Reports

Sulfur: Role in Genesis of Petroleum

Abstract. *Sulfur reacts readily with cholesterol at 150°C, and the product of the reaction contains aromatic hydrocarbons, some with a benzene, some a naphthalene, and some a phenanthrene ring system as part of the molecule. The reaction of farnesol with sulfur takes place at 135°C. Cadalene (1,6-dimethyl-4-isopropylnaphthalene) is one of the products of the reaction. These reactions at relatively low temperatures support the proposition that a thermal reaction of sulfur with terpenoids and steroids plays a part in the genesis of petroleum.*

The thought that sulfur may play a role in the genesis of petroleum is not new. Because the amount of sulfur in the organic material from plants and animals seems to be too small to account for the large amounts of sulfur compounds in some petroleums, Hanson (*1*) has proposed that a thermal reaction between elemental sulfur and the organic material of the sediment may be responsible for the genesis of the sulfur-containing compounds.

The similarity of the structures of certain petroleum hydrocarbons (naphthalenes, phenanthrenes, and cyclopentanophenanthrenes) and those produced by the reaction of sulfur with terpenoids and steroids has been noted (*2*). Dehydrogenation of terpenoids, steroids, and other natural products with sulfur is a common method for the elucidation of structure, but the temperature employed is usually 200° to 220°C. Since this temperature is higher than those believed present during the genesis of petroleum, it seemed desirable to determine whether the dehydrogenation of terpenoids and steroids to give petroleum-type aromatic hydrocarbons would take place at lower temperatures.

We have found that cholesterol reacts readily with sulfur at 150°C with the evolution of hydrogen sulfide and that the product of the reaction contains hydrocarbons. Some of these have a benzene, some a naphthalene, and some a phenanthrene ring system as part of the molecule. The reaction of farnesol with sulfur takes place at 135°C. Cadalene (1,6-dimethyl-4-isopropylnaphthalene) has been identified as one of the products of the reaction.

The reactions with cholesterol and sulfur were carried out at 150°C. In one reaction cholesterol (5 g) and sulfur (2.5 g) were heated together for 30 days; hydrogen sulfide (0.28 g) was collected as cadmium sulfide, and the reaction product (4.6 g) was obtained as a viscous black tar. In another reaction, cholesterol (60 g) and sulfur (12 g) were stirred together. After 6 days some product (26 g) was removed, and after 31 days the reaction was stopped, yielding an additional 42 g of product. One day after the start of the experiment hydrogen sulfide was evolved at a rate of 0.05 g per hour; after 5 days the rate fell to a few milligrams per hour.

The tar, dissolved in a minimum quantity of benzene, was chromatographed on activated alumina. A pale yellow oil amounting to 7 to 10 percent of the reaction product was obtained by elution with cyclohexane and then with cyclohexane containing benzene in increasing proportions. The remainder of the reaction product was eluted from the column with chloroform and then methanol. Some of the dark viscous gums recovered from these eluates contained 7 to 11 percent of sulfur; they were not investigated further.

The pale yellow oils were rechromatographed on alumina and the ultraviolet absorption spectra of selected fractions, recovered from the eluates, were recorded. Fractions with similar spectra were combined, and their nuclear magnetic resonance (NMR) spectra were recorded. Corresponding fractions from several experiments showed similar ultraviolet spectra and similar NMR spectra.

The first material eluted yielded impure Δ^4-cholestene as judged by optical rotation, melting point, ultraviolet, mass, and NMR spectra. Succeeding fractions gave oils with ultraviolet spectra characteristic of benzenoid hydrocarbons. The sulfur content was low, 0.20 to 0.29 percent. In the NMR spectrum of one of these fractions (Fig. 1) we assign the strong peak at $\tau = 3.00$ to benzenoid protons and the peak at $\tau = 7.76$ to the protons of a methyl group attached directly to a benzene ring. A comparison of this

