arsenic compounds.[5] An un-

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† The oil shale sample from Anvil Points Co. (NBS Standard Reference Material) was found to contain *ca.* 20 p.p.m. of total arsenic.

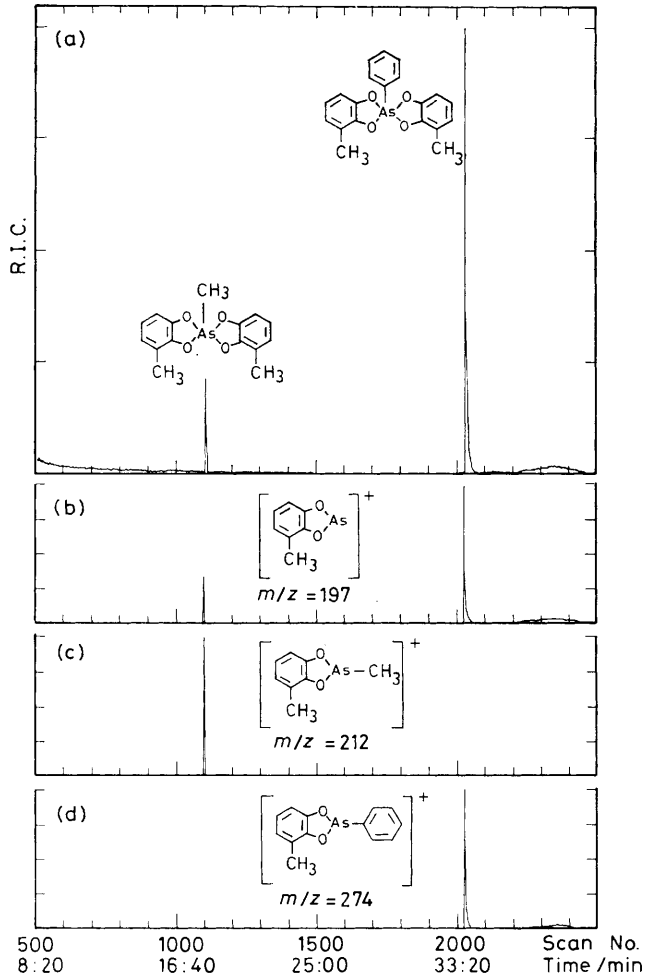

Figure 1. G.c.–e.i.m.s. analysis of the 3-methylcatecholates of methyl- and phenyl-arsonic acids (1 scan/s). (a) Reconstructed ion chromatogram (R.I.C.) of standards. (b) Selected ion chromatogram of *m/z* 197. (c) Selected ion chromatogram of *m/z* 212. (d) Selected ion chromatogram of *m/z* 274.

known neutral organoarsenic compound eluted with the solvent front.‡

We have shown recently that reactions of methyl- and phenyl-arsonic acids with substituted catechols provide five-co-ordinate organoarsenic catecholates.[6] Since many of these organoarsenic catecholates could be gas chromatographed on fused silica capillary columns and characterized by electron impact mass spectroscopy (e.i.m.s.), we decided to apply this derivatization technique to the unequivocal identification of methyl- and phenyl-arsonic acids present in the oil shale extract.

The methanol extract was purified by preparative h.p.l.c., lyophilized, and dissolved in benzene. To this solution was added an excess of 3-methylcatechol and the reaction mixture was refluxed for 5 h and worked up to remove the excess of 3-methylcatechol. A concentrated sample was subjected to g.c.–e.i.m.s. analysis§ and gave spectra and retention times that were identical to the known samples of the 3-methylcatecholates of both methyl- and phenyl-arsonic acids.

