maining vertexes of the tetrahedrons are linked in a sphalerite-like fashion to a second set of tetrahedrons. The second set of tetrahedrons, in turn, share vertexes with other octahedrons. Inspection of Fig. 1 shows that the structure differs from a sphalerite arrangement in that (i) three of the four sulfur atoms which would be given by an equipoint with coordinates $\frac{1}{8}\,\overline{\frac{1}{8}}\,\frac{1}{8}$ are absent, while the fourth has been displaced to 000, and (ii) Sb is substituted for those Cu atoms which lie closest to the octahedral arrangement.

While consideration of the metal polyhedrons facilitates visualization of the structure, the reasons for this curious arrangement become more apparent when the coordination of sulfur about the metal atoms is considered. The Cu(1) is coordinated by four S(1) at distances of 2.343 Å. The bond angles for this tetrahedron are all 110°47′, which represents only a slight distortion from a regular tetrahedron. The Cu(2) is coordinated by two S(1) at 2.292 Å and one S(2) at 2.210 Å. This group of four atoms lies in a symmetry plane and is therefore planar. This coordination has been found in other copper sulfides such as CuS (*5*), Cu_2S (*6*), and CuAgS (*7*). Triangular coordination for a B-subgroup metal is very unusual and, for inorganic compounds, appears to be unique to copper sulfides. Three S(1) atoms are coordinated to Sb at distances of 2.436 Å. The bond angles, S(1) to Sb to S(1), are 90°32′. This polyhedron represents a trigonal pyramid with Sb at its apex.

The metal polyhedrons are linked in a complex fashion. Six CuS_3 triangles share a corner at 000, and form a six-bladed "spinner." Since the triangles lie in the (110) symmetry planes of the cell, the corners of three different triangles are in close proximity. The base of a SbS_3 pyramid links these three corners. In addition to the vertex of the SbS_3 pyramid, each corner of a triangle is further shared by vertexes from two different CuS_4 tetrahedrons. Each corner of a tetrahedron links four different spinners in this fashion.

The coordination of S about Sb gives the key to the reason for the formation of the structure. The structures of several other sulfosalts containing Sb have been determined. The coordination of S about Sb in these structures is similar to that found in the present study, except that the bond distances are not equal. The Sb atom in these structures displays a minimum distance of 2.4 Å to only *one* closest neighboring S. The three short bond distances and the orthogonal disposition of these bonds in tetrahedrite suggests a very strong bond involving the p^3 electrons of Sb. The failure of a fourth S atom to coordinate with Sb accounts for the S atoms which are missing from a completed sphalerite-like arrangement. The nature of the Sb to S bond also explains why the tetrahedrite structure is not merely a derivative structure of sphalerite in which the different metal atoms substitute in an ordered fashion (for example, chalcopyrite, $CuFeS_2$). It is misleading to describe the structure of tetrahedrite in terms of Sb atom substitution for a tetrahedrally coordinated Cu. The SbS_3 group is really a different sort of coordination polyhedron (*8*).

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6 June 1963

Photochemical Generation of the Hydrated Electron

Abstract. *A transient species with properties similar to the hydrated electron produced previously by electron irradiation has been observed by flash photolysis of aqueous solutions of inorganic salts and aromatic compounds including amino acids.*

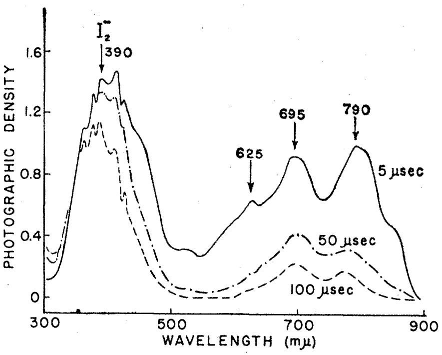

Fig. 1. Transient spectra from the flash photolysis of air-free 0.0005*M* potassium iodide at *p*H 7. The band at 390 mµ is due to the diiodide ion; the shorter-lived red absorption bands are due to the hydrated electron.

Hart and Boag (*1*) have identified with the hydrated electron an optical absorption produced by irradiating deaerated water and aqueous solutions with electron pulses of 1.8 Mev. A species with similar properties has been obtained by ultraviolet-light flash photolysis of compounds showing "electron-transfer" spectra. The irradiations were performed in a 26-cm long fused-silica cell on solutions evacuated to 1×10^{-5} mm-Hg. The light source was of 40 µsec duration from a 700 joule capacitor discharge. The spectra were taken with a 10-µsec xenon spectroflash lamp on a Hilger E 498 (medium) quartz-prism spectrograph and Kodak I-N plates.

Figure 1 shows transient spectra from aqueous 0.0005*M* KI. The band at 390 mµ is due to diiodide ion (I_2^-), which was investigated by Grossweiner and Matheson (*2*, *3*). The shorter-lived bands at 625, 700, and 790 mµ have a spectrum and lifetime that agree with the hydrated-electron absorption reported by Hart and Boag (*1*). These shorter-lived bands are not observed for air-saturated KI solutions, although the I_2^- absorption is enhanced in that case. On the assumption that each I_2^- present immediately after the flash corresponds to one hydrated electron, and by using the reported value of the I_2^- molar absorbance (*3*), the hydrated-electron molar absorbance is estimated to be 15,000 ± 30 percent at 695 mµ. Strong hydrated-electron spectra were observed by flash photolysis of air-free, aqueous solutions of 0.05*M* Na_3PO_4, 0.1*M* Na_2CO_3, and 0.07*M* $Ca(OH)_2$. Associated radical products were not detected in these cases. A very weak absorption was found for air-free, doubly-distilled water, presumably due to residual salts.

The same hydrated-electron spectrum was obtained from air-free, aqueous solutions of aromatic compounds buffered at *p*H 11.8 with Na_3PO_4. Figure 2 shows transient spectra from 0.05*M* *p*-cresol irradiated through a filter of 0.20*M* Na_3PO_4, so that light absorption by the buffer was negligible. The narrow bands at 388 and 405 mµ identify the phenoxyl radicals, as reported from the flash photolysis of phenol, phenolate ion, and their de-

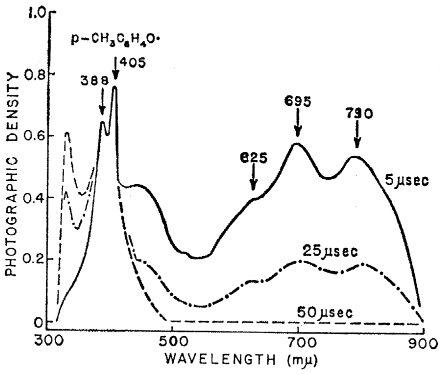

Fig. 2. Transient spectra from the flash photolysis of air-free, aqueous 0.05*M* *p*-cresol at *p*H 11.8. The bands at 388 and 405 mμ are due to the *p*-methylphenoxyl radical; the shorter-lived red absorption bands are due to the hydrated electron.

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 *p*H of 4 to 5 gave the free radical spectrum but not the hydrated electron absorption.

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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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_1 to C_7 and higher is to be found. The naphthenes are represented by both cyclopentane and cyclohexane and their alkyl-substituted derivatives. For the 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 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_{10} (*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_2 through C_6 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 1.04×10^{-4} and 4.2×10^{-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