

## A NEW STRUCTURAL MODEL OF OIL SHALE KEROGEN

T. F. Yen

Departments of Medicine (Biochemistry),  
 Chemical Engineering, and Environmental Engineering  
 University of Southern California  
 Los Angeles, California 90007

Kerogen is usually defined as the insoluble fraction of organic components of oil shale in contrast to the soluble fraction which is called bitumen (1). Structural elucidation of kerogen is difficult due to the following:

- (a) Kerogen is a large complex molecule belonging to the multipolymer class (2).
- (b) The insoluble nature of the kerogen is closely related to the non-uniform 3-dimensional gel nature of a giant crosslink network.
- (c) Inhomogeneity due to biogenesis.

All of these have challenged a number of researchers (3,4,5); so far the molecular structure of kerogen remains unsolved.

A method has been developed for the structural elucidation of amorphous and mesomorphic carbonaceous organic materials (6). It is possible to obtain a number of structural parameters from x-ray diffraction (7). The kerogen concentrate of Green River oil shale was obtained from W. E. Robinson of the Bureau of Mines. The bitumen-free sample was subjected to the usual acid leaching procedure to remove the carbonate and silicate minerals with ca. 10% of the ash content remaining; from the elemental analysis, %C is 66.4 and %H is 8.8.

The powdered sample of kerogen concentrate was packed in an aluminum holder and mounted in a goniometer. A Norelco diffractometer was used to measure the intensities ranging from  $2\theta = 8$  to  $100^\circ$ . The reduced intensity data were obtained by:

- (a) Adjusting the data for polarization by  $(1 + \cos^2 2\theta)/2$ .
- (b) Fitting the data to electronic units, A, by normalization of the amplitude to the region of  $0.40 \leq (\sin \theta)/\lambda \leq 0.50$ .
- (c) Substrating tabulated values of incoherent scattering, C.
- (d) Dividing each value by the proper value (for isolated carbon atoms) of the independent coherent scattering, E.

This reduced intensity, (A-C)/E of the Green River oil shale kerogen concentrate over the angular range of  $(\sin \theta)/\lambda$  of 0.02 to 0.50 is shown as the solid line in Fig. 1.

The first band in the low angle region does not appear as a doublet. The distance of the single peak centers at  $(\sin \theta)/\lambda = 0.11 \text{ \AA}^{-1}$  definitely corresponds to a  $\gamma$ -band ( $\sin \theta/\lambda = 0.10 \text{ \AA}^{-1}$ ). There is no peak or shoulder of the 002-band at  $(\sin \theta)/\lambda = 0.14 \text{ \AA}^{-1}$ . Based on this information alone, it is concluded that there is little or no aromatic carbon skeletons in the kerogen matrix. This is further substantiated by the fact that the controlled oxidation-derived products from oil shale contain no aromatic protons (8). The low angle peak in the x-ray graph of Fig. 1 is shifted slightly to the high-angle side (from 0.10 to  $0.11 \text{ \AA}^{-1}$ ). This fact may indicate that in the saturated structure there are some isolated double bonds.

The next two strong bands which center around  $(\sin \theta)/\lambda = 0.25$  and  $0.42 \text{ \AA}^{-1}$  are generally, classified as [10] and [11] reflections, respectively. These two bands correspond to the first and second nearest neighbors (2.1 and 1.2 Å) in cyclic compounds for both aromatics and naphthenics. Since these fall in the 2-dimensional reflective region, a number of theoretical calculations has been made (9,10). The simplest procedure will be the profile matching procedure. From calculated patterns of 10 and [11] regions, only the contour of [11] of the kerogen fits the saturated-ring (naphthenic) from Fig. 1. For example the dash-dotted line (Fig. 1) is perhydro-agbi-dibenzoperylene and the dash line (Fig. 1) is perhydro-anthracene. The maxima of both patterns check quite well with the maximum of the pattern of kerogen. If there is an aromatic-ring structure in kerogen, it is anticipated to have a 2 or 3 unit-shift in  $\sin \theta/\lambda$  to the high angle region. An example is provided by the dotted line (Fig. 1) which corresponds to a polycyclic aromatic compound, anthracene. It is evident that the pattern of aromatic compounds does not match that of the oil shale kerogen.

Another important feature for these 2-dimensional patterns is the bandwidth. As the ring number increases, usually the bandwidth decreases (6). The profile for both [10] and [11] bands of the kerogen do indeed correspond to a 3-ring naphthenic (dash line, Fig. 1) better than a 7-ring naphthenic (dash-dotted line, Fig. 1). In this instance matching should be emphasized on the band shape (x-axis), not on the vertical y-direction since the intensities are relative. From this alone it is plausible to conclude that the saturated clusters within oil shale kerogen are small, in the 3-4-ring range.