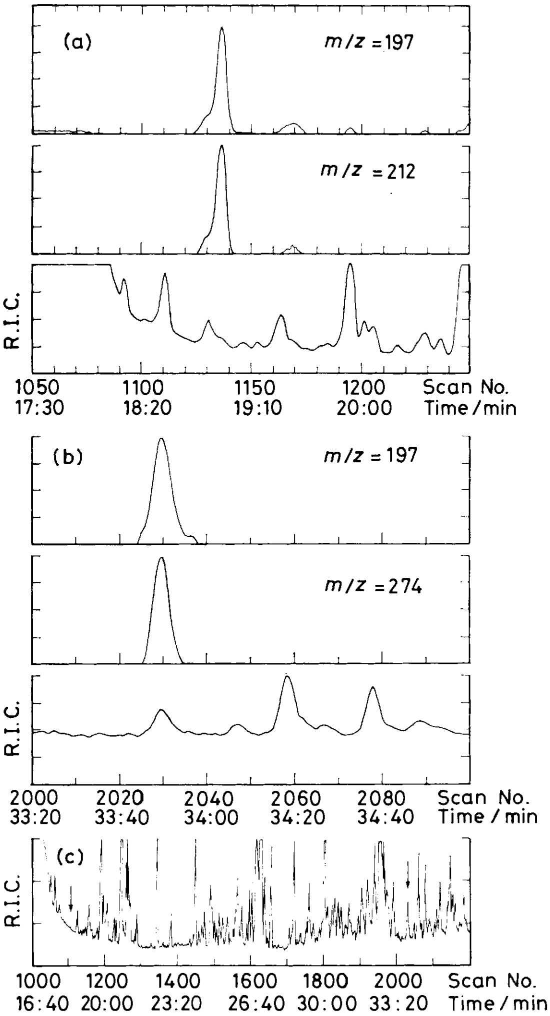

Figure 2. G.c.–e.i.m.s. analysis of the derivatized and h.p.l.c. purified extract (1 scan/s). (a) Selected ion chromatograms near scan 1137 for *m/z* 197 and 212. (b) Selected ion chromatograms near scan 2030 for *m/z* 197 and 274. (c) Reconstructed ion chromatogram (R.I.C.) of h.p.l.c. purified methanol extract with the arrow on the left designating the 3-methylcatecholate of methyl-arsonic acid and the arrow on the right the 3-methylcatecholate of phenylarsonic acid.

Figure 1(a) shows the reconstructed ion chromatogram (R.I.C.) of the two standards and the single ion chromatograms show pertinent fragments of interest at *m/z* 197 and 212 for the methylarsonic acid derivative [Figure 1(b),(c)] and *m/z* 197 and 274 for the phenylarsonic acid derivative [Figure 1(b),(d)]. Figure 2 (c) shows the region purified by h.p.l.c. containing the organoarsonic acids, which were derivatized, and the expanded sections of this chromatogram containing the organoarsenic catecholates with the important ions, *m/z* 197, 212, and 274, clearly evident for the 3-methylcatecholates of methyl- [Figure 2(a)] and phenyl-arsonic [Figure 2(b)] acids.

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‡ We examined this material, after preparative h.p.l.c. isolation, on a C-18 reverse phase h.p.l.c. column with methanol as solvent and determined that the compound(s) eluting at the solvent front was not triphenylarsine or triphenylarsine oxide.

§ The g.c.–m.s. analyses were performed on a Finnigan 4023 mass spectrometer system with a 30 m × 0.3 mm DB-5 (J&W) capillary column. Conditions: 55 °C (3 min) to 300 °C at 4 °C/min. Data analysis and preparation were performed using the INCOS data system.

Additionally, the presence of the arsenate ion (AsO_4^{3-}), was verified similarly by preparation of the tris(trimethylsilyl) derivative of the ammonium arsenate salt and analysing the purified extract by g.c.–e.i.m.s. for ions at *m/z* 207, 343, and 358.[7] The organoarsenic compound(s) that elutes with the solvent front has not been identified.

We believe these identifications of the organoarsonic acids to be the first such molecular characterizations of trace organometallic compounds to be reported for any fossil fuel precursors and initiates the area of organometallic geochemistry, a field that has hitherto been totally unexplored. The implications are that these organoarsonic acids are natural products and hence have a biogeochemical origin in the oil shale taphonomy process. It is also interesting to note that no examples of biophenylation have been reported, whereas the biomethylation of arsenic compounds is well known.[8]

Finally, the fact that these organoarsonic acids are released upon oil shale pyrolysis has important implications in synthetic fuel processes, where the role of organometallic compounds in poisoning process catalysts and contributing to environmental problems, is paramount.

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