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The analysis of the kerogen of Green River oil shale by controlled potential oxidation with perchloric acid

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The analysis of the kerogen of Green River oil shale by controlled potential oxidation with perchloric acid

by

Chris Wyatte McGowan

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

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For the Graduate College

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1979

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I. INTRODUCTION

A. History of the Oil Shale Industry in the United States

The first discovery of oil shale in the western United States was made in 1874. During the construction of the Union Pacific Railroad through the Green River region of Colorado, a portion of the rail passed through a cutting made in twenty to forty feet of rock. In the preparation of a cook fire, workmen used some of the excavated rock for protection. It was soon observed that the rock ignited (4). The above events were recorded in the March 14, 1874, issue of Scientific American. The same article also stated that oil could be produced for a few cents a gallon and that the Pacific coast and all places west of the Mississippi would soon be supplied with the oil obtained from the Green River oil shales. Over a hundred years later, a significant portion of the energy needs of the United States has not yet been derived from oil shale.

As long as crude petroleum oil could be obtained easily, there was little interest in developing an oil shale industry. However, when the supply of crude oil has been in jeopardy, interest in the production of oil from oil shale has risen. During the early 1920's production of domestic crude oil began to fall behind demand and the U.S. Geological Survey estimated that domestic reserves would last only nine years. During this time over 30,000 mining claims were made in the Green River region and some 200 companies were formed to produce oil from oil shale.

The discovery of the large East Texas oil fields in the late 1920's quickly quenched this development. Again, interest in oil shale was revived during World War II. Reserves of domestic crude oil were becoming low and a reliable source of fuel was absolutely necessary during time of war. Congress passed the Synthetic Fuel Act in 1944, which directed the Bureau of Mines to establish a reliable source of fuel from oil shale deposits. The Bureau then established a research program. After World War II, interest again declined as oil from the Middle East became available and oil deposits were discovered on the north slope of Alaska. The oil embargo of 1973 initiated a renewed interest in the oil shale industry. Several commercial companies have now established pilot plants in the Green River region (5, 12, 51, 59).

B. Geology of Oil Shale

The term "oil shale" is used to describe a rock which yields an oily material upon heating at 400° to 500°. Oil shale actually does not contain an oil; very little of the organic material within the shale can be extracted by organic solvents. The term oil shale is a common designation and does not describe the lithology of the rock (32).

Oil shales were deposited from shallow seas or large lakes. Shales deposited from shallow seas are usually thin, on the order of tens of feet thick, but cover hundreds or thousands of square miles. The Devonian age Chattanooga shales of the eastern and central United States were deposited from shallow seas. Shales deposited from lakes represent some of the largest and most extensive deposits (18).

The largest oil shale deposits in the world occur in the Green River formation of Colorado, Utah and Wyoming (32). The Green River oil shales were deposited from large lakes during the Eocene period. The Green River oil shales are up to 2,000 feet thick and cover an area of 23,000 square miles (63). Potential reserves have been estimated as high as 750 billion barrels of oil (51).

Green River oil shale is a massive, non-fissile, dolomitic marlstone. Green River shale is highly varved. Correlation of the varves indicates a lateral persistence of identical depositional conditions which explains the uniformity in the composition of the minerals. Minerals in the Green River shale are authigenic (the minerals were formed and precipitated at the present site) and strikingly similar from place to place (55). Over 50 minerals have been identified in Green River oil shale, some of which are unique to the Green River formation (33). Carbonate minerals, primarily dolomite and calcite, make up 50 per cent of the mineral portion. Quartz, feldspars and clays make up most of the remaining mineral portion with pyrite constituting about one per cent (33, 51).

C. Organic Composition of Oil Shale

The organic carbon in the Green River oil shale constitutes on the average 8.3 per cent of the shale (39). The organic matter is rich in hydrogen having a carbon-hydrogen ratio of 7.8 (54). Smith (54) determined the composition of the organic material as 80.5 per cent carbon, 10.3 per cent hydrogen, 5.8 per cent oxygen, 2.4 per cent nitrogen and 1.0 per cent sulfur. The organic material exists in two forms, bitumen and kerogen. The bitumen is a mixture of low molecular weight materials which are soluble in common organic solvents. Kerogen is a high molecular weight polymer which is insoluble in common organic solvents. Kerogen constitutes about 90 per cent of the organic material (5).

