

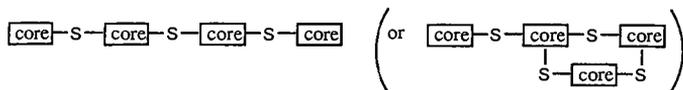
COVALENT STRUCTURE AND MOLECULAR ARCHITECTURE OF ATHABASCA ASPHALTENE

O.P. Strausz, Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada; P. Peng, Guangzhou Institute of Geochemistry, Guangzhou 510640, People's Republic of China; J. Murgich, Centro di Quimica, Instituto Venezolano de Investigaciones Cientificas, Apartado 21827, Caracas 1020-A, Venezuela.

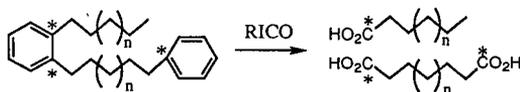
INTRODUCTION

Extensive research in the recent past has led to new insights into the composition,¹ covalent structure² and molecular architecture^{3,4} of Athabasca asphaltene (AA). Employing thermolytic and chemolytic degradations such as the nickel boride (Ni/B) cleavage of the C-S bonds in sulfides, the ruthenium ions-catalyzed oxidation (RICO) of the C_{arom}-C_{arom/aliph} bonds, the basic hydrolytic cleavage of the ≡CO-C(O)-C ester bonds and the BBr₃ cleavage of the ≡C-O-C≡ ether bonds yielded an array of products representing structural elements in the asphaltene molecules. Thus, the principal products from the mild thermolysis were homologous series of thiolanes, thianes, thiophenes, benzothiophenes, dibenzothiophenes, methylbenzenes and fluorenes. All these structures were *n*-alkyl substituted—in the C₁₂-C₂₈ total carbon range—in such a fashion that upon ring cleavages at appropriate places the entire carbon skeleton of the molecules could be stretched out into an *n*-alkane chain, pointing to the *n*-alkanoic origin of these cyclic structures. Significantly, cyclic terpenoid sulfides, abundant in the maltene fraction of the parent bitumen, appear to be lacking in the asphaltene. Additional products identified were: series of partially hydrogenated di-, tri- and tetrabenzothiophenes, two- and three-ring aromatics and hydroaromatics, and one-through three-ring naphthenes, all alkyl substituted with a total carbon number up to ~28, *n*-alkanes, iso- and anteisoalkanes and isoprenoids. Among the polar products the dominant ones were *n*-alkanoic acids, *n*-alcohols and *n*-alkanoic amides (originally hydrogen-bonded acid-amine complexes?), all exhibiting a marked even-to-odd carbon preference. The latter feature is the fingerprint of a relatively recent origin related to secondary microbial degradation of the precursor oil of the present-day bitumen. Small quantities of alkyipyridines and alkyquinolines were also detected.

The Ni/B cleavage of the sulfide bonds in acetone-extracted AA afforded about 2.5% aromatics, 2.5% polars and 0.1% saturates. The saturates comprised entirely biomarkers, *n*-alkanes, di-, tri- and pentacyclic terpenoids including γ -cerane and regular steranes, all corresponding to distribution representing a significantly lower level of thermal maturity than that of the maltene of the parent bitumen. These compounds were originally present in the asphaltene molecule as sulfur-bound appendages and possibly bridges. And, what is from a structural point of view an even more noteworthy phenomenon, is the drastic fourfold drop in the MW of the residual asphaltene after Ni/B reduction, proving a molecular architecture in which four asphaltene core segments are bound together by three (or more) sulfur atoms, e.g.

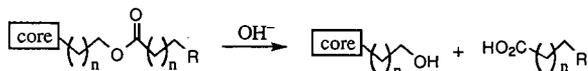


The RICO produced, among other products, series of *n*-alkanoic and α,ω -di-*n*-alkanoic acids, signifying the presence of *n*-alkyl side chains and bridges attached to aromatic carbons.

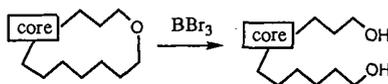


Lastly, cleavage of ester and ether bonds resulted in the formation of *n*-alkanoic acids and *n*-alcohols, again dominated by the even carbon members.

In the present context the important structural elements in the asphaltene molecules are the alkyl (polymethylene) bridges connecting aromatic or naphthenic rings, the alkyl, ether and ester appendages as well as other types of appendages. Long bridges (up to C₂₈) can connect distant carbon sites and create loops and internal cavities. From RICO studies the evidence for the existence of long polymethylene bridges connecting two aromatic carbons and an aromatic carbon with a naphthenic carbon is unambiguous. The Ni/B cleavage of the C-S bonds in sulfides shows that there are small amounts of long alkyl sulfide bridges as well. In the cleavage of C-O bonds it is only the external moiety in the bond that is liberated, e.g.



If the ether or ester represents a bridge anchored at both ends to the core then no GC-detectable products would result from the cleavage reaction, e.g.



The total amounts of acids and alcohols liberated in the C-O cleavage reaction are quite substantial, alcohols ~3.0% and acids ~ 0.5%, and therefore it would be reasonable to assume that there are some ethers and esters present in bridge positions as well as in side-chain appendages. Indirect experimental evidence appears to support this conclusion. The total number of bridges can be estimated to be about eight per asphaltene molecule or about two per core segment. Consequently, internal cavities of varying sizes have to be an integral feature of the molecular structure of asphaltene. This has been discussed previously in connection with a model for asphaltene structure and has been confirmed by molecular mechanics computations on the isolated model.

The present communication deals with some aspects of the adsorption properties of AA and the question related to its pore structure.

RESULTS AND DISCUSSION

Several series of studies have been carried out on the adsorption properties of AA. Here, only some, yielding information on the pore structure and adsorption capacity, will be discussed.

When, in a series of experiments,⁵ the adsorption of C₉-C₃₂ alkanes, squalane and squalene was investigated in CH₂Cl₂ solutions, it was observed that the *n*-alkanes were not adsorbed, squalane was adsorbed moderately and squalene, substantially. Thus, AA in a 10% solution adsorbed 0, 20 and 46% of 10,000-ppm dissolved *n*-alkanes, squalane and squalene. If the adsorption mechanism were purely physical adsorption by van der Waals forces, then *n*-alkanes should adsorb more readily than squalane because the presence of the branched methyl groups in squalane hinders a close contact between the methylene groups of the alkane chain and the adsorbent. Since the experimental finding was the reverse of this intuitive expectation, other factors must be involved. The simplest explanation at hand would be the operation of an adduct mechanism, implicating an appropriate-size pore structure. *n*-Alkanes have a molecular diameter of about 3.0 Å and can be adducted to molecular sieves 5 Å which have an internal pore diameter of 3.0 Å. Molecular sieves 5 Å would not adduct squalane because the effective molecular diameter of squalane exceeds 3 Å. Squalane (along with other isoprenoids) with a molecular diameter of about 7 Å could, however, be clathrated with substrates of appropriate size pore structure, such as thiourea. On the other hand, *n*-alkanes cannot be clathrated with thiourea because the narrow *n*-alkane molecules would not be held firmly enough in the wide pores.

Thus, from the experimental observation that squalane can be adsorbed on AA whereas *n*-alkanes cannot, we conclude that the adsorption is, in effect, an adduction of the squalane molecule into an appropriate-size cavity in the asphaltene structure. The cavity may be present in the covalent molecular structure, in the micelle-like aggregates or in the form of a combination of the two. The simplest assumption one can make is that the cavity is located in the covalent molecular structure because in the micelle-like aggregate the dynamic equilibrium continuously rearranges the structure, rendering the adduction (clathration) process ineffective.

The high value of the adsorbed squalane can be viewed as the result of the combined effects of adduction and adsorption, the latter being due to the higher dispersion force in the interaction of the olefinic π bond with the aromatic ring systems of the asphaltene.

Another important question in this regard is the capacity, that is, the maximum amount of squalane a unit weight of the asphaltene is capable of adducting. This would provide a measure of the number of cavities (in the appropriate size range) present in the asphaltene. The same question is also relevant to the amount of resins the asphaltene can hold, and whether a precipitated asphaltene (say *n*-C₅-AA with 21.1% adsorbed maltene, resins and low-MW asphaltene fragments) represents a (unimolecularly) saturated state of the asphaltene-adsorbate system or rather a steady-state equipartition distribution of the adsorbate between the oil and the adsorbed phase.

In order to answer this question, an experiment was carried out⁶ in which *n*-C₅-AA was sequentially re-precipitated seven times and the desorbed material combined. A portion of this desorbed material was then dissolved in *n*-pentane and freshly *n*-C₅-precipitated solid asphaltene was added to the *n*-C₅/CH₂Cl₂ (40:1) solution. After standing overnight the asphaltene adsorbed 44% of the desorbed material (corresponding to 8.8% of the asphaltene), clearly manifesting that the precipitated solid asphaltene is capable of adsorbing significantly more resinous material than it contained.

ACKNOWLEDGEMENT

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REFERENCES

1. Payzant, J.D.; Montgomery, D.S.; Strausz, O.P. *AOSTRA J. Res.* **1988**, *4*, 117-131; Payzant, J.D.; Lown, E.M.; Strausz, O.P. *Energy & Fuels* **1991**, *5*, 445-453.
2. Mojelsky, T.M.; Montgomery, D.S.; Strausz, O.P. *AOSTRA J. Res.* **1985**, *2*, 131-137.
3. Peng, P.; Morales-Izquierdo, A.; Hogg, A.; Strausz, O.P. *Energy & Fuels* **1997**, *11*, 1171-1187.
4. Strausz, O.P.; Mojelsky, T.W.; Faraji, F.; Lown, E.M. *Energy & Fuels* **1999**, *13*, 207-227.
5. Strausz, O.P.; Ignasiak, T.M.; Kotlyar, L.; Montgomery, D.S. to be published.
6. Strausz, O.P.; Torres, M. to be published.