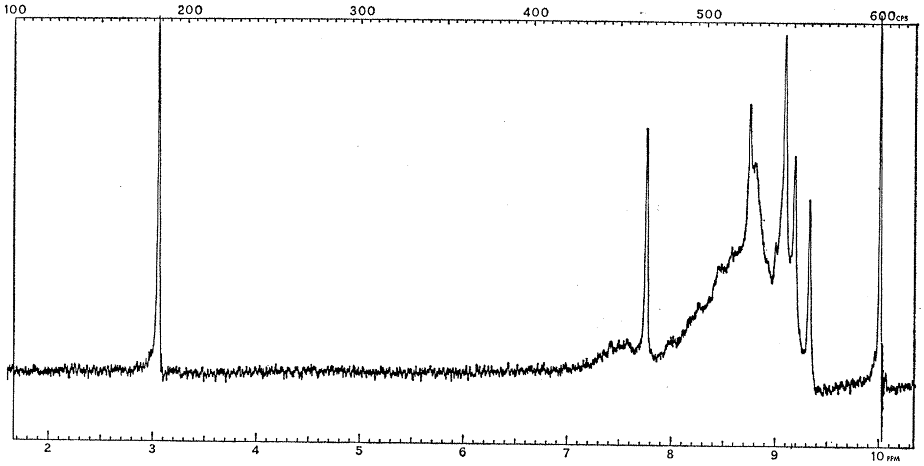


Fig. 1. NMR spectrum showing molecules with benzene ring with a methyl group attached directly to that ring.

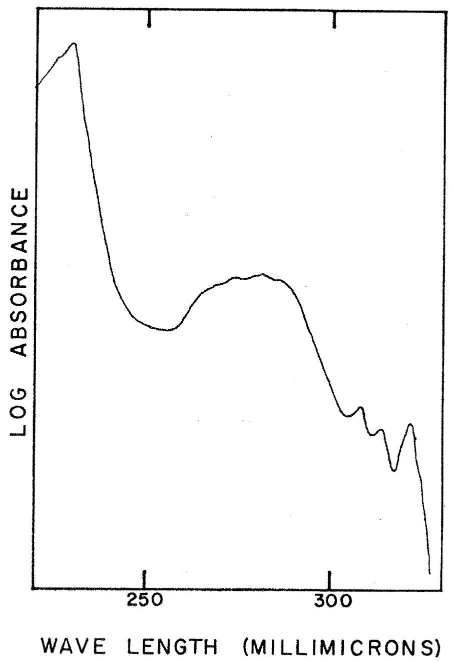
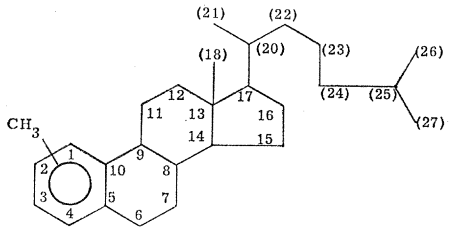


Fig. 2. Ultraviolet spectrum showing molecules with naphthalene nucleus.

spectrum with that of cholesterol (*3*) shows the loss of the methyl at C-19 while the methyl proton signals in the range $\tau = 9.09$ to 9.32 indicate the retention of the methyl at C-18 and the side chain. Thus, a structure one might reasonably write is



However, the mass spectroscopic data showed that this fraction contained 63 percent of a compound, or compounds, with a mass of 368 units and 21 percent with a mass of 370 units. The structure illustrated, with a mass of 366 units, clearly is not in accord with these data. The combined mass and NMR spectra data lead us to propose a structure in which one of the rings has been opened, for example, a structure similar to that illustrated, except that the bond between the C-9 and C-10 atoms is broken. It may be noted that cholestadiene has a mass of 368 units; however, the NMR spectrum shows that this is not present in significant amounts. Succeeding chromatographic eluates had naphthalene-like ultraviolet spectra (Fig. 2) some of which were similar to that of 1,2-dimethylnaphthalene. The NMR spectra of these showed aromatic proton absorption in the region of $\tau = 2.0$ to 3.0 (Fig. 3) which agrees with an interpretation that compounds with a naphthalene nucleus are present. The mass spectroscopic analysis of one of the fractions indicated 68 percent of compound with a mass of 348 units, which corresponds with that of a 26-carbon naphthalene with two cycloparaffin rings in the molecule.

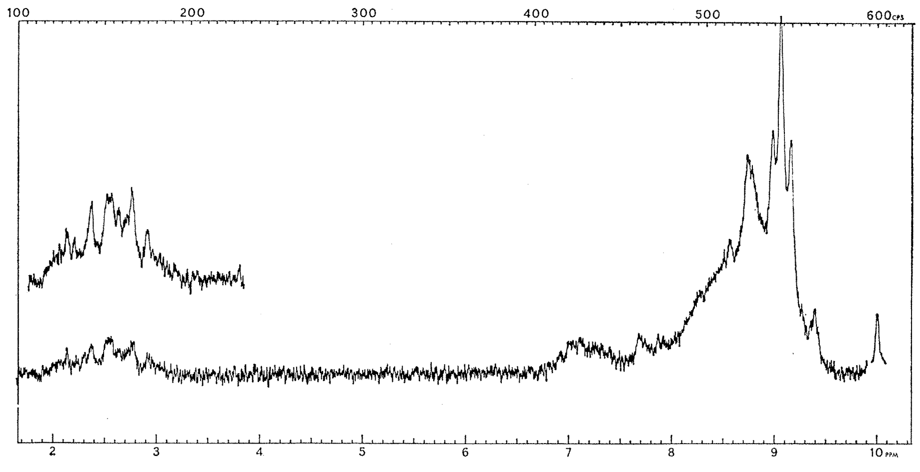


Fig. 3. NMR spectrum showing molecules with a naphthalene nucleus.

Finally, chromatographic fractions eluted with 20 to 50 percent benzene had ultraviolet spectra with phenanthrene-like absorption; Fig. 4 shows the ultraviolet spectrum of a small amount of impure solid isolated from one such fraction.

The reactions with farnesol and sulfur were done at 135°C. One reaction carried out at 150°C evolved hydrogen sulfide vigorously to produce, within a few hours, a viscous black tar. When farnesol (25 g) and sulfur (3 g) were heated with stirring at 135°C for 23 days, hydrogen sulfide was slowly evolved, and the reaction product was obtained as a black tar (26 g). It was chromatographed on alumina as already described. Rechromatography on alumina of the oil from the first portion of eluate gave a series of fractions which were then separated by preparative scale gas-liquid chromatography on a 7.2-m column containing 20 percent of *m*-bis [*m*-(*m*-phenoxyphenoxy)phenoxy] benzene on 42- to 60-mesh fire brick. Capillary-column chromatography (168 m, 0.05 cm stainless steel capillary coated with silicone nitrile) showed that these fractions were still complex mixtures. The NMR spectra of some of these mixtures showed aromatic proton absorption in the range from $\tau = 2.90$ to 3.20, and also absorption at $\tau = 7.73$ typical of a methyl group bonded directly to an aromatic ring. Also, the ultraviolet spectra were consistent with those for substituted benzenes. We propose that some compounds are present which contain a substituted benzene ring obtained by ring closure of farnesol. Succeeding portions of the eluate from the alumina column contained cadalene (1,6-dimethyl-4-isopropylnaphthalene) which was isolated as the picrate. The identity of this hydrocarbon was established by direct comparison with an authentic sample (NMR and ultraviolet spectra and relative retention time on a capillary column and also by comparing the picrates, melting point 111°–112°C, and

Fig. 4. Ultraviolet spectrum showing molecules with a phenanthrene nucleus.

melting point mixed with an authentic sample, 111°–112°C).

Thus petroleum-type hydrocarbons are produced relatively rapidly by the reaction of cholesterol and farnesol with sulfur at temperatures no more than 50°C above those prevailing in some sediments which are commonly regarded as source beds of petroleum. The reaction at a temperature near 100°C would take place very slowly but over a long time period may be expected to produce the same or similar hydrocarbons. Our experiments do not conform with the geological conditions in other respects. These include dilute solutions of the components, an aqueous reducing environment, and the presence of acid clays. With regard to the latter Kawai and Kobayshi (*4*) report that squalene and cholesterol give petroleum-like mixtures of hydrocarbons when heated with acid clays.

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References and Notes

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5. Grateful acknowledgment is made to P. R. Mommessin, Shell Development Company, Houston, Texas, for the mass spectrograph analyses; to R. O. Clark, Gulf Research and Development Company, Harmarville, Pennsylvania, for the sulfur analyses; and to E. J. Eisenbraun, Oklahoma State University, Stillwater, for the synthetic sample of cadalene. Supported by grant from the American Chemical Society Petroleum Research Fund.

13 November 1964

Carbonate in Hydroxylapatite

Abstract. *Unit cell dimensions of hydroxylapatite synthesized hydrothermally are* $a_0 = 9.42_6$ *Å and* $c_0 = 6.88_5$ *Å, whereas carbonate apatite (2.29* CO_2*) gave* $a_0 = 9.43_6$ *Å and* $c_0 = 6.88_5$ *Å. A deficiency of both calcium and phosphorus in the carbonate apatite suggests a coupled substitution of hydronium and carbonate ions in the structure.*

Chemical analyses of dental enamel, bone, phosphorite rock, and even single crystals of apatite commonly show carbon dioxide. However, the manner of its occurrence has been a subject of controversy for many years. Some investigators suppose that carbon dioxide is present as an absorbed layer on the crystallites of teeth and bone. Others suppose that the carbonate is a separate phase, presumably calcite or aragonite; however, if such a separate phase exists, it cannot be detected by any experimental method that has been applied. Still other investigators are aware of the solid solution of carbonate ions in calcium phosphate minerals and dental enamel, and they believe that such solid solution is also possible in crystallites of dentin and bone. The purpose of this study is to determine precise values for the unit cell dimensions of apatite, with and without substitution of carbonate ions, and the effect on the omega index of refraction.

Table 1. Analyses of apatite. The product after heating to 1460°C in each case was apatite, and the Ca : P ratios were 1.760 for the carbonate and 1.665 for the hydroxylapatite (Calcd. 1.667).

Item	Carbonate (64-AP-2)		Hydroxyl (64-Ap-4)		Calcd. for $Ca_{10}(OH)_2(PO_4)_6$ (%)
	Weight (%)	Molecular proportions	Weight (%)	Molecular proportions	
CO_2	2.29	0.0520	0.00		
CaO	53.87	.9620	55.22	0.9860	55.78
P_2O_5	38.74	.2728	41.97	.2955	42.43
H_2O					1.79
Total weight loss after drying at 130°C, cumulative values					
~ 800°C, 12 hr	0.9		0.0		
~ 1120°C, 3 hr	2.0		0.0		
~ 1460°C, ½ hr	3.1		1.5		

Many periodicities for hydroxylapatite are recorded in the literature (McConnell has reviewed the problem, *1*). The differences probably result from x-ray analysis of nonstoichiometric materials. Most analyses were made on precipitates that were very fine-grained; only rarely was hydrothermal synthesis used. Reported periodicities for hydroxylapatite represent a range of nearly 0.1 Å for both c_0 and a_0.

McConnell (*2*) and Altschuler *et al.* (*3*) found that carbonate fluorapatite from Staffel, Germany, has a significantly smaller a_0 dimension and a slightly larger c_0 dimension than does fluorapatite from Durango, Mexico.

To establish the effect of the carbonate ion on the unit cell dimensions of apatite, control of the purity and stoichiometric composition of the material is essential. Carbonate apatite was prepared from reagent grade dibasic calcium phosphate ($CaHPO_4$) having a Ca : P ratio of 1.03 and low-alkali calcium carbonate. These two solids were well mixed. This mixture, with a calcium-to-phosphorus ratio of 1.67, was then sealed in a gold tube. No water was added to the mixture prior to sealing because the dibasic calcium phosphate contained sufficient water for the formation of apatite. Carbonate-free hydroxylapatite was prepared after heating the same reagents to a temperature in excess of 900°C. Dibasic calcium phosphate was heated to form β-calcium pyrophosphate. The pyrophosphate and low-alkali calcium carbonate were mixed to yield a calcium-to-phosphate ratio of 1.67, and the mixture was then heated to 900°C for 8 hours to eliminate the CO_2 from the system. The resulting mixture of lime and β-calcium pyrophosphate was packed in a closed-end gold tube and then reheated for 4 hours. It was reheated until the sample attained a constant weight. A slight amount of water was added to this sample and the tube was immediately closed by welding to prevent the absorption of CO_2.

The sealed gold capsules containing the carbonate hydroxylapatite mix and and the carbonate-free hydroxylapatite mix were then placed in a "cold-seal"

Table 2. Lattice dimensions of apatite (values in angstroms).

Reference	a_0	c_0
	Carbonate apatite	
*	9.43_6	6.88_3
	Hydroxylapatite	
*	9.42_6	6.88_5
	Fluorapatite†	
*	9.39_8	6.89_9
(*2*)	9.39_5	6.88_2
(*3*)	9.38_6	6.87_8
	Hydroxylapatite	
(*5*)	9.418 ± .003	6.883 ± .003
(*6*)	9.420 ± .001	6.885 ± .001
(*7*)	9.421 ± .003	6.881 ± .003
(*8*)	9.416 ± .002	6.883 ± .002
	Dahllite	
(*6*)	9.454 ± .004	6.892 ± .0025

* This work. † Durango, Mexico.