D. Characterization of the Bitumen

The soluble bitumen material has been well-characterized. For characterization, the soluble bitumen was separated into neutral, acidic and basic fractions. The neutral fraction was further separated into polar and non-polar fractions. Analysis was then made by gas chromatography and mass spectrometry.

The largest component of the bitumen was the saturated hydrocarbon fraction (non-polar) (40). A series of n-alkanes (C_{12}-C_{33}) and isoprenoid alkanes (C_{15}-C_{20}) were identified (14, 20, 22, 40). Robinson et al. (40) reported the presence of cycloalkanes as a major constituent of bitumen. Burlingame et al. (7) reported the presence of three steranes (C_{27}-C_{29}) and one triterpane (C_{30}) and Hill et al. (29) identified the pentacyclic triterpane, gammacerane (C_{30}). Henderson et al. (28) identified four steranes (C_{27}-C_{29}), two tetracyclic triterpanes (C_{28}, C_{29}), two tricyclic triterpanes (C_{30}), and seven pentacyclic triterpanes (C_{29}-C_{31}). Anders et al. (2) identified the presence of three Steranes (C_{27}-C_{29}). Gallegos (22) identified 35 branched and cyclic hydrocarbons including a series of branched alkanes (C_{21}, C_{22}, C_{25}, C_{27}, C_{29}), five pentacyclic triterpanes (C_{29}-C_{30}), two tetracyclic diterpanes (C_{23}), eleven tricyclic triterpanes (C_{20}, C_{21}, C_{23}-C_{26}), seven tetracyclic steranes (C_{21}, C_{27}-C_{29}) and two perhydro-β-carotenes (C_{40}). Wardroper et al. (57) identified ten steranes (C_{27}-C_{29}) and eleven triterpanes (C_{27}, C_{29}-C_{31}).

The acidic fraction of the bitumen constituted the second largest component. A series of n-carboxylic acids (C_7-C_{35}), isoprenoid carboxylic acids (C_9-C_{12}, C_{14}-C_{17}, C_{19}-C_{21}) and n-dicarboxylic acids (C_8-C_{18}) were identified and represent the major portion of the acidic fraction (3, 17, 19, 24, 35). Methyl keto acids (C_{11}-C_{14}), aromatic acids (C_7-C_{17}) and cyclic acids (C_5-C_{16}) were also identified (9, 25, 26, 27). Burlingame et al. (8, 9) isolated acid salts similar to the free acids isolated. A series of n-carboxylic salts (C_5-C_{32}), branched carboxylic salts (C_8-C_{22}), n-dicarboxylic salts (C_3-C_{18}), methyl keto carboxylic salts (C_4-C_{16}), cyclic carboxylic salts (C_5-C_{18}), aromatic carboxylic salts (C_7-C_{15}) and pentacyclic carboxylic salts (C_{28}-C_{34}) was identified.

Basic compounds represented a very small fraction of the soluble material. Basic compounds for which evidence exists consisted primarily of quinolines and isoquinolines (C_9-C_{20}), tetrahydroquinolines and tetrahydroisoquinolines (C_8-C_{18}), pyridines (C_7-C_{17}) and indoles (C_8-C_{20}) (49, 50). Anders et al. (1) identified three tetrahydroquinolines, one quinoline (C_{11}), four alkoxyquinolines (C_6, C_8, C_9) and one imide (C_7).

A number of polar and aromatic compounds was identified and again represent only a small portion of the soluble material. Cox et al. (13) identified a series of primary isoprenoid alcohols (C_{14}-C_{16}, C_{19}, C_{20}) and secondary (two-carbon) isoprenoid alcohols (C_{13}, C_{18}, C_{20}). Anders et al. (1) identified an isopropylcyclohexanol and two isoprenoid methyl ketones (C_{13}, C_{18}). These two ketones represent the highest oxidation state for isoprenoid chains 13 and 18 carbons in length and fill the gap for the missing C_{13} and C_{18} isoprenoid carboxylic acids. Gallegos (23) tentatively identified 24 monoaromatic hydrocarbons most of which have structures similar to saturated steranes and triterpanes. Anders et al. (1) identified α-tetralone (C_{10}), five indanones (C_{13}, C_{14}), tetralin (C_{10}), two napthalenes (C_{12}, C_{13}) and dimethylbenzylbenzene (C_{15}).