In the  $\gamma$ - and 002-band region we have so far failed to locate the sharp doublet of [110] and 200 bands, as these are prerequisites for wax-like long chain alkane-containing compounds (11). Usually these two peaks, 4.15 and 3.74 Å, occur close to the  $\gamma$ -band in polymethylene chain-like-containing materials. These crystalline reflections are in all pure long chain paraffins. The absence of these two bands suggests there is no free end or flexible long-chain polymethylene in the kerogen of Green River oil shale. This is supported by the fact that we have not observed any  $725 \text{ cm}^{-1}$  band which is so characteristic of the  $-(\text{CH}_2)_n-$ , ( $n > 4$ ) structure in our infrared work, even at a lower temperature. However one cannot rule out the possibility of condensed or isolated cycloparaffin in which the flexibility has been inhibited.

Finally the multiple weak peaks between the  $(\sin \theta/\lambda = 0.28-0.35 \text{ \AA}^{-1})$  range in Fig. 1 of the kerogen could suggest the presence of diamond-like crosslink structures. One such example is the [102] band of hexagonal diamond crystallite. Of course, there are also possibilities of other contaminations.

To summarize, the present x-ray diffraction method strongly supports the following for Green River oil shale kerogen:

(a) There is little or nil aromatic carbon skeleton in kerogen. Aromaticity for this kerogen approaches zero. There is a possibility of the presence of isolated double bonded carbon structure (12).

(b) The bulk of the carbon structure is naphthenic containing 3-4 rings. It is possible that these are clusters and are linked by heterocyclic atoms and short-chain bridges.

(c) There is no free-end and flexible long-chain linear polymethylene structures in this kerogen. This does not rule out the possibility of the presence of the crosslink structure of elaterite (2) which could be condensed polycycloparaffin. Such a structure could be foreseen as poly-

mantane-like (1), since alkyl adamantanes are easily converted by Lewis acid from a great number of precursors including steroids and terpenoids.

(d) The C/O atomic ratio of kerogen is 18. The distribution of oxygen functional groups in this kerogen is predominantly of ether type (53%) and ester type (25%)(13). The crosslink sites of the structure of (b) is anticipated to be largely oxygen.

(e) The age of the Eocene formation of Green River oil shale kerogen is considered to be youthful (18). The diagenesis is expected to be still in progress. Actually the difference of bitumen versus kerogen is of degree, not of kind. The analogy is similar to the difference between asphaltenes and the insoluble carbonenes and carboids in source rocks. In this sense the structure of kerogen can be reflected from the structure of bitumens.

(f) The structure of kerogen is a multi-polymer consisting of monomers which are the molecules so far identified from bitumen. These molecules in bitumen are steranes, triterpanes and isoprenoids, such as squalene, lycopene, cyclic carotenoids of  $C_{40}$  (15), etc. The monomers also can be inferred as the mild oxidation products when the kerogen is subjected to oxidation by aqueous permanganate (8). In this instance the products are mono- and di-carboxylic acid homologs.

(g) There is as anticipated, not only the primary bonding but secondary and tertiary bonding as well. The inter- and intramolecular hydrogen bondings as well as the charge-transfer bonding plays an important role. Molecular entrapment of which the molecular force is in the van der Waals range, become important. This is especially true since the nature of kerogen is comparable to a molecular sieve and can retain small molecules present in bitumens.

In conclusion, a hypothetical structural model is proposed to summarize the above statement (Fig. 2).

#### ACKNOWLEDGEMENT

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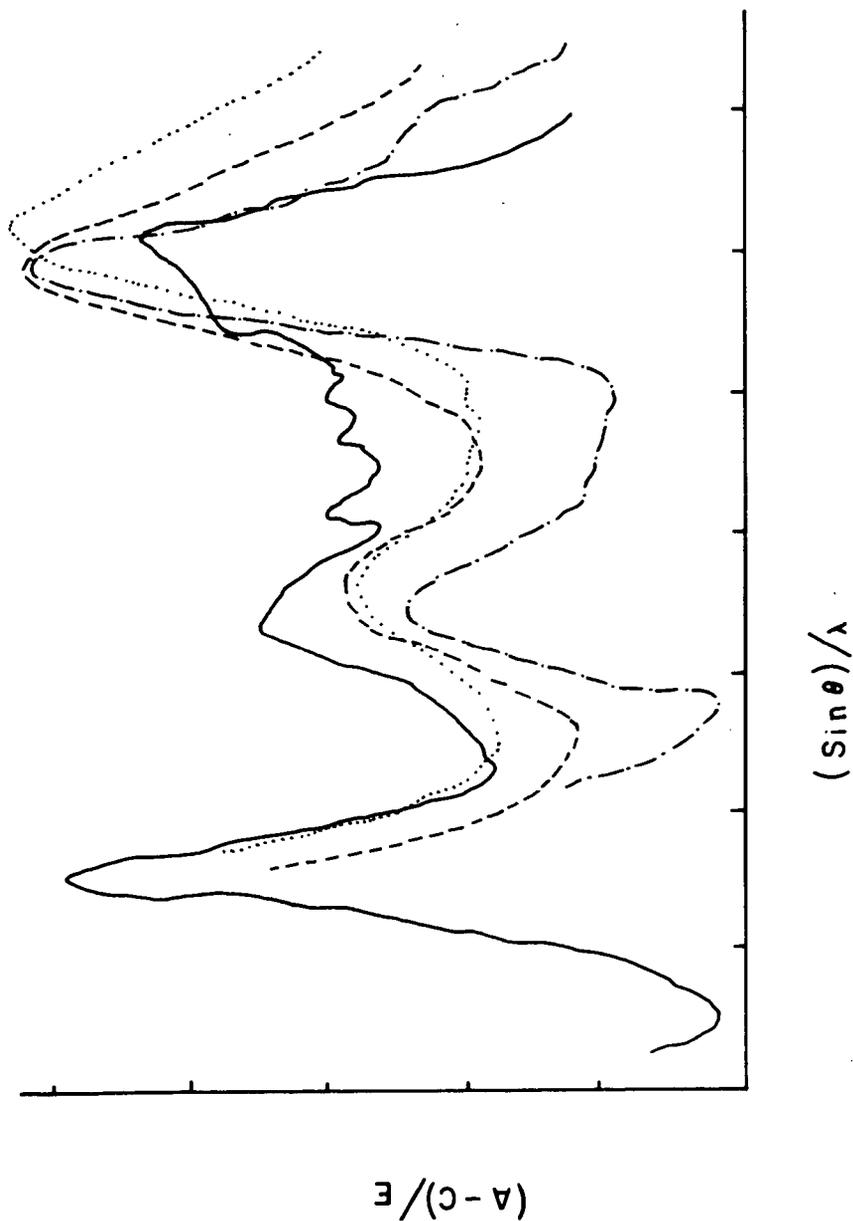


Fig. 1. X-ray Spectrum of Green River Oil Shale Kerogen and Calculated Intensities of some Hydrocarbons. Solid line is kerogen; dotted line is the calculated intensities of anthracene; dash line is those of perhydroanthracene; the dash-dotted line represents those of perhydro-dibenzo(a,g,b,i)perylene.

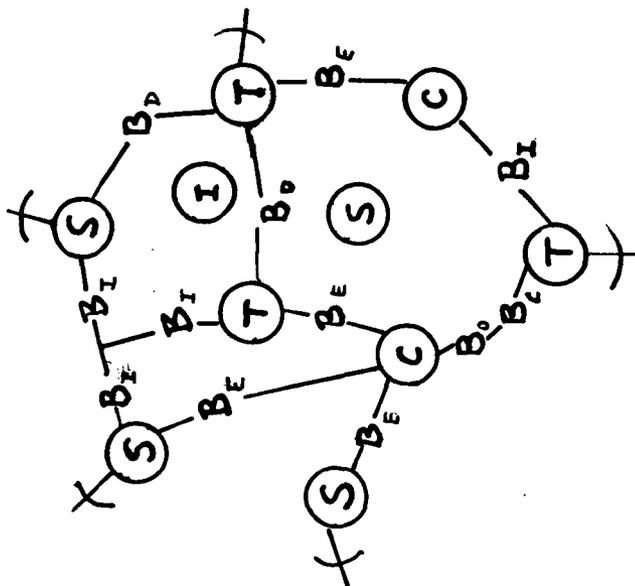
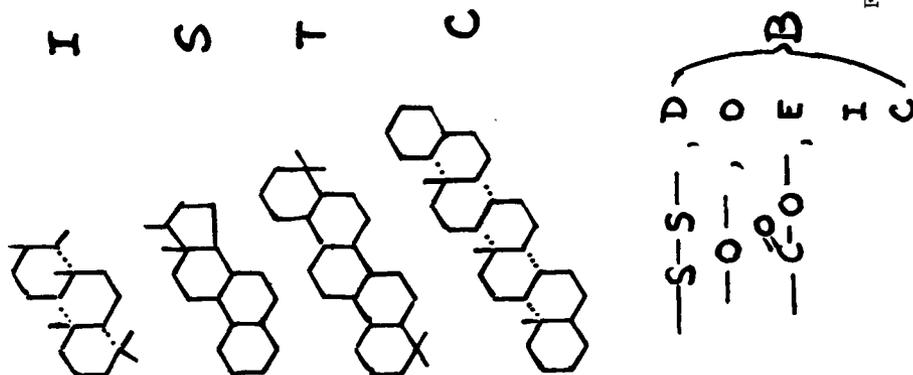


Fig. 2. Hypothetical Structural Model of Green River Oil Shale Kerogen. The left are the monomers of the multipolymer. I, represents isoprenoids; T, terpenoids; C, carotenoids; and B, bridges (molecules have been isolated from Green River oil shale, see Ref. 13-17). Bridges can be disulfide (D), ether (E), ester (E), isoprenoid (I), and carotenoid (C) linkages. The entrapped molecules in the matrix of the network is not bonded.