

Chapter 1

Geochemistry of Sulfur in Petroleum Systems

Wilson L. Orr¹ and Jaap S. Sinninghe Damste²

¹Dallas Research Laboratory, Mobil Research & Development Corporation,
13777 Midway Road, Dallas, TX 75244-4312

²Faculty of Chemical Engineering and Materials Science, Organic
Geochemistry Unit, Delft University of Technology, De Vries
van Heystplantsoen 2, 2628 RZ Delft, Netherlands

A renaissance in the 1980s concerning geochemistry of sulfur in fossil fuels makes an update of the subject timely. Papers developed from the 1989 ACS Symposium in Dallas provide a cross-section of recent research and progress in our understanding of the abundance and nature of organically bound sulfur in fossil fuels. This chapter furnishes an overview of our understanding of sulfur introduction into the geologic systems and biogenic materials that produce petroleum and natural gas. Many of the geochemical considerations also apply to coal and lignite deposits. A brief historical account leads to a summary of the most recent advances, an appraisal of current understanding, and some remaining challenges and opportunities for further research.

This chapter provides a historical perspective and overview of the status of knowledge regarding the geochemistry of sulfur in fossil fuels with emphasis on petroleum related systems. The major reason for considering the diverse fossil fuel systems in a single symposium is that many aspects of the geochemistry are common to all classes of fossil fuels (petroleum, natural gas, coal, lignite and oil shales). However, the technologies, terminologies, methods of study, and technical problems are sufficiently different that some topics are specific to a given fuel class while others are relevant to all fuel classes. The broad scope of this volume will make it easy to appreciate the similarities and differences in the various fuel systems.

The chemistry of sulfur in fossil fuels is of both practical and academic interest. The behavior of sulfur during processing high-sulfur crude oils, coals and natural gas to make environmentally acceptable fuels poses special

engineering problems and economic penalties. Sulfur must be reduced to appropriate levels for each intended application. The *acid rain problem*, resulting largely from combustion of sulfur in fossil fuels, is a pressing national and international concern. The magnitude of sulfur dioxide emissions in the United States is discussed by Manowitz and Lipfert (1). Pending U.S. legislation will mandate major reductions in emissions of sulfur dioxide and nitrogen oxides into our air in the near future. The fuel and utility industries will make major expenditures to meet these requirements. Although naturally formed biogenic sulfur compounds are recognized as harmful environmental pollutants, they appear to make up only about 0.13% of total sulfur emissions into the atmosphere (2,3).

The chemistry of desulfurization involved in processing fuels is, of course, dependent on molecular structures or form of sulfur in the fuel material. This is true for lignite, coal, and oil shales as well as for petroleum, petroleum fractions, and natural gas. Desulfurization of natural gas presents few problems because the technology for removing hydrogen sulfide and traces of thiols is relatively simple and well-developed. In contrast, crude oils and other fossil fuels vary considerably both in total sulfur content and in modes of combination that make sulfur removal more difficult. The more we know about chemical structure, thermal stability, and reactivity of sulfur in a given fuel, the more guidance we have for improving sulfur removal processes.

The emphasis of this symposium is on the geochemistry of sulfur rather than on processing, utilization or environmental consequences. Nevertheless the factual information, generalizations and insights provided by these current research topics should be informative and should suggest practical applications for many concerns of the fossil fuel industry.

Although petroleum processing is not treated in this symposium, it is evident that industrial treatment of crude oils at relatively high temperatures and short times involves many of the same chemical reactions that occur in the geologic environment at lower temperature on a much longer time-scale. Therefore, experience from refining and geochemistry support each other in a symbiotic relationship. A number of studies reported here utilize pyrolysis or thermal treatments for either the simulation of geochemical processes or the analytical characterization of materials. These studies supply information relating to the chemistry of high temperature reactions.

Refining engineers and chemists are most interested in the ease of desulfurizing petroleum using thermal and thermocatalytic treatments. The sulfur is removed primarily as hydrogen sulfide. Thermal and thermocatalytic studies have established that non-thiophenic sulfur (aliphatic as in thiols, acyclic and cyclic sulfides) evolve H_2S much more readily than thiophenic sulfur (aromatic heterocyclic compounds). Thus, the relative abundances of nonthiophenic (aliphatic) and thiophenic (aromatic) sulfur is a critical characteristic for all fuels with respect to ease of desulfurization. Analytical methods were developed in the 1960s for classifying the total sulfur in crude

oils into types or fractions that correlate with ease of desulfurization (4-7). Although these analytical methods left a significant fraction of the total sulfur (commonly 30-60%) as "sulfur not recovered" or "an unknown fraction", this fraction was considered to be part of the more resistant category (complex thiophenic components).

Application of these methods showed that the distribution of types of organic sulfur compound(s) (OSC) in crude oils is variable. In other words, the ratio of thermally labile to more resistant sulfur has a large range in crude oils. Geochemically, the large range is expected and understandable because of variations in source, maturity and other alteration processes.

The industry prefers to refine low-sulfur crude oils, and usually handles high-sulfur crudes by blending them with much lower sulfur oils. Refinery design and operation determine the sulfur level that can be processed. In the future, more high-sulfur oil containing 3-6% sulfur will be exploited, and refining processes must be modified accordingly. The shift to higher sulfur crudes will be gradual and the time frame for the transition is not evident. However, the world's potential reserves of "heavy oils" and "tar sands" (generally high in sulfur content) greatly exceed known reserves of conventionally produced low-to-moderate-sulfur crude oils (8, 9). Increasing use of these potential resources will be required unless alternative energy sources replace fossil fuels.

The bottom line for the fuel industry is that a more complete understanding of the origin and evolution of sulfur in fossil fuels can lead to improved practical applications in a number of areas such as:

1. Guiding exploration for fossil fuels, particularly for oil and gas with a concern for fuel quality.
2. Providing clues that help rationalize the wide range of oil and gas compositions and properties found in natural occurrences (fuel quality).
3. Suggesting reasons why different fuels and fuel fractions behave differently during processing.
4. Developing improved processes and uses for fossil fuels.

The Geochemical Focus

Geochemists attempt to understand the chemistry that takes place in the geologic environments where fossil fuels originate and evolve over periods of millions of years. With respect to sulfur this science is concerned with: (1) how and when sulfur is introduced into the natural biogenic materials that lead to fossil fuels; (2) why and how the abundance and forms of sulfur differ in various geologic environments and; (3) how abundance and forms of sulfur evolve (change) with subsequent geologic history.

Limitations in methods for analysis of sulfur in complex materials and complex mixtures determine the extent of our knowledge and understanding of sulfur in fossil fuels. Historically, as new and improved methods of analysis

became available, increased knowledge and insights followed quickly. Therefore, improvements in analytical methods continue to be critical research topics. A major current limitation is our inability to characterize adequately the forms of sulfur (functional groups) in solids (kerogen, coals, etc.) and in the higher-molecular-weight fractions of petroleum (resins, asphaltenes and refinery residues).

The scope of geological and geochemical considerations related to sedimentary organic matter and fossil fuels embraces many different disciplines including oceanography, sedimentology, biology (especially microbiology), mineralogy, petrology, tectonics of basin development, etc., and concerns inorganic/organic interactions involving water, minerals, biogenic organic materials and gases. The literature on these subjects is extensive and many specialized reference works and reviews are available.

Although A. Treibs is regarded as the founder of modern organic geochemistry for his work on porphyrins in the 1930s (10, 11), organic geochemistry did not become established as an active science until the 1950s and 1960s and interest has increased significantly since 1970. The first reference book on organic geochemistry appeared in 1963 (12) (edited by the late I. Breger) and the second in 1969 (13) (edited by Eglinton and Murphy). Erdman made significant contributions to petroleum geochemistry in the 1950s and 1960s; his 1965 paper (14) on the origin of petroleum summarized various historical views and the accepted view at that time. Silverman (15) pioneered studies of carbon isotopes in petroleum geochemistry and made many important contributions. A later review of the use of carbon isotopes in exploration for petroleum was given by Fuex in 1977 (16). The pioneering work of Thode on sulfur isotopes in petroleum, which started in the 1950s, had a major impact on sulfur geochemistry (17,18). The use of sulfur isotopes in petroleum exploration was reviewed by Krouse in 1977 (19), and broader aspects of sulfur isotopes were covered by Nielsen (20). Sulfur isotopes continue to make important contributions in studies of the geochemistry of sulfur.

An early comprehensive review of the organic geochemistry of sulfur was provided by the late Claude E. Zobell in 1963 (21) with some emphasis on microbiological involvement. The sulfur cycle in oceans and sediments was treated by Goldhaber and Kaplan in 1974 (22). Berner and others have published extensively on sulfur in sediments with emphasis on pyrite (23,24). Interestingly, biogenic sedimentary organic matter has often been considered mainly as the substrate necessary for bacteria to reduce sulfate to hydrogen sulfide which is the major source of sulfur forming pyrite in early sedimentary environments. The reaction of H_2S with the organic matter to form sulfur-rich precursors of fossil fuels has often been ignored or has been treated as insignificant in many discussions of sediments and of the global sulfur cycle. This is unfortunate from our viewpoint because the sulfurization of organic matter is the major concern regarding sulfur in fossil fuels. A number of papers

in this symposium relate to the early introduction of sulfur into sediments in both organic and inorganic forms and the environmental factors controlling the operative processes. A recent book dealing with biogenic sulfur in the environment also reports major progress in understanding sulfur interactions with organic matter in sediments and in biological systems (2).

Comprehensive monographs by Tissot and Welte (25) and Hunt (26) are available on geology and geochemistry of oil and gas occurrences. These works have incorporated concepts developed in the 1960s and 1970s with later works to derive general schemes for the origin of petroleum, coal, and natural gas. These schemes are comprehensive and generally accepted. Sedimentary environmental conditions necessary for source-rock deposition are well known. The oil generation process is understood to be largely a thermal conversion of kerogen and associated immature bitumens into petroleum and gas (see later discussion). This evolutionary stage (catagenesis) occurs with increasing temperature and time as source-rocks are progressively buried. The nature of the migration process, which moves oil generated in a source-rock to oil trapped in a reservoir, remains the least understood process. Subsequent petroleum alteration processes are reasonably well understood but remain current topics of investigation. These include: (1) in-reservoir maturation that changes oil composition and properties, and in the extreme includes cracking of oil to gas, and (2) biodegradation and water-washing of petroleum in shallow reservoirs, which not only decrease oil quality but also destroy large amounts of hydrocarbons. The general scheme allows for the formation of kerogens with different compositions that reflect different biogenic source materials and different conditions in the initial sedimentary environments. The composition and nature of the kerogen then determine the nature of the oil and/or gas that it generates; i.e., differences in initial oil properties and gas/oil ratio. Subsequent alteration processes account for additional changes in composition and properties after generation. Current research continues to examine and refine these concepts.

The importance of the heteroatoms nitrogen, sulfur and oxygen (NSO) is recognized in all of the processes involved in the origin and alteration of petroleum (25,26). The nitrogen containing tetrapyrrole pigments (porphyrins and the vanadyl and nickel metalloporphyrins) have received more attention than most NSO compounds (10,11). The abundance of vanadium and/or vanadyl porphyrins is highly correlated with sulfur content of bitumens and crude oils, but it is not clear whether this correlation reflects mainly chemical associations or sensitivity to preservation processes with different oxic-anoxic sedimentary conditions (25-27). Aside from porphyrins, major emphasis over the years has been on studies of hydrocarbons (i.e., compounds that contain only carbon and hydrogen). Hydrocarbons are the major useful fuel components and are the simplest compounds to characterize. Naturally, hydrocarbon geochemistry has advanced more rapidly than that of heteroatomic (NSO) compounds.

Sulfur in Petroleum and Related Bitumens

Sulfur content in crude oils and natural bitumens varies from less than 0.05 to more than 14 weight percent, but few commercially produced crude oils exceed 4% sulfur. Tissot and Welte (25) show a frequency distribution of crude oils based on over 9,000 samples and report the average sulfur content as 0.65%. The distribution is clearly bimodal with a minimum at about 1% sulfur. Oils with less than 1% sulfur are classified as low-sulfur, and those above 1% as high-sulfur. In general, high-sulfur oils are derived from carbonate or carbonate-evaporite rock sequences whereas low-sulfur oils are derived largely from clay-rich clastic sequences (25-26, 28-29).

Most of the sulfur present in crude oils and bitumens is organically bound, (i.e., bound to carbon) because dissolved hydrogen sulfide and elemental sulfur usually represent only a minor part of the total sulfur. Organic sulfur is present in low- to medium-molecular-weight molecules, but the largest fraction is in the high-molecular-weight components (25-26, 28-29).

OSC vary in polarity and chromatographic behavior such that some elute during liquid chromatography with the aromatic hydrocarbon fraction while others elute with the more polar NSO fractions that include the resins and asphaltenes. Until recently, precise organic molecular structures have been established only for relatively low molecular weight sulfur compounds, generally with fewer than 15 carbon atoms and from fractions with boiling points below 250-300 °C. This unsatisfactory state of knowledge is aggravated by the fact that generally 60-80% of the sulfur is in fractions boiling above 300 °C. We now know a great deal about the types of OSC and functional groups in perhaps 20-40% of the total sulfur. The same types of functional groups (and perhaps others) are believed to extend into uncharacterized fractions in increasingly complex combinations with many of the more polar and higher molecular-weight compounds containing more than one heteroatom. The most thoroughly characterized OSC are those which separate chromatographically with lower-molecular-weight aromatic hydrocarbons.

A number of reviews related to the identification of sulfur compounds in petroleum should be mentioned. Dean and Whitehead (30) summarized work on separation and identification of sulfur compounds in petroleum and shale oil in 1967. Drushel (7) reviewed sulfur compound types with an emphasis on the available analytical methods as of 1970. Mehmet (31) and Gal'pern (32) also reviewed sulfur compounds in petroleum in 1971 with some speculation on their origin. The major contributions of API Project 48 reported by Coleman et al. in 1971, Rall et al. in 1972, and Thompson in 1981 will be discussed below (33-35). More recent summaries of sulfur compounds by Aksenov and Kamyranov in 1981 (36) and by Gal'pern in 1985 (37), discuss OSC in petroleum, processed petroleum fractions, shale oil, coal derived liquids and related products. These reviews include much of the Soviet literature. In 1975 and 1978 Orr (28-29) discussed sulfur in the petroleum system with somewhat

more emphasis on geochemistry. For the most part, all of these papers preceded advances made in the identification of OSC in sediments and bitumens during the last decade by GC-MS analysis.

Rall et al. (34) gave a detailed account of the U. S. Bureau of Mines work under The American Petroleum Institute (API) Project 48, which devoted about 50 man-years of research to sulfur in petroleum during the time from 1948 to 1966. Their report is a comprehensive summary of the project accomplishments and also reviewed most prior work with 469 literature citations. Only 25 sulfur compounds had been reported in petroleum prior to 1948. Structures of these 25 compounds were confirmed and 176 additional compounds were isolated and identified during the life of this project (Table I). Figures 1 and 2 illustrate major structural types for lower-molecular-weight OSC in petroleum. Structures of higher-molecular-weight OSC compounds in more complex aromatic ring systems and in higher boiling fractions of petroleum and bitumen are largely unknown. Most characterizations of higher molecular weight fractions are by group type analysis (mass spectrometry supported by other techniques) rather than by isolation and rigorous structural determination (38-40).

The API project settled a number of questions that had been debated for years. API 48 took special precautions to isolate and identify sulfur compounds from virgin crude oils using mild thermal conditions. They investigated the thermal stability of crude oils and reactions of oils and hydrocarbons with elemental sulfur to settle long standing debates about whether the OSC identified were in fact present in virgin crude oils or were produced by processing practices. They made quantitative or semiquantitative estimates of the abundance of many of the OSC identified. New techniques for separation, analysis and characterization of the compounds were investigated and developed. Limitations of the project were mainly that the work was slow and tedious, and the state-of-the-art limited separations and identifications to low-molecular-weight compounds.

The question of the presence of elemental sulfur in crude oils was also a matter of controversy for many years. Many virgin crude oils contain small but significant amounts of H_2S that is easily oxidized to elemental sulfur by exposure to air. API 48 confirmed that elemental sulfur indeed does exist in some crude oils but it is not common; in most cases dissolved S_8 is a minor part of the total sulfur.

API 48 not only established that the types of sulfur compounds listed in Table I were common in virgin crude oils, but also found that the relative abundance of these compounds was highly variable in the different crude oils studied. Geochemical reasons for these differences are more easily rationalized now than they were in 1972.

Ho et al. (41) applied "sulfur-compound-type" analytical methods (4-7) to 79 crude oils having a range of sulfur contents from 0.05 to 7.82 % with results that were very informative from a geochemical viewpoint. Sulfur type

Table I. Number and Types of Sulfur Compounds Identified by API Project 48^(a)

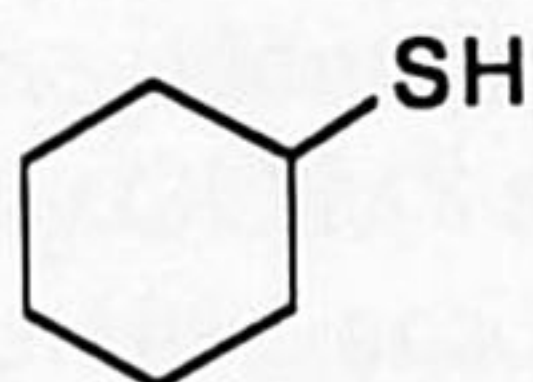
| Compound Type | Wasson W. Texas | Wilmington California | Agha Jari Iran | Deep River Michigan | Total |
|-------------------------------------|--------------------|--------------------------|-------------------|------------------------|-------|
| THIOLS | | | | | |
| Alkyl- | 40 | 0 | 6 | | 46 |
| Cyclic- | 6 | | | | 6 |
| Aromatic- | 1 | | | | 1 |
| SULFIDES | | | | | |
| Dialkyl- | 38 | | 5 | | 43 |
| Alkylcycloalkyl- | 5 | | | | 5 |
| Alkylaryl- | 4 | | | | 4 |
| Cyclic- | 21 | 19 | | | 40 |
| Thiaindans | 18 | | | | 18 |
| DISULFIDES | | | | | |
| | 1 | | | 3 | 4 |
| THIOPHENES | | | | | |
| Alkyl- | 0 | 11 | | | 11 |
| Benzo- | 22 | | | | 22 |
| Thieno- | 2 | | | | 2 |
| Dibenzo- | 2 | | | | 2 |
| TOTAL IDENTIFICATIONS | | | | | |
| | 160 | 30 | 11 | 3 | 204 |
| UNDUPLICATED IDENTIFICATIONS | | | | | |
| | 160 | 14 | 0 | 2 | 176 |

(a) From Rall et al. (34)

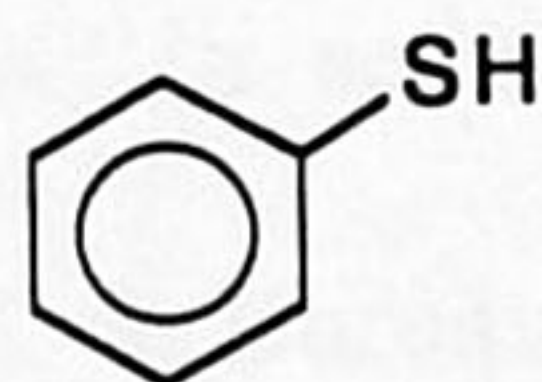
Thiols (Mercaptans)



1-pentanethiol

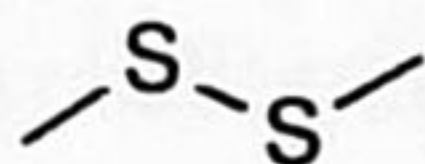
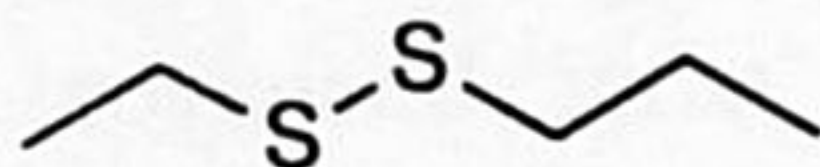
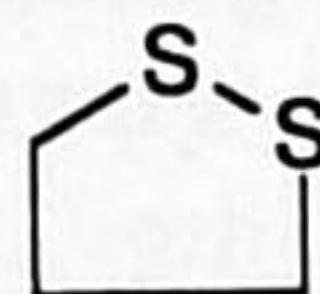