E. Characterization of the Kerogen

Unlike the soluble bitumen, the structure of the kerogen of Green River oil shale has not been well characterized. Because of the insolubility of the kerogen, direct analysis has produced very little information. Breaking down the kerogen to soluble components has been necessary. Subsequent analysis of the lower molecular weight components of the kerogen has yielded information which can be used to propose model structures. As will be shown later, the proposed structures differ depending on the process used to break down the kerogen.

1. Direct analysis

Brower and Graham (6) ran several reactions on a kerogen concentrate. The kerogen concentrate was prepared by reacting the raw oil shale with one to one hydrochloric acid to remove carbonate minerals. Chlorine gas was swept over a portion of the kerogen concentrate for three hours. Elemental analysis showed an increase in the percentage of chlorine from 1.54 per cent to 18.96 per cent. The addition of hypochlorous acid to the kerogen concentrate showed an increase to 10.8 per cent chlorine.

The kerogen concentrate also underwent hydrobromination and nitration giving an increase in the percentage of bromine and nitrogen respectively. The kerogen concentrate was sulfonated with chlorosulfonic acid. The resulting material had an ion exchange capacity of 1.68 meq./g. The magnesium salt of the sulfonated kerogen was a low capacity desiccant. The sulfonated kerogen contained one sulfonic acid group for each 12.5 carbon atoms. The addition of hydrogen bromide to the kerogen concentrate resulted in a product containing 23.9 per cent hydrogen bromide. This corresponded to one double bond for approximately 16 carbon atoms. The kerogen concentrate failed to undergo a Friedel-Crafts reaction with acetic anhydride and stannic chloride. The kerogen concentrate failed to undergo a Diels-Alder reaction with maleic anhydride. Conclusions drawn were that the kerogen was non-benzenoid, and typical of unsaturated substances containing isolated double bonds.

Fester and Robinson (21) investigated the oxygen functional groups contained in Green River kerogen. A kerogen concentrate was prepared by extracting raw oil shale with benzene, to remove some soluble organics, then reaction with hydrochloric acid to remove carbonate minerals and finally attrition grinding in the presence of water and cetane to remove the remaining minerals. Minerals consisting of quartz, feldspars and pyrite constituted 14 per cent of the resulting kerogen concentrate. Total oxygen in the organic portion of the concentrate was determined by difference using data from combustion analysis for carbon and hydrogen, Kjeldahl analysis for nitrogen, and Eshka analysis for sulfur. The amount of carboxyl groups was determined by a modified Fuchs calcium exchange method. Ester groups were determined by alkaline hydrolysis followed by precipitation of liberated acids as calcium salts. Amide groups were determined by strong alkaline hydrolysis followed by determination of released ammonia and soluble amines; nitrogen was also determined on the kerogen residue remaining after hydrolysis. Carbonyl groups were determined by reaction with hydroxylamine and determination of the increase in nitrogen. Hydroxyl groups were determined by acetylation. Ether groups were determined by difference. The results of elemental analysis showed that kerogen contained one oxygen atom for every 12 carbon atoms. The distribution of oxygen functional groups was found to be 53.5 per cent unreactive or ether oxygen, 24.7 per cent ester oxygen, 15.3 per cent carboxyl oxygen, 4.7 per cent hydroxyl oxygen, 1.2 per cent carbonyl oxygen and 0.6 per cent amide oxygen.

Yen (62, 63) studied the X-ray diffraction pattern of a kerogen concentrate prepared from Green River oil shale. Preparation of the sample was not given except that the bitumen free oil shale was subjected to the usual acid leaching procedure to remove the carbonate and silicate minerals. The kerogen concentrate contained 10 per cent ash. The X-ray diffraction pattern of the powdered kerogen concentrate was compared to the diffraction pattern of pernydrodibenzoperylene, dibenzo-(a, g, h, i)-perylene, anthracene, perhydroanthracene and long-chain paraffins. The X-ray pattern for the kerogen concentrate most closely resembled that of perhydroanthracene. As a result of this work, several generalizations were made concerning the kerogen. There was little aromatic content in the kerogen. Aromaticity approached zero. The presence of isolated double bonds was not precluded. The bulk of the kerogen was napthenic containing three to four rings. No free-end and flexible polymethylene chains longer than C_4 existed in the kerogen. The presence of paraffin molecules which have been inhibited by twisting and entanglement was not precluded. Several other points were noted in this paper. The Green River oil shale of Eocene age was geochemically youthful; diagenesis was still occurring. The difference between bitumen and kerogen was of degree not kind. The structure of kerogen was a multipolymer consisting of monomers similar to molecules composing the bitumen. The author expected that secondary and tertiary bonding as well as primary bonding existed in the kerogen. The author noted that like molecular seives, kerogen had the ability to retain smaller molecules.

2. Indirect analysis

Brower and Graham (6) oxidized raw oil shale with air. The ground shale, 30 to 50 mesh, was oxidized in a heated static bed. Air was introduced at the bottom of the bed. At temperatures above 200°, oxidation could be controlled only by limiting the supply of air. A hot zone moved upward through the bed as combustion proceeded. At a temperature of 375° the organic matter was completely oxidized to carbon dioxide and volatile acids. At 200° and atmospheric pressure, oxidation was general throughout the bed. There was no hot zone and the exit gases contained 18 to 19 per cent oxygen. The principal products at 200° were water, oxides of carbon and water-insoluble regenerated humic acids. As oxidation proceeded, the production of carbon dioxide and acids increased and the weight of the oil shale decreased slightly. The water insoluble acids were hard, amorphous substances soluble in dimethylformamide. The acids were insoluble in water and acetone but dissolved readily in a one to one mixture of acetone and water. The sodium salts were water soluble and were extracted from the shale residue with hot aqueous alkali. The equivalent weight of the acids ranged between 123 and 153. The potentiometric titration of the sodium salts with acid produced a titration curve similar to the titration of salts of polyfunctional weak acids.

Robinson and coworkers used air, oxygen, ozone, nitric acid (44) and alkaline potassium permanganate (41, 42, 43, 44) to oxidize Green River oil shale. Raw oil shale and three kerogen concentrates were oxidized. Kerogen concentrates were prepared by flotation, HF-HCl treatment, and attrition grinding. The flotation concentrate was prepared by centrifuging the finely ground carbonate free shale with mixtures of carbon tetrachloride and benzene having densities of 1.2 to 1.4 g./ml. to separate the more dense silicate minerals from the less dense organic material. The HF-HCl concentrate was prepared by treating the oil shale with concentrated hydrochloric and hydrofluoric acids to remove both carbonates and silicates. The attrited concentrate was prepared by grinding a thick paste of the carbonate free shale and cetane with water to remove most of the silicate minerals.

The raw oil shale, HF-HCl concentrate and attrited concentrate were air oxidized in open pans. The oxidation was carried out at 170° for 14 weeks. Weight loss occurred at a faster rate in the first part of the oxidation and then stabilized in the latter parts. The rate of oxidation was faster in the kerogen concentrates. The atomic hydrogen to carbon ratio decreased from 1.59 to 0.63 as the oxidation proceeded;

the oxygen to carbon ratio increased from 0.10 to 0.46. The total number of acidic groups increased as the time of oxidation increased.

Raw oil shale was oxidized with oxygen at elevated temperatures and pressures. A 200-g. sample of raw oil shale, 105 g. of potassium hydroxide and 400 ml. of water were placed in a bomb. The bomb was charged with oxygen to 900 p.s.i.g. and heated to 250° from 2 to 24 hrs. After 24 hrs. of heating the pressure was 2400 p.s.i.g.; after cooling the residual pressure was 900 p.s.i.g. The alkaline solution and shale residue were washed and filtered. The filtrate was acidified and the solvent evaporated. The resulting solid was extracted with methyl ethyl ketone to separate organic oxidation products from inorganic salts. The acids obtained were similar to those obtained from the oxidation of oil shale with alkaline potassium permanganate described later in this review.

A sample of raw oil shale was oxidized by ozone at room temperature. Samples containing 1 g. of organic carbon were suspended in 0.4 N sodium hydroxide. An ozone-oxygen mixture containing 2 per cent ozone was bubbled through the solution for 100 hrs. The major products were carbon dioxide and nonvolatile nonoxalic acids.

The flotation concentrate was oxidized with 60 per cent nitric acid at 60° to 70° for 40 hrs. The crude oxidation products separated into yellow brown solid acids (73 per cent of the product); oily liquid products, which floated; and products soluble in nitric acid. The solid acids were soluble in acetone and 5 per cent sodium hydroxide. The atomic hydrogen to carbon ratio was 1.49; reduced from 1.58. The oxygen to carbon ratio was 0.35. The nitric acid solution was steam distilled.

The volatile acids were further separated on silicic acid columns. Some acids were extracted with ether and separated by fractional crystalization of the free acids and amide derivatives. Butanