

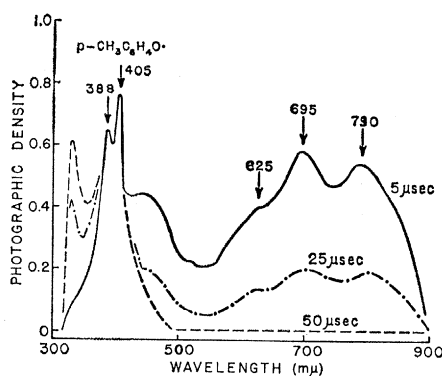


Fig. 2. Transient spectra from the flash photolysis of air-free, aqueous 0.05M *p*-cresol at pH 11.8. The bands at 388 and 405 mμ are due to the *p*-methylphenoxyl radical; the shorter-lived red absorption bands are due to the hydrated electron.

rivatives (4, 5). Again, the red bands of the hydrated electron were observed only for air-free solutions. A band at 330 mμ that grows as the band of the hydrated electron disappears probably represents a reaction product of the *p*-methylphenoxyl radical. Equivalent results were obtained with phenol, L-tyrosine, 3-(*p*-hydroxyphenyl)-propionic acid, glycyl-L-tyrosine, and DL-leucyl-DL-tyrosine, except for small variations in the appropriate phenoxyl radical spectra. Similarly, the hydrated electron was obtained from alkaline solutions of DL-phenylalanine and DL-tryptophan, where the observed radicals were benzyl and 3-indolyl, respectively (5, 6). For each of the above cases, irradiation at a pH of 4 to 5 gave the free radical spectrum but not the hydrated electron absorption.

## Genesis of Hydrocarbons of Low Molecular Weight in Organic-Rich Aquatic Systems

**Abstract.** *Mild heat treatment of water-wet marine muds resulted in the genesis of three aromatic hydrocarbons characteristic of crude oils, but which are seldom found in significant quantities in recent sediments. Whereas part of the toluene and xylenes may have stemmed from carotenoid pigments, the source of the benzene as well as the larger amount of the toluene and xylene is as yet unknown.*

Hydrocarbons of low molecular weight comprise an important part of most petroleum accumulations and, indeed, are widely distributed in unweathered, organic-rich ancient rocks. In the paraffin series, every chain length from C<sub>1</sub> to C<sub>7</sub> and higher is to be found. The naphthenes are represented by both cyclopentane and cyclohexane and their alkyl-substituted derivatives. For the

The nonspecificity of the results is an argument against a direct production of the hydrated electron by photoelectric detachment from the anion. Furthermore, this type of process is inconsistent with the view that the excited electron is bound in a discrete state by the coulombic field of the adjacent hydration shell, as propounded by Platzman and Franck (7) for halide ions. An alternative mechanism is the photooxidation of the water itself, sensitized by light absorbed in the anion. In this case, the radical products could result from a subsequent oxidation of the anion by a hydroxyl radical produced by dissociation of the photoionized water. However, whether the photoionization step is direct or sensitized, the process by which the photoelectron becomes hydrated requires further clarification (8).

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more than traces of ethane, propane, the butanes, pentanes, and hexanes. Apparently, the first paraffin above methane to occur in appreciable quantities is *n*-heptane (3). In the aromatic series, the first member to appear in any abundance in living organisms is *p*-cymene, C<sub>10</sub> (4). During the last 10 years recent aquatic sediments, representing various environments of deposition, have been investigated. The methods ordinarily used involved drying and/or extraction of the sediments, with the result that the hydrocarbons isolated comprised only relatively high-molecular-weight material of low volatility. Emery and Hoggan (5) made one of the few direct efforts to quantitatively determine hydrocarbons of low molecular weight in aquatic sediments. In all cases, the most abundant hydrocarbon was methane. In addition, traces of the C<sub>2</sub> through C<sub>6</sub> paraffins, cyclobutane, cyclopentane, benzene, toluene, and the xylenes were detected.

Using Emery and Hoggan's data, we calculated the concentrations of benzene and toluene in the 4- to 28-inch section of a core from the Santa Barbara Basin to be approximately  $1.04 \times 10^{-4}$  and  $4.2 \times 10^{-4}$  parts per million, respectively, based on dry weight of sediment. The amounts are exceedingly small, even though the sample is exceptionally rich in organic matter and was deposited under conditions considered to be highly favorable for the genesis of petroleum. Considering that benzene and toluene represent approximately 0.2 and 0.4 percent, respectively, of an average crude (2), and assuming that no more benzene and toluene are formed during geologic time and that none of that present is lost, this sediment, therefore, could have a crude oil productivity of only about 160 to 320 μg/kg.

In an earlier paper (6), one of us suggested that likely progenitors of at least some of the low-molecular-weight aromatic hydrocarbons are polyene compounds such as the carotenoids. The carotenoids are to be found in considerable quantity in most terrestrial and aquatic plants and animals. Further, these compounds have been shown by Fox *et al.* (7) to be contained in marine sediments which are as old as 8000 years. On the other hand, carotenoids have never been detected in ancient rocks.

A systematic study of sediments deposited in aquatic environments ranging from fresh-water swamps to the deep marine has been carried out in this

aromatics there is the comparable series of alkyl-substituted benzenes of which toluene and *m*-xylene (1, 2) often are the most abundant.

Whereas living organisms produce certain hydrocarbons, there are striking gaps in the above-mentioned series. Among the paraffins there is little evidence for the presence, either in body substance or metabolic products, for

Table 1. Identification of aromatic hydrocarbons of low molecular weight in thermally treated aquatic sediments (188°C for 72 hours in sealed glass ampoules). For Core 3 from the Santa Barbara Basin, the ratio, parts per million of carotenoids before heating to parts per million of toluene after heating, equals 23/12, equals 1.8. For the Gulf of Mexico material, this ratio equals 2.1/0.44, equals 4.7.

| Compound                           | Santa Barbara Basin |        | Gulf of Mexico, continental shelf |
|------------------------------------|---------------------|--------|-----------------------------------|
|                                    | Core 2              | Core 3 |                                   |
| Benzene                            | 4.5                 | 3.04   | 0.14                              |
| Toluene                            | 15.2                | 12.0   | 0.44                              |
| <i>m</i> - and/or <i>p</i> -Xylene | 3.5                 | 2.7    |                                   |
| <i>o</i> -Xylene                   | 3.6                 | 2.3    |                                   |

laboratory during the past decade. In all cases where the samples did not contain reworked ancient organic matter or man-made pollutants, the concentration of aromatic hydrocarbons of low molecular weight was found to be less than the limit of detection, namely, approximately 0.5 ppm based on the dry weight of the sediment (6). In brief, the method consisted of freeze-drying the sediment sample, extracting the volatile aromatic hydrocarbons from the sublimate with iso-octane, and determining the aromatics by ultraviolet spectroscopy. More recently, the method has been modified by carrying out the extraction with *cis*-decalin, and aromatic and other hydrocarbons in the extract are determined by gas-liquid chromatography.

The objective of the present study was to determine whether the genesis of hydrocarbons of low molecular weight could be accelerated by mild thermal treatment. In a preliminary experiment pure crystalline  $\beta$ -carotene was dispersed in an aquatic sediment containing 60-percent water, and was sealed in a glass ampoule and heated at 188°C for 72 hours. The ultraviolet spectrum of the extract from the sublimate showed that a considerable quantity of benzenoid hydrocarbons, presumably toluene and *m*-xylene, and a small amount of naphthalene, presumably 2,6-dimethylnaphthalene, had been generated. An attempt to demonstrate that these hydrocarbons also would be formed from carotenoid and related polyene substances naturally present in the sediment was prevented because of high background absorption.

The development of the gas-liquid chromatographic procedure made possible a continuation of these experiments, whereby detection limits of approximately 0.5 ppm could be achieved for heated as well as unheated sediment samples. For this study, two marine sediments were chosen, one from the Santa Barbara Basin off the coast of California, the other from the conti-

mental shelf of the Gulf of Mexico, approximately 19.3 km south of the city of Pascagoula, Mississippi, and about 2.4 km outside the barrier island. The samples obtained by coring had been frozen immediately upon collection and maintained frozen until ready for freeze-drying. As a control, aliquots of the Santa Barbara Basin, Core 2, and Gulf of Mexico samples were worked up without heat treatment. In neither case could any trace of benzene, toluene, or xylenes be detected, that is, their individual concentrations were less than the detection limit, which is 0.5 ppm. After heat treatment, aromatic hydrocarbons were found to be present in all three samples. In those from the Santa Barbara Basin the aromatic hydrocarbons detected and determined were benzene, toluene, *m*- and/or *p*-xylene, and *o*-xylene. In the less organic-rich sample from the continental shelf of the Gulf of Mexico, only benzene and toluene were detected, the concentrations of the xylene being probably below the detection limit.

Comparison of the concentrations of benzene and toluene generated in the Santa Barbara sediment by heat treatment, with the values for unheated sediment as calculated from the data of Emery and Hoggan, shows increases of 36,000 and 31,000, respectively. On the basis of these concentrations of benzene and toluene, the Santa Barbara sediment might be expected to yield up to 5 to 10 g of a typical crude oil per kilogram dry weight, assuming no loss of these constituents during the elapse of geologic time.

The genesis of benzene and *o*-xylene by heat treatment of the mud slurries cannot be easily explained by degradation of the conventional carotenoid pigments. Further, model experiments have shown that the yield of toluene from a typical carotenoid pigment, carotene, is approximately 0.3 percent. In the upper portion of Table 1, the yields of toluene on heat treatment are compared with the concentrations of

total carotenoids in the unheated sediment samples. The amount of carotenoids is insufficient in both cases to account for all of the toluene generated.

At the present time, the additional precursors of these hydrocarbons are not known. Likely precursors of benzene are polyunsaturated fatty acids. *o*-Xylene might arise from similar non-isoprenoid branched polyunsaturated chains. In the case of toluene and *m*-xylene, the precursors are probably isoprenoid polyenes where the conjugated chain is too short to develop the characteristic color on which the determination of total carotenoids is based. Such substances, of which vitamin A is an example, might be natural products, as such, or may represent intermediate stages in the degradation of the conventional carotenoid pigments.

In the course of the thermal treatment of the mud slurries, it was observed that a positive pressure existed in the ampoules after cooling to room temperature. In the runs reported in Table 1, the ampoules were equipped with breakoff tips so that the gas could be collected for analysis. Gases apparently generated, or at least released from the sediment, were, in order of abundance: carbon dioxide, methane, carbon monoxide, and, in variable small amounts, ethane, ethylene, propane, propylene, and *n*-butane. The presence of carbon monoxide, while at first surprising, is explained by the fact that carbon monoxide is generated by certain living organisms as a normal part of their life processes (8; 9).

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