cyclohexanethiol

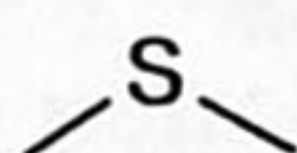
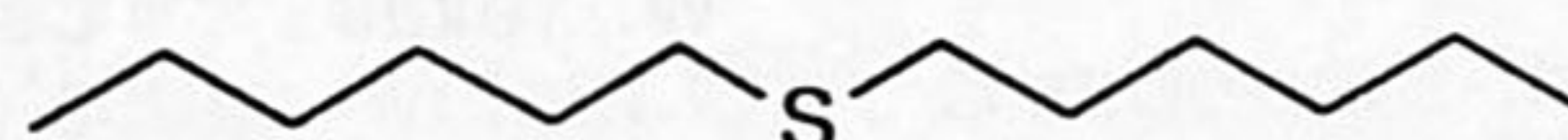
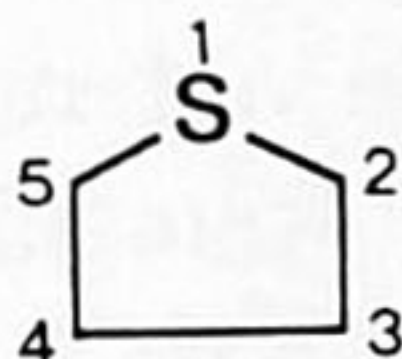
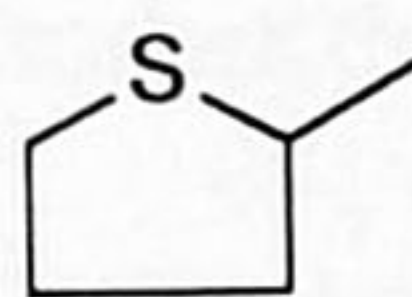
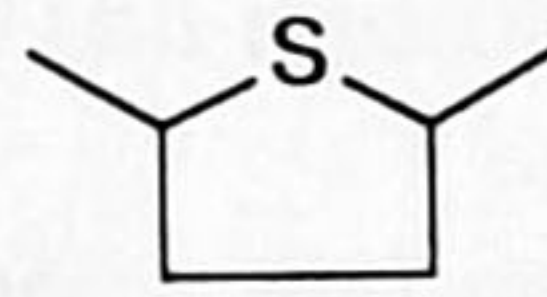
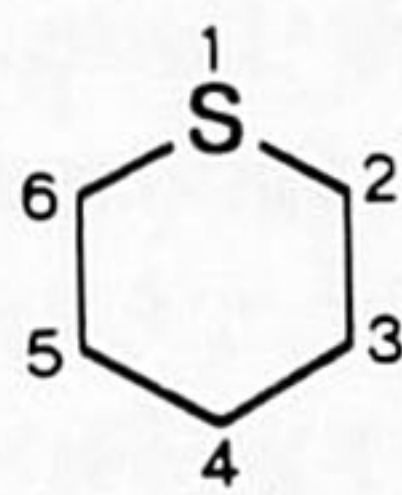
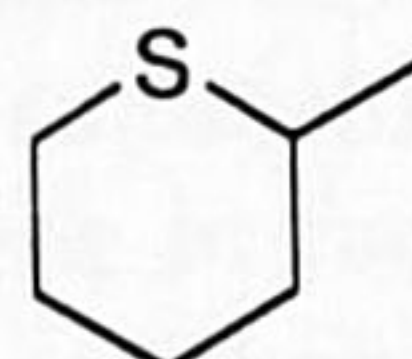
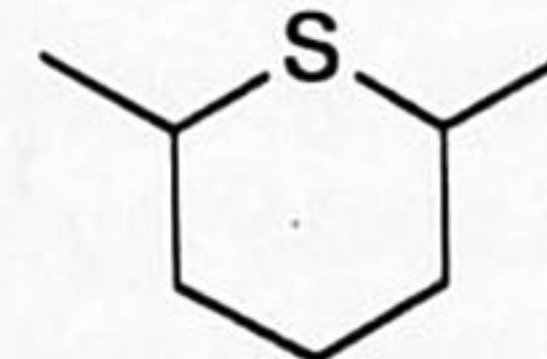
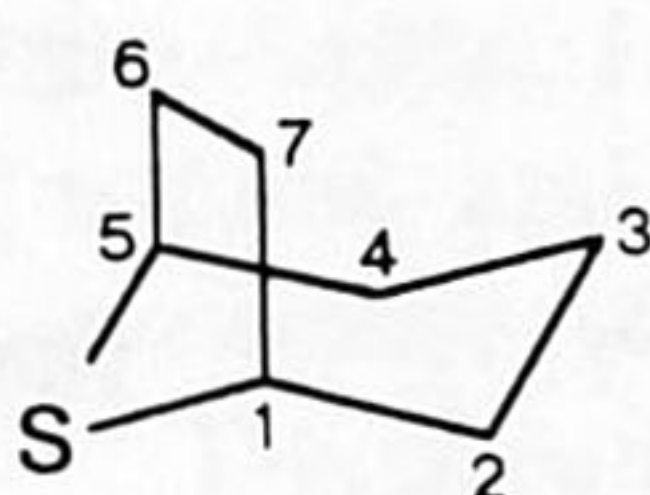


benzenethiol

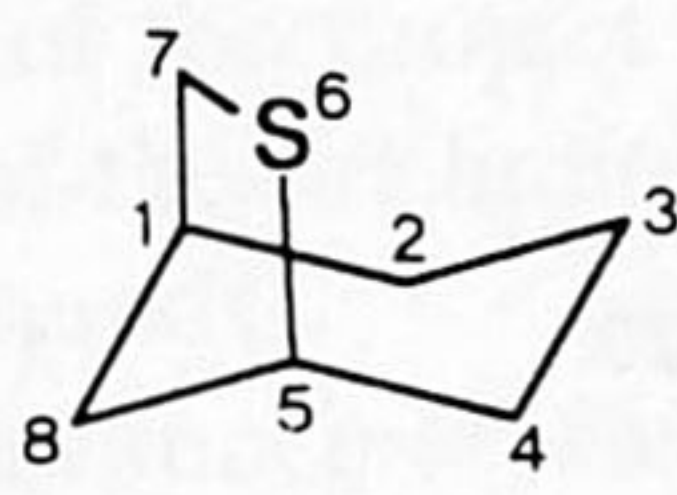
Disulfides

2,3-dithiabutane
(dimethyl disulfide)3,4-dithiaheptane
(ethyl propyl disulfide)1,2-dithiacyclopentane
(1,2-dithiolane)

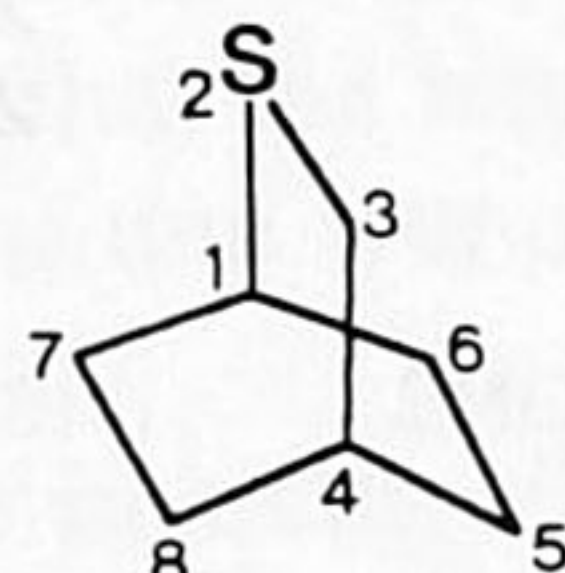
Thiaalkanes and Thiacycloalkanes (Sulfides)

2-thiapropane
(dimethyl sulfide)2-thiapentane
(methylpropyl sulfide)7-thiatridecane
(dihexyl sulfide)thiacyclopentane
(thiolane)2-methylthiacyclopentane
(2-methylthiolane)2,5-dimethylthiacyclopentane
(2,5-dimethylthiolane)thiacyclohexane
(thiane)2-methylthiacyclohexane
(2-methylthiane)2,6-dimethylthiacyclohexane
(2,6-dimethylthiane)

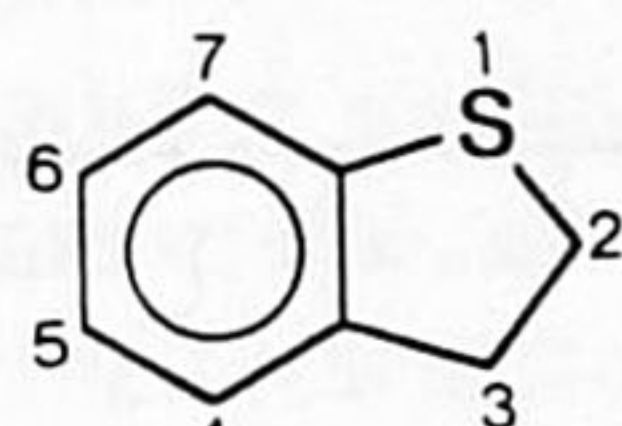
8-thiabicyclo[3,2,1]octane



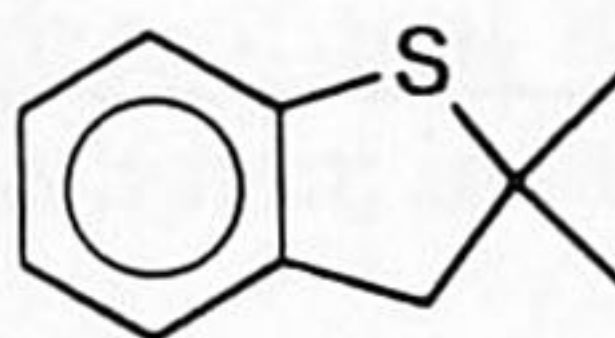
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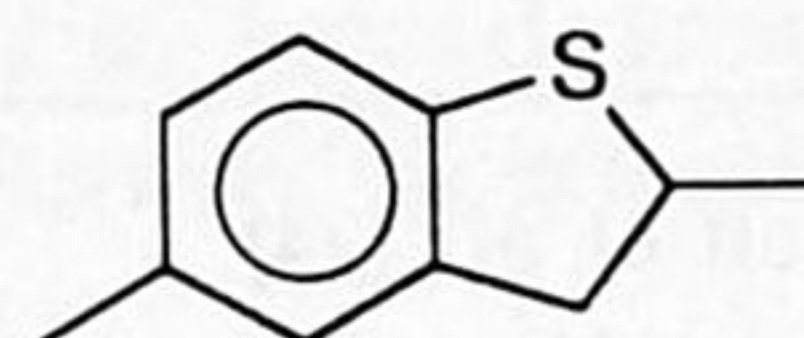
2-thiabicyclo[2,2,2]octane



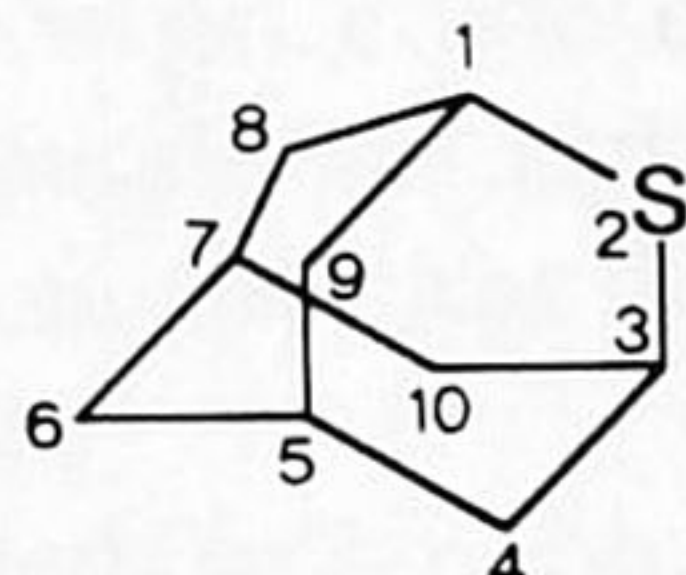
1-thiaindan



2,2-dimethyl-1-thiaindan



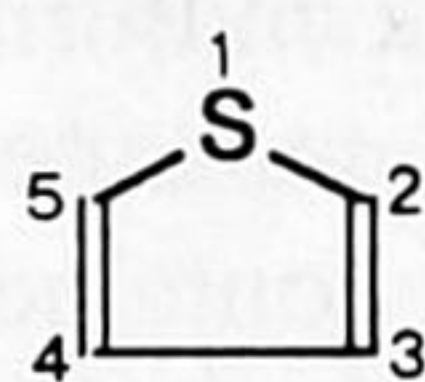
2,5-dimethyl-1-thiaindan



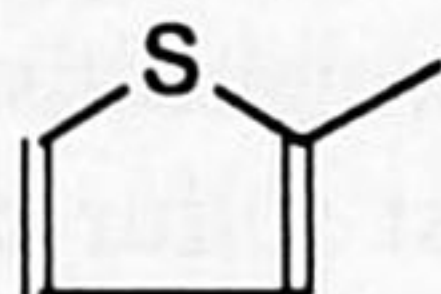
2-thiaadamantane

Figure 1. Examples of non-thiophenic sulfur compounds in petroleum and related materials.

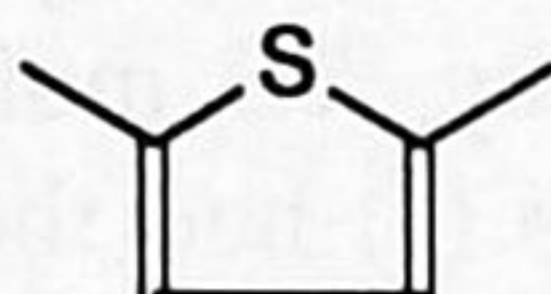
Thiophenes



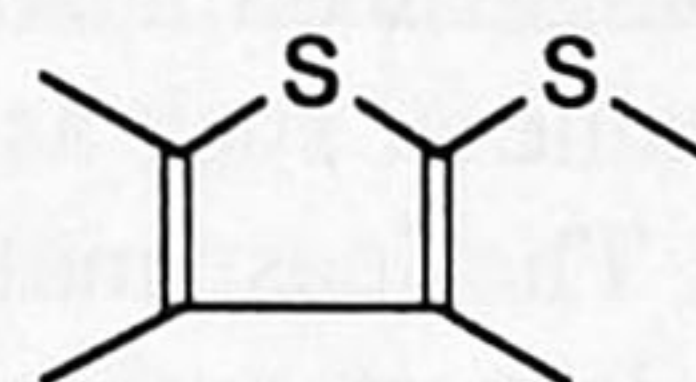
thiophene



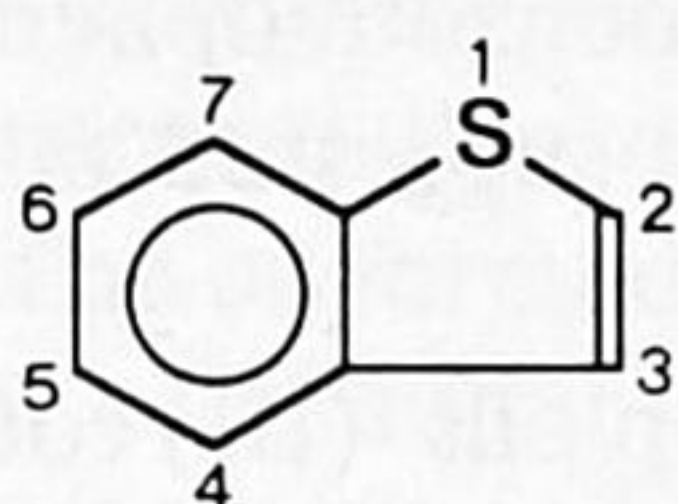
2-methylthiophene



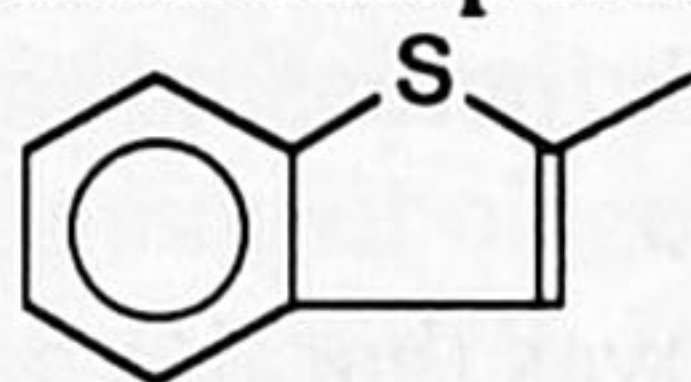
2,5-dimethylthiophene

3,4,5-trimethyl-2-(1-thiaethyl)-
thiophene

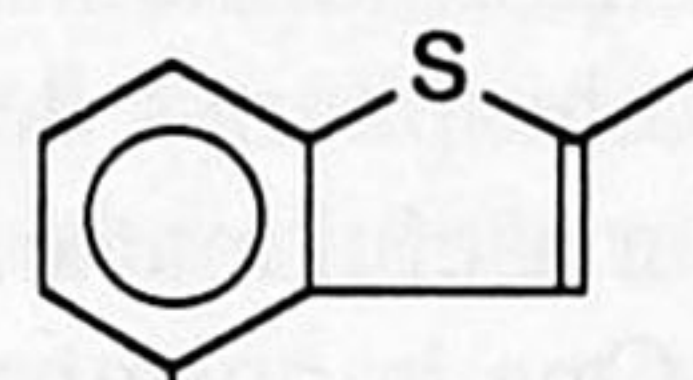
Condensed Thiophenes



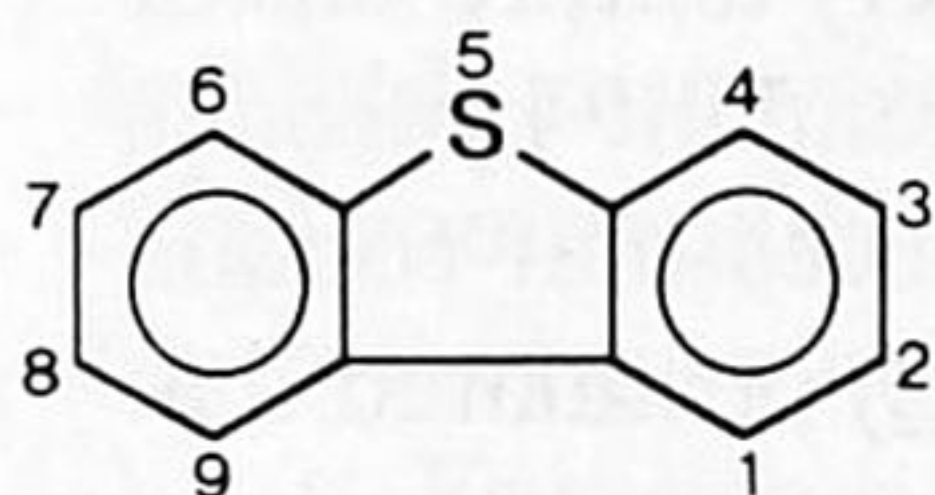
benzo [b] thiophene



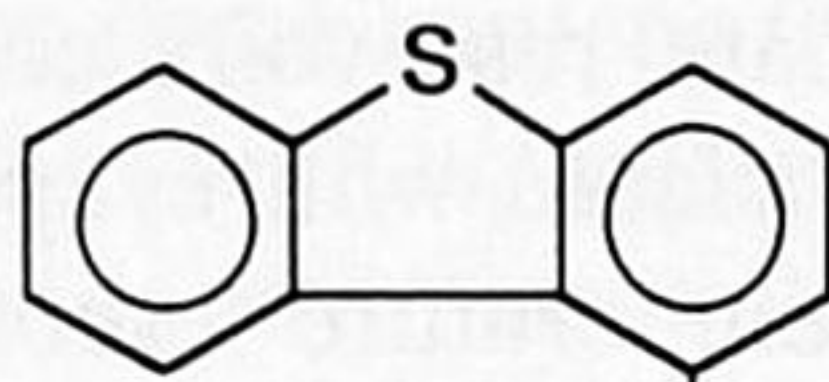
2-methylbenzo [b] thiophene



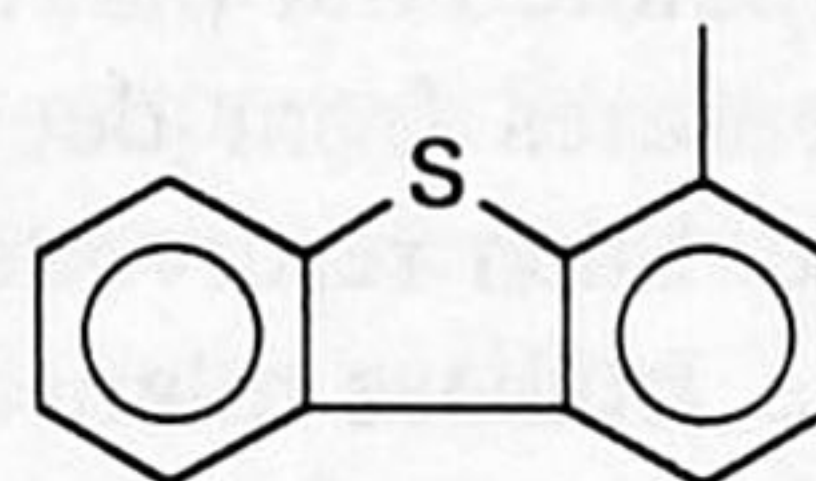
2,4-dimethylbenzo [b] thiophene



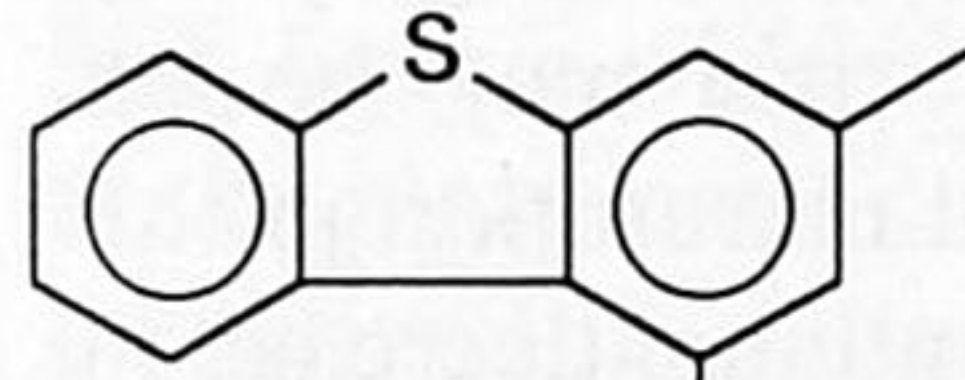
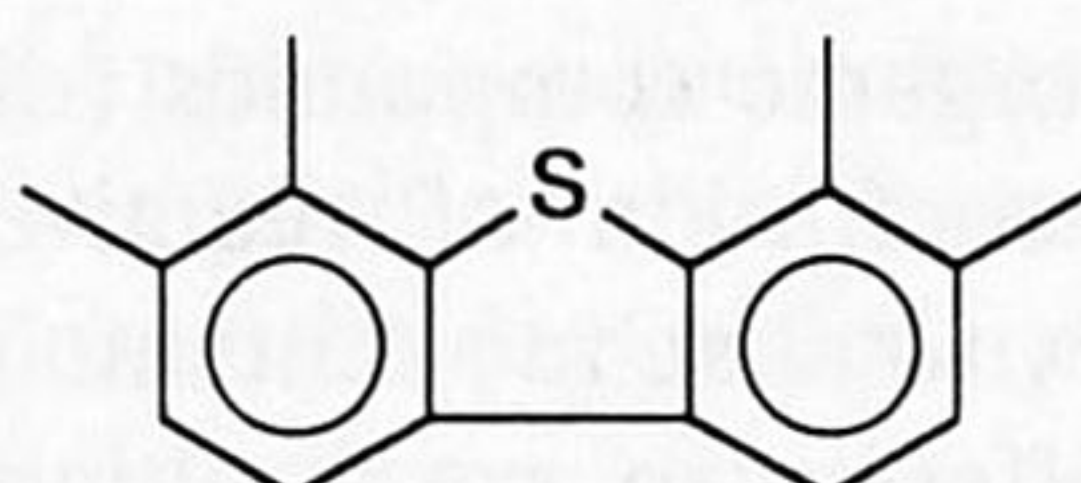
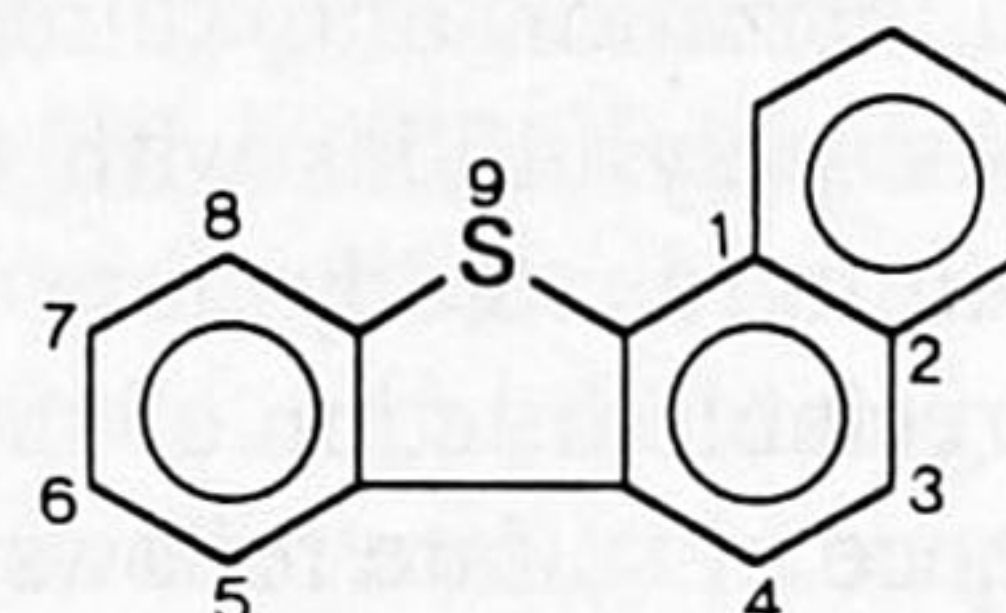
dibenzo [bd] thiophene



1-methyldibenzo [bd] thiophene



4-methyldibenzo [bd] thiophene

1,3-dimethyl-
dibenzo [bd] thiophene3,4,6,7-tetramethyl-
dibenzo [bd] thiophene

9-thia-1,2-benzofluorene

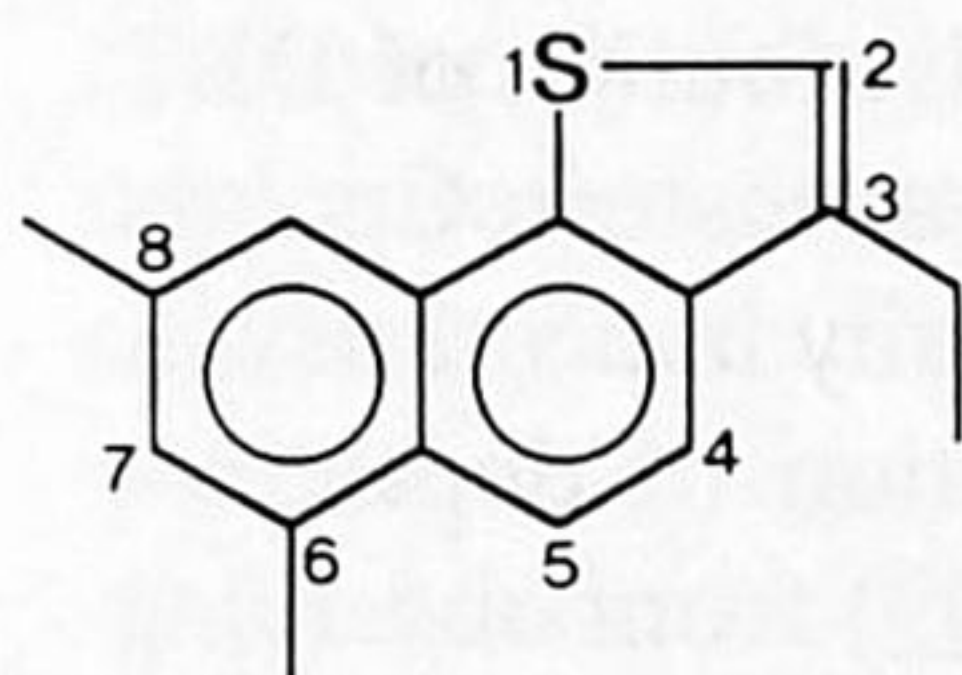
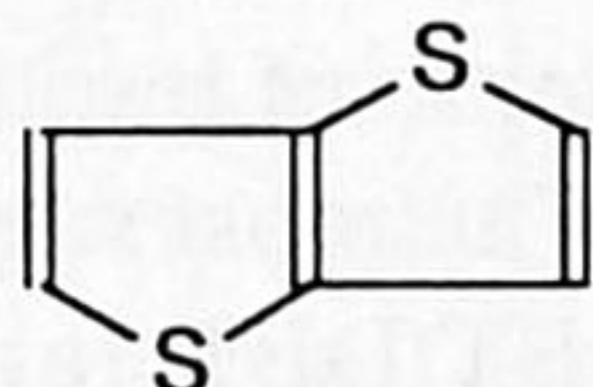
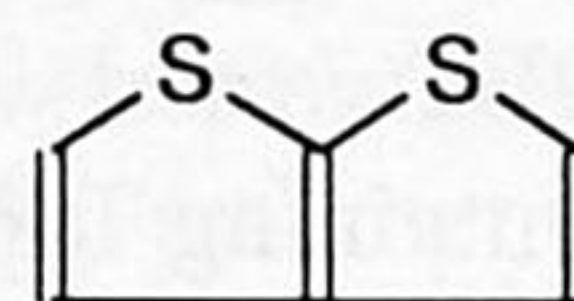
3-ethyl-6,8-dimethylnaphtho
[1,2-*b*] thiophenethieno [3,2-*b*] thiophenethieno [2,3-*b*] thiophene

Figure 2. Examples of thiophenic sulfur compounds in petroleum and related materials.

distributions were determined for the following compound types: (1) nonthiophenic sulfur, (2) thiophenes, (3) benzothiophenes, (4) dibenzothiophenes, (5) benzonaphthothiophenes, and (6) sulfur not recovered.

They classified the oils into three groups based on the distribution of types of sulfur compounds. These groups were immature (I), altered (II) and mature (III). This classification by sulfur distributions was consistent with geological data such as depth and age and with conventional bulk maturity parameter such as API gravity, %S, molecular-weight-distribution of n-alkanes, etc. The least mature group (I) had the highest sulfur content and contained the largest amount of nonthiophenic sulfur (the thermally labile type). The most mature group (III) was from deeper high-temperature reservoirs, contained less total sulfur but relatively more of the thermally stable OSC such as dibenzothiophenes. They showed that the ratio of benzothiophenes to dibenzothiophenes decreased with increasing maturity and suggested that this ratio is a useful maturity indicator.

One important conclusion was that the mature group oils (III) could be divided into two types. One was relatively low in thiols and the other quite high. They pointed out that the high-thiol type is characteristic of very mature oils or condensates from deep carbonate reservoirs containing abundant hydrogen sulfide. Such reservoirs are associated with evaporitic sequences that contain sulfate. In these relatively high temperature reservoirs, Orr (42) postulated that thermochemical sulfate reduction leads to the abundant hydrogen sulfide (and polysulfides) and to conditions that result in a dynamic sulfur system where desulfurization and sulfurization reactions are competing. Reactions of H₂S and/or polysulfides with the organic compounds (oil, condensate or gas) can result in a steady-state concentration of reactive thiols that may be an appreciable fraction of the low total-sulfur content. Thermal maturation in the absence of sulfate follows a different course resulting in a continual decrease in total sulfur and a low thiol content in mature oils and condensates (42).

More recently, increasing interest has been shown in the distributions of dibenzothiophenes (DBT) and methyl dibenzothiophenes (MDBT) (43-49). Radke et al. (43) observed that the relative abundance and distribution of DBT and MDBT varied with increasing depth of burial in a well in a western Canada Basin containing Type III kerogen. The most suggestive maturity indication was shown as a decrease in the 4-MDBT/DBT ratio as a function of depth. A related maturity trend was suggested by Leythaeuser et al. (49) from observing a regular decrease in the 1-MDBT/DBT ratios with depth for extracts from two wells in the North Sea basin. Maturity related changes are also observed within the MDBT isomers. The decrease in 1-MDBT isomer relative to the 2-, 3- and 4-MDBT isomers with increasing maturity is attributed to the relatively lower thermal stability of the 1-isomer (44-48). A decrease in the 1-MDBT/4-MDBT ratio with maturity appears to be common for all types of organic matter, but the value of this ratio at a certain vitrinite reflectance level varies with the type of organic matter (44). Hughes (45) reported that a characteristic

distribution pattern of MDBT isomers was useful to identify oils derived from carbonate source rocks. However, Radke et al. (44) found that this MDBT pattern was also observed in bitumens from siliciclastic rocks containing immature to marginally mature Type II kerogen.

These examples illustrate recent interest in investigating the potential of sulfur compound distributions for improving our understanding of geologic influences in determining variations in composition of crude oils with relation to source and evolution history.

Sulfur in Kerogens and Asphaltenes

The sulfur content of oil is determined primarily by the sulfur content of the source kerogen. The classic paper by Gransch and Posthuma (50) clearly demonstrated this relationship which has been confirmed by all subsequent work. The oil formed at the beginning of oil generation has the maximum sulfur content. Oil sulfur content decreases with increasing maturity as a result of dilution by further generation of non-sulfur compounds as well as by removal of sulfur. The sulfur loss is partly as H₂S and partly by retention of sulfur in insoluble reservoir bitumens or pyrobitumens formed by disproportionation of NSO compounds including resins and asphaltenes into lower-molecular-weight liquid and gaseous hydrocarbons and an insoluble carbonaceous residue.

Kerogen is defined as the fraction of sedimentary organic matter that is insoluble in common organic solvents. This operational definition provides a label or category for the material that is regarded as the major source material for oil and gas but does not imply a unique substance (25-26,51). Kerogens, in fact, have a wide range of composition that depends on the original nature of the organic matter, conditions in the depositional environment, and the stage of evolution or maturity. Kerogens are considered as mixtures of complex macromolecules derived in part from modified biopolymers and in part from new macromolecules formed by condensation, polymerization and crosslinking reactions of initial biogenic precursor materials (51-52). Sulfur may react with the biopolymers and precursor molecules and also may enter into the condensation cross-linking reactions forming kerogen with variations in sulfur content, depending on the depositional environment. As sediment burial increases, kerogens undergo evolution (diagenesis and catagenesis) involving disproportionation into lower molecular weight molecules (oil and gas) on the one hand, and a more condensed carbonaceous residue (residual kerogen) on the other.

Commonly, immature sedimentary organic matter consists of 85-97% kerogen accompanied by 3-15% of extractable organic matter (EOM, or bitumen). Both kerogen and bitumen contribute to petroleum by thermal degradation reactions (catagenesis) as sediments are heated during burial, but quantitatively, the bulk of the oil must come from kerogen.

Petroleum geochemists need the best possible insights into kerogen structure because the amount and composition of oils formed during kerogen evolution depend on its chemical composition. The sulfur content of a crude oil is determined primarily by the sulfur content of the source kerogen and secondarily by the maturity level. High-sulfur kerogens produce high-sulfur oils (42,50,53). In spite of this important relationship, little is known about the amount and forms of sulfur in most kerogens. Even total organic sulfur in kerogens is not routinely determined, mainly because of common contamination by pyrite that makes the analysis difficult. Nevertheless, determination of the total organic sulfur content is possible and the analyses supply very useful information (51,53,54). Examples of complete elemental analysis of kerogen (corrected for pyrite impurities) are given in Table II and show a wide range in organic sulfur content.

Various investigators have proposed that high-sulfur kerogens start to generate oil at lower thermal exposures than classical Type II kerogens, probably because of weaker carbon-sulfur and sulfur-sulfur bonds (25, 53, 55-59). Furthermore, it has been proposed that oil-prone kerogens with an atomic S_{org}/C ratio greater than 0.04 have sufficiently different properties from the classical Type II kerogens that they should be given a distinctive designation "Type II-S" kerogen (53).

Not only the total organic sulfur content but also exact structures of sulfur-containing functional groups in kerogens and their relative abundances may be key factors in determining kinetics of petroleum generation from high-sulfur kerogens. However, satisfactory functional group analysis of sulfur in kerogens is not presently possible. Therefore, this property is not used in establishing kinetic models except for the recognition that different kinetic parameters are required for different types of kerogen (56-59).

Organic sulfur in kerogens is thought to be present as sulfide, disulfide, and heterocyclic moieties; i.e., structures similar to those found in smaller extractable bitumen and oil components. However, the high atomic S_{org}/C ratios in the range of 0.04 to 0.09 for Type II-S kerogens (Table II) suggests either that disulfide and/or polysulfide moieties must be significant or that a large number of sulfur cross-linkages (e.g., $>C-S-C<$ bonds) must be present. At the atomic S_{org}/C ratio of 0.04 (ca. 7-8 wt %S), there is one sulfur atom for every 25 carbon atoms; at an atomic S_{org}/C ratio of 0.08 to 0.09 (ca. 13-14 wt %S), this is one sulfur atom for every 11 to 13 carbon atoms. Trying to accommodate these high sulfur abundances into a kerogen molecular structural model, such as proposed by Behar and Vandembroeck (52), is difficult and informative.

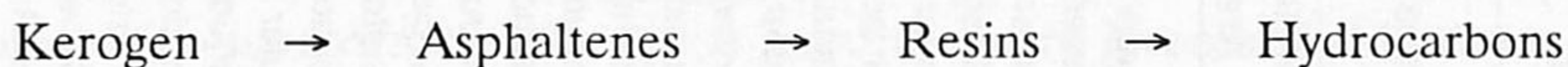
Relationship between kerogens and asphaltenes have taken on new meaning in the last few years especially for relatively low maturity oils. Asphaltene composition can give inferences about the source kerogen composition when kerogen data are unavailable (53,58-59). Asphaltenes are defined as materials soluble or peptized in oil or bitumen that precipitate when

Table II. Examples of Organic Sulfur Content of Oil-Prone Kerogens

| | Elemental Analysis of Kerogens (Normalized Ash-Free) | | | | | | Atomic Ratio | | | Sample Information | |
|----|--|------|-------|--------------|------|------|--------------|-------|--------------|--------------------|--------------|
| | Weight Percent | | | Atomic Ratio | | | Formation | | Geologic Age | | |
| | C | H | O | N | S | H/C | O/C | N/C | S/C | Formation or Area | Geologic Age |
| 1 | 56.40 | 6.80 | 20.10 | 2.50 | 14.2 | 1.44 | 0.268 | 0.038 | 0.094 | Monterey | Miocene |
| 2 | 59.28 | 6.62 | 18.53 | 2.26 | 13.2 | 1.33 | 0.235 | 0.033 | 0.084 | Monterey | Miocene |
| 3 | 63.95 | 7.15 | 12.19 | 2.44 | 14.3 | 1.33 | 0.143 | 0.033 | 0.084 | Monterey | Miocene |
| 4 | 69.44 | 5.20 | 8.53 | 2.18 | 14.6 | 0.91 | 0.092 | 0.027 | 0.079 | Monterey | Miocene |
| 5 | 73.58 | 7.37 | 4.40 | 1.85 | 12.8 | 1.19 | 0.045 | 0.022 | 0.065 | Monterey | Miocene |
| 6 | 74.89 | 8.01 | 3.75 | 1.77 | 11.6 | 1.27 | 0.038 | 0.020 | 0.058 | Monterey | Miocene |
| 7 | 75.57 | 6.65 | 4.83 | 1.59 | 11.4 | 1.05 | 0.048 | 0.018 | 0.056 | Kimmeridge | Jurassic |
| 8 | 74.26 | 8.40 | 4.64 | 2.00 | 10.7 | 1.35 | 0.047 | 0.023 | 0.054 | Monterey | Miocene |
| 9 | 76.19 | 7.89 | 3.59 | 2.06 | 10.3 | 1.23 | 0.035 | 0.023 | 0.051 | Monterey | Miocene |
| 10 | 74.27 | 8.40 | 5.50 | 2.02 | 9.8 | 1.35 | 0.056 | 0.023 | 0.050 | Monterey | Miocene |
| 11 | 74.50 | 7.50 | 6.20 | 2.80 | 9.0 | 1.20 | 0.063 | 0.032 | 0.045 | Phosphoria | Permian |
| 12 | 68.70 | 7.81 | 13.48 | 3.65 | 6.5 | 1.32 | 0.147 | 0.046 | 0.036 | Sisquoc | Miocene |
| 13 | 70.47 | 6.97 | 13.76 | 2.58 | 6.4 | 1.15 | 0.147 | 0.031 | 0.034 | Phosphoria | Permian |
| 14 | 67.77 | 7.33 | 15.63 | 3.75 | 5.5 | 1.29 | 0.173 | 0.047 | 0.031 | Sisquoc | Miocene |
| 15 | 72.60 | 7.90 | 12.40 | 2.10 | 4.9 | 1.30 | 0.128 | 0.025 | 0.025 | Toarcian | Jurassic |
| 16 | 78.20 | 7.70 | 7.00 | 2.10 | 5.0 | 1.17 | 0.067 | 0.023 | 0.024 | Woodford | Devonian |
| 17 | 70.85 | 7.47 | 13.58 | 4.03 | 4.1 | 1.26 | 0.144 | 0.049 | 0.022 | Sisquoc | Miocene |
| 18 | 77.25 | 7.51 | 8.03 | 3.09 | 4.1 | 1.16 | 0.078 | 0.034 | 0.020 | Nodular Sh. | Miocene |
| 19 | 75.95 | 8.15 | 8.46 | 3.62 | 3.8 | 1.28 | 0.084 | 0.041 | 0.019 | Sisquoc | Miocene |
| 20 | 77.52 | 8.05 | 7.76 | 2.97 | 3.7 | 1.24 | 0.075 | 0.033 | 0.018 | McDonald Sh. | Miocene |
| 21 | 78.08 | 7.28 | 9.13 | 2.09 | 3.4 | 1.11 | 0.088 | 0.023 | 0.016 | Kimmeridge | Jurassic |
| 22 | 85.40 | 3.50 | 5.60 | 2.10 | 3.3 | 0.49 | 0.492 | 0.021 | 0.015 | N. Sahara | Silurian |
| 23 | 75.90 | 9.10 | 8.40 | 3.90 | 2.6 | 1.43 | 0.083 | 0.044 | 0.013 | Green River | Eocene |
| 24 | 73.50 | 8.30 | 15.60 | 0.40 | 2.2 | 1.35 | 0.139 | 0.005 | 0.011 | Kukersite | Ordovician |
| 25 | 69.30 | 8.30 | 18.00 | 2.60 | 1.8 | 1.43 | 0.195 | 0.032 | 0.010 | Messel Sh. | Eocene |

the sample is diluted with an excess of n-alkane (e.g., pentane, hexane or heptane). Another definition is the fraction that is soluble in benzene and insoluble in n-alkanes (52,53,60-63). These solubility characteristics are a function of both molecular size and polarity; the latter is related to both the NSO heteroatom functional groups and the aromatic/aliphatic carbon ratio.

Tissot pointed out in 1984 (58) that "*asphaltenes can be thought of as small fragments of kerogen, having a comparable structure. Thus kerogen, asphaltenes, resins, and hydrocarbons might be considered to form a continuum, with decreasing size, heteroatom content, and polarity.*" This continuum is a reaction or transformation sequence that proceeds with increasing maturity:



Pyrolysis of kerogens and asphaltenes has demonstrated the nature and logic of this conversion sequence (58,63-64). Relative to elemental composition, initial asphaltenes have a much lower atomic O/C ratio, a slightly lower atomic S/C ratio, and almost the same H/C and N/C ratios as their source kerogens (53).

We should caution that the above concept of the genetic relationship between kerogens and asphaltenes differs from the more historic view that asphaltenes are condensation and/or alteration products of hydrocarbons and resins. Certainly, in some petroleum processing treatments and probably at higher maturation levels in nature, various reactions do form new products with asphaltene solubility characteristics. These new condensation products may be regarded as altered asphaltenes and intermediates in the coke or pyrobitumen formation process (62-64). Contamination of original asphaltenes by subsequently formed or altered products, of course, will result in a less definitive correlation between an asphaltene and its source kerogen.

Presently, the unsatisfactory state of knowledge regarding structure of organic sulfur in kerogens and asphaltenes is also the case for coals. Coal is a special form of kerogen derived largely from higher terrestrial plant organic matter. Advances in analytical methods for solids with respect to sulfur characterization will benefit all fuel sciences. Sulfur K edge X-ray absorption spectroscopy (XANES and XAFS) shows promise (65). This technique applied to petroleum asphaltenes is reported by George et al. (66) in this volume, and is being investigated for quantitative determination of sulfur forms in other complex solid materials such as coals and kerogens.

Sulfur in Natural Gas

Natural gases vary in H₂S content from negligible amounts to over 90 mole percent, but most gases have a negligible H₂S content. Natural gases with high H₂S contents often also contain dissolved elemental sulfur and polysulfides. Gases with more than a few percent H₂S are generally limited to carbonate reservoirs at relatively high temperatures and in strata associated with

evaporites. These rocks and associated waters furnish sulfate (from anhydrite) that can be reduced to H₂S by bacteria at low temperatures and by thermochemical sulfate reduction at higher temperatures. The H₂S from thermochemical sulfate reduction can accumulate in high concentrations if the reservoir contains little reactive iron. Geologic and geochemical controls on the distribution of H₂S in natural gas have been reviewed (67). Several informative papers were given in the symposium dealing with thermochemical sulfate reduction and other aspects of sulfur in natural gas (see abstracts of 197th ACS Meeting), but most of these papers did not become available for this volume. Hopefully, some will be published elsewhere.

Recent Advances in Molecular Structure of OSC

Major advances in analytical chemistry in the last two decades have greatly accelerated the geochemical study of fossil fuels. In particular, high resolution capillary gas chromatography coupled with mass spectrometry (GC-MS) has allowed the determination of molecular structure more precisely, with smaller samples, and with less prior separation and purification than was required previously. As a result, knowledge about petroleum composition has increased greatly. Composition of petroleum is now used much more effectively to infer source-rock facies (reflecting depositional environments), maturation levels (thermal history), migration pathways, and the various secondary alteration processes (biodegradation and water washing). The so-called biomarker molecules retaining structures indicative of their biological precursors are now used routinely in petroleum geochemistry for these applications and inferences. Hydrocarbon biomarkers, especially the steranes, hopanes, isoprenoids and n-alkanes have been the major molecules used for these purposes (68-70).

Advances in petroleum characterization at the molecular structure level by GC-MS methods renewed interest in OSC. Within the past few years, at least one-thousand new and novel OSC that previously were not known to be present in petroleum and bitumens have been reported. Tentative molecular structures inferred from GC-MS and other techniques have been confirmed in many cases by synthesis of authentic reference-compounds. The difficult and time-consuming synthetic work has been crucial in validating many of the novel structures. Another key finding has been that immature bitumens and crude oils (samples that have not received significant thermal stress) differ markedly from the previously known OSC in that they have carbon-skeletons resembling ubiquitous biomarker hydrocarbons (e.g., n-alkanes, isoprenoid alkanes, steranes, and hopanes). This similarity, of course, suggests that the hydrocarbons and OSC have common biogenic precursors.

In this overview we can only illustrate by selected examples the general structural types of OSC that have been identified in recent years and point out major conclusions to be drawn from these studies (71-92). Additional studies representing current trends in OSC research are included in this volume under

the heading *Molecular Structure of Sulfur Compounds and Their Geochemical Significance*. These papers largely relate to: (1) early diagenetic reactions in initial sedimentary deposits, (2) immature bitumens and associated kerogens, (3) initial reactions involved in the transformation of kerogen and bitumen to crude oil, and (4) molecular indications of depositional environmental and thermal maturity conditions.

Structures I-XIII in Figure 3 illustrate the new generation of OSC quite different from those previously known (cf. Figures 1 and 2). The beginning of the new era in OSC research was the identification of two series of terpenoid sulfides I and II in petroleum reported by Payzant et al. in 1983 and 1985 (71-72) dealing with Alberta oils and oil sands, and of the C₃₅ thiophene-containing hopane III reported by Valisolalao et al. in 1984 (76) from studies of bitumen extracted from an immature black shale. The structure of compound III strongly suggested that it was formed by incorporation of sulfur into bacteriohopanetetrol as shown in Figure 4A. The hopanetetrol is a cell membrane constituent of prokaryotes. This case was the first definitive indication at the molecular level of sulfur incorporation into a specific biogenic precursor molecule.

Additional precursor-product relationships were indicated by the identification of a C₂₀ isoprenoid thiophene (IV; Figure 3) by Brassell et al. in 1986 (77) in both recent and ancient deep-sea sediments. This structure strongly suggested an origin by incorporation of reduced inorganic sulfur species into phytol and/or archaeobacterial phytanes or their diagenetic products as indicated in Figure 4B. Other C₂₀ isoprenoid thiophenes (e.g., V and VI; Figure 3) have been identified subsequently as reported by Sinninghe Damsté et al. in 1986 and 1987 (80,81), Sinninghe Damsté and de Leeuw in 1987 (82) and by Rullkötter et al. in 1988 (83).

Further examples are the C₂₅ highly branched isoprenoid thiophenes (e.g., VII; Figure 3) which have been identified as abundant OSC from upwelling areas forming diatomaceous sediments such as in the Monterey Formation of California by Sinninghe Damsté, et al. (87,89). Precursors for these thiophenes are believed to be C₂₅ highly-branched isoprenoid alkenes with two to four double bonds as shown in Figure 4C. These isoprenoid alkenes are known to be ubiquitous in young sediments as reported by Robson and Rowland (92) and were recently found to occur in Antarctic sea-ice diatoms by Nichols et al. (93). Therefore, this thiophene series has been suggested as biological markers for diatoms (88).

These examples convincingly demonstrate that specific OSC are formed during the early stages of diagenesis by reactions of reduced sulfur species with specific biogenic substrates. The reactive substrates are proposed to contain either carbon-carbon double bonds or other reactive functional groups that react with either hydrogen sulfide or polysulfides to form the OSC (88). These views are consistent with evidence from sulfur isotopes that H₂S produced by microbial sulfate reduction is the major source of reduced sulfur in sediments

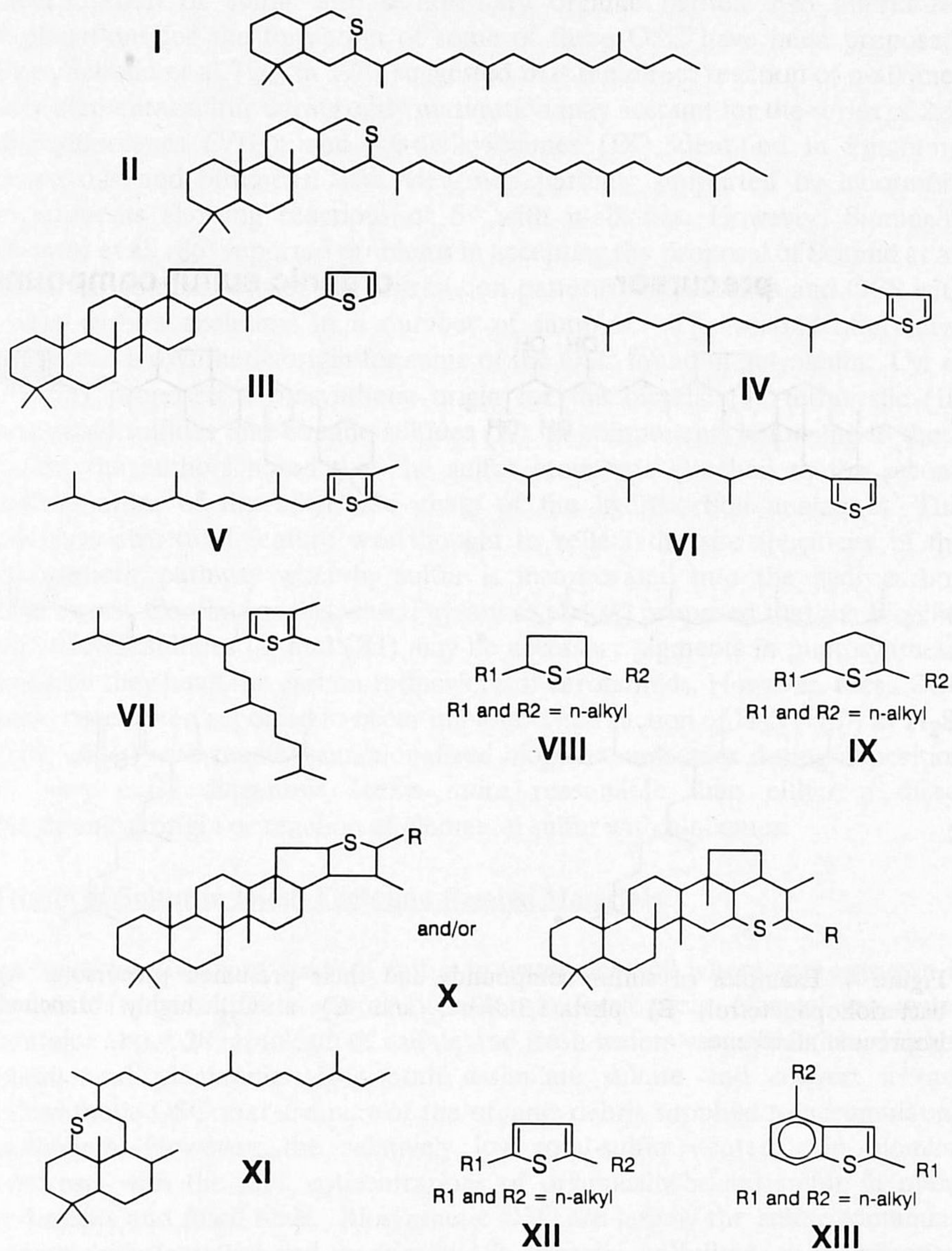


Figure 3. Examples of sulfur compounds with structures related to well known biological markers.

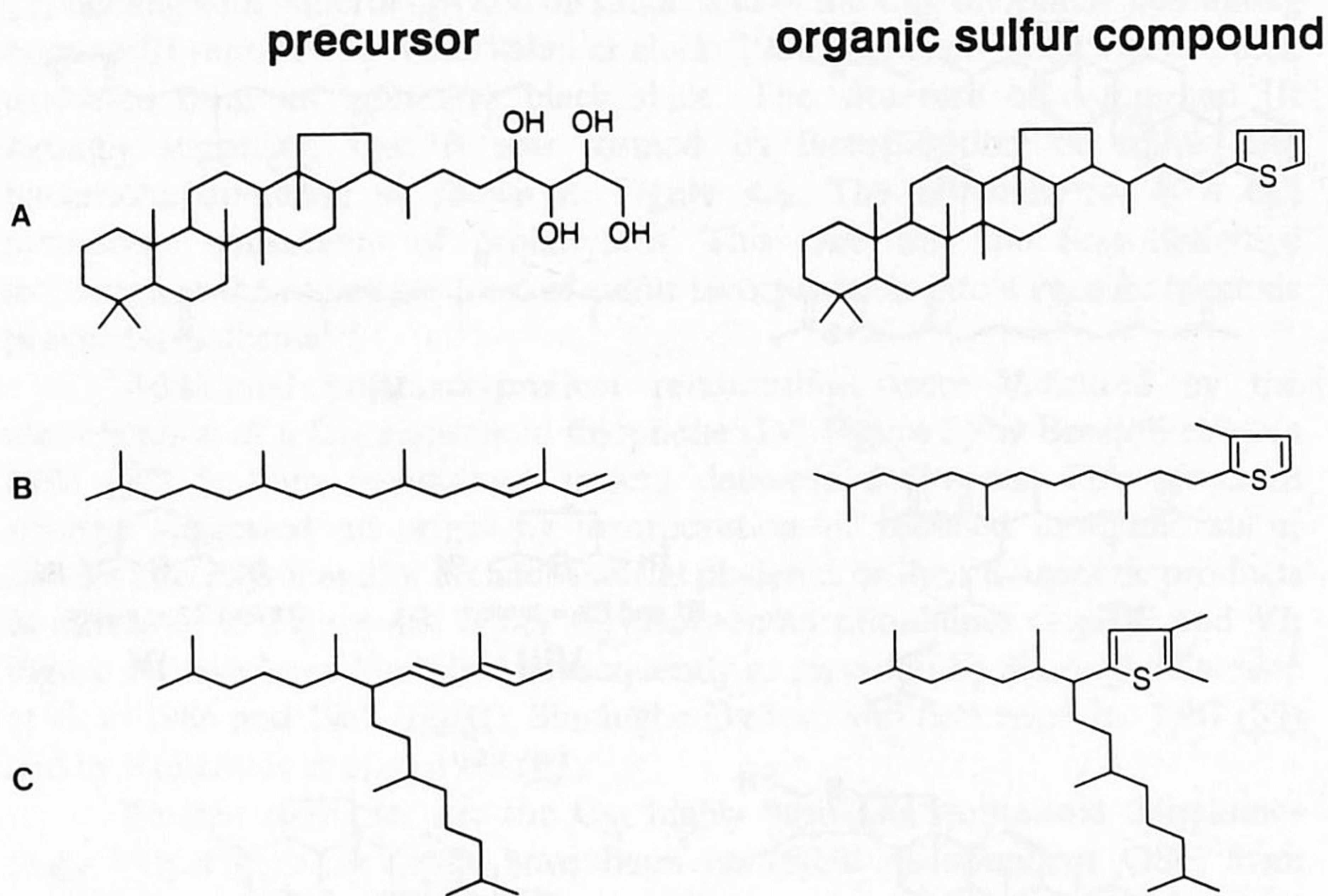


Figure 4. Examples of sulfur compounds and their presumed precursors: A) bacteriohopanetetrol, B) phyta-1,3-diene, and C) a C_{25} highly branched isoprenoid alkadiene.

and crude oils (17-20,22-24,28-29), and they are in agreement with other evidence presented in this volume and elsewhere (53, 99-106).

Despite the overwhelming evidence for the very early chemical incorporation of sulfur into sedimentary organic matter, two alternative explanations for the formation of some of these OSC have been proposed. First, Schmid et al. (90) in 1987 suggested that the direct reaction of n-alkanes with elemental sulfur during early maturation may account for the series of 2,5-dialkylthiolanes (VIII); and 2,6-dialkylthianes (IX) identified in immature crude oils and bitumens. This view was partially supported by laboratory experiments showing reactions of S^0 with n-alkanes. However, Sinninghe Damsté et al. (86) reported problems in accepting the proposal of Schmid et al. based on comparisons of the distribution patterns of n-alkanes and OCS with linear carbon skeletons in a number of samples. The second alternative suggests a biosynthetic origin for some of the OSC found in petroleum. Cyr et al. (73) proposed a biosynthetic origin for the bicyclic (I), tetracyclic (II) terpenoid sulfides and hopane sulfides (X). In components belonging to these series, the authors noted that the sulfur atom was attached to the second carbon atom of the alkyl side chain of the hydrocarbon analogues. This common structural feature was thought to reflect the site specificity of the biosynthetic pathway whereby sulfur is incorporated into the hydrocarbon framework. Continuing this view, Payzant et al. (74) proposed that the bicyclic- and tricyclic sulfides (I) and (XI) may be accessory pigments in photosynthesis because they have the carbon framework of carotenoids. However, these OSC have never been reported to occur in biota. The reaction of H_2S (HS^-) or H_2S_x (HS_x^- , S_x^{2-}) with reactive functionalized biogenic molecules during deposition or very early diagenesis seems more reasonable than either a direct biochemical origin or reaction of elemental sulfur with n-alkanes.

Origin of Sulfur in Fossil Fuels and Related Materials

Sulfate, the dominant form of sulfur in water and soil where some oxygen is present, is the ultimate source of sulfur in fossil fuels. Normal sea water contains about 28 mmol/L of sulfate and fresh waters very much less. Higher plants and planktonic algae both assimilate sulfate and convert it into biosynthetic OSC that are part of the organic debris supplied to accumulating sediments. However, the relatively low total-sulfur content in biomass contrasts with the high concentrations of organically-bound sulfur in many sediments and fossil fuels. Biosynthetic OSC are largely the sulfur containing amino acids (cysteine and methionine) in proteins, sulfolipids in membranes, and sulfate esters in cell wall carbohydrates (96-101). Therefore, original OSC in biological debris not only have structures very different from those in fossil fuels, but they also are easily degraded by microbial and enzymatic processes that release sulfur. The released sulfur is largely in H_2S , methyl mercaptan and dimethyl sulfide in young sediments, but some is converted to more oxidized

inorganic forms such as elemental sulfur, polysulfides, thiosulfate, polythionates, sulfite and sulfate (2,100). A number of other OSC are found in biological systems but they are quantitatively less important (96). For many years, it has been evident that original biomass is a minor sulfur source for sedimentary organic matter that contains moderate to large amounts of sulfur, but it may furnish a significant fraction of the total sulfur in low-sulfur kerogen and coal.

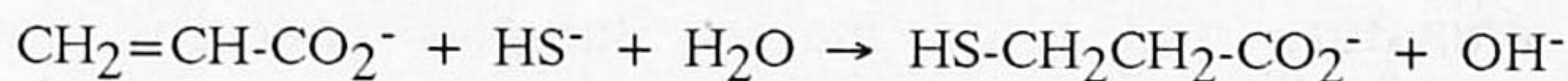
The major source of sulfur incorporated into pyrite and sedimentary organic matter is the dissimilatory H_2S formed by sulfate-reducing bacteria acting on aqueous sulfate (e.g., sea water in marine environments) either at the sediment-water interface or at shallow depths in organic-rich sediment. Sulfur isotope studies have been critical in establishing this fact (16-21). In some environments with restricted deep-water circulation (silled basins) or in highly productive upwelling areas in oceans, microbial sulfate reduction also may occur in the water column and lead to bottom-waters containing H_2S .

Hydrogen sulfide does not exist alone in natural sediment systems, but is always associated with variable concentrations of partially oxidized species with intermediate valence states between -II (H_2S , HS^- , S^{2-}) and +VI (HSO_4^- , SO_4^{2-}). Sulfate is kinetically inactive at low temperatures and generally is not in equilibrium with other sulfur species. On the other hand, reduced forms of sulfur in general are very reactive and concentrations are controlled by both thermodynamics and kinetics for the various species. The oxidation of microbially produced H_2S can be caused by (1) dissolved oxygen at anoxic/oxic boundaries, (2) by reducible cations such as Fe^{3+} released from minerals and (3) by microbial processes involving biochemical oxidation and reduction reactions in both oxic and anoxic environments. Currently, research directed toward understanding anoxic oxidation of H_2S in biological systems is very active (2,100). The capacity of chemoautotrophic bacteria to oxidize hydrogen sulfide as an energy source for CO_2 fixation is well known, however the relatively recent realization that entire biological communities exist in deep ocean sites (using sulfide derived from hydrothermal vents) has stimulated new interest in the ability of biological systems to derive energy by sulfide oxidation in the dark. These studies are producing improved analytical methods for determining the numerous sulfur species (organic and inorganic) in biological systems and in sediments (2,100). Although details of sulfide oxidation mechanisms in anoxic environments are not completely understood, elemental sulfur and polysulfides H_2S_x are ubiquitous in sediments, as are at least traces of other intermediate oxidation state species such as thiosulfate, polythionates, and sulfite. Hydrogen sulfide and elemental sulfur (S^0 valence state) react rapidly and reversibly without biological mediation to form various catenated polysulfides (H_2S_x ; $x = 2,3,4,5$ etc.) and establish the reactive aqueous $H_2S/S^0/H_2S_x$ system in sediments. This system is the major Eh controlling mechanism in reducing sediments (23,102).

Pyrite is a major sink for reduced sulfur from the $\text{H}_2\text{S}/\text{S}^0/\text{H}_2\text{S}_x$ system to the extent that reactive iron is available. In sediments with limited amounts of reactive iron, reduced sulfur species in the $\text{H}_2\text{S}/\text{S}^0/\text{H}_2\text{S}_x$ system are available for reaction with the sedimentary organic matter.

Polysulfides are extremely reactive in both oxidation and reduction reactions and readily incorporate sulfur into labile biogenic compounds that have functions such as the keto ($\text{R}_2\text{C}=\text{O}$), hydroxyl ($\text{RCH}_2\text{-OH}$), amino ($\text{R}_2\text{-NH}$) groups and/or carbon-carbon double bonds ($>\text{C}=\text{C}<$). Polysulfides also can cause oxidation of almost any functional group to a carboxylic acid or reduction to a hydrocarbon without sulfur remaining in the final organic product (103). LaLonde (104-105) discusses the importance of polysulfides in forming OSC and sulfur-rich kerogen in young sediments at low temperatures. As discussed in the previous section, thiolanes, thianes, thiophenes and organic polysulfides are concluded to be formed very early in this manner. Polysulfides probably also assist the natural polymerization process (kerogen formation) in sulfur-rich environments by forming sulfide and/or polysulfide cross-linkages (perhaps similar to the vulcanization of rubber). Francois (106-107) and others have demonstrated the early incorporation of sulfur into humic acids in modern marine sedimentary environments and stress the probable importance of polysulfides in these reactions. Aizenshtat et al. also reported on the involvement of polysulfides in reactions with recent organic matter in the hypersaline Solar-Lake environment (108).

Further evidence for the addition of H_2S to carbon-carbon double bonds very early in sediments, and further insights into reaction mechanisms, have been reported by Vairavamurthy and Mopper in 1987 and 1989 (109,110). They identified 3-mercaptopropionic acid (3-MPA) as a major thiol in anoxic intertidal marine sediment and demonstrated that the thiol formation could occur by the reaction of HS^- with acrylic acid in sediment water and seawater at ambient temperature: The formation of 3-MPA was hypothesized to occur by a Michael addition mechanism whereby the nucleophile HS^- adds to the activated double bond in the α,β -unsaturated carbonyl system:



They suggested that this could be a major pathway for the incorporation of sulfur into sedimentary organic matter during early diagenesis.

In the later work (110) they reported the relative rates of additions of both bisulfide (HS^-) and polysulfide (S_4^{2-}) to acrylic acid and to acrylonitrile ($\text{CH}_2=\text{CH-CN}$) for a range in pH and ionic strength. Results showed that at equal nucleophile concentrations, the addition of the polysulfide ion was much faster than that of the bisulfide ion. The difference in rate for the two nucleophiles was greater for acrylic acid, which is largely the anion under the pH conditions, than for acrylonitrile which is neutral. Effects of ionic strength

on rates led to the suggestion that hypersaline environments also may favor organosulfur formation by the Michael addition mechanism.

Expectations for the Future

Although recent advances have led to a number of important conclusions and insights with respect to sulfur in fossil fuels, many remaining questions provide challenging opportunities for further research.

One area of intrigue relates to preliminary reports (78,86,111) of sulfur cross-linked polymers isolated from low maturity high-sulfur crude oils. Presumably, these materials are still being investigated, and further evaluation of their character and their significance can be expected.

An important opportunity related to petroleum exploration concerns the nature of transformations of OSC occurring between immature oils (or bitumens) and more mature crude oils. Easily identified OSC in immature oils and bitumens are mainly alkylthiolanes, alkylthianes, and alkylthiophenes whereas more mature crude oils (i.e., conventional crude oils) are dominated by rather low-molecular-weight benzo- and dibenzothiophenes. This difference signals potentially useful maturity reaction sequences in the OSC that require further investigation. Cyclization and aromatization of 2-alkyl- and 2,5-dialkylthiophenes (XII) containing side chains with four or more linear carbons may be a major pathway to the alkylbenzothiophenes as suggested by Perakis (79) and Sinninghe Damsté et al. (84,89). This explanation is supported by the relatively high abundance of 2- and 4-alkyl- and 2,4-dialkylbenzothiophenes (XIII) in crude oils and bitumens (79,84) and the observation that more mature samples contain relatively higher amounts of these benzothiophenes (89). Similar cyclizations may account for benzothiophene moieties inferred to be present in some macromolecules (85,95). Eglinton et al. (94) found an increased abundance of alkylbenzothiophenes over alkylthiophenes in flash pyrolysis of artificially matured kerogens that suggests these reactions may proceed within the macromolecules during diagenesis and maturation. Of course the entire problem of understanding the differences in composition of OSC between immature and more mature samples concerns not only molecular changes in the early OSC, but also the newly generated product that may form later with increasing maturity.

Further advances in various areas of OSC research can be expected in the next few years and many will be connected with continuing investigations of the mode of occurrence of sulfur in macromolecules (kerogens, asphaltenes and resins). The difficult problem of understanding sulfur bonding and distribution of sulfur containing functional groups in macromolecules will continue to be given high priority because it is strongly related to the important implication of early oil generation from sulfur-rich kerogens. Determining the nature and abundance of polysulfide functions in kerogens, asphaltenes and resins remains a very important challenge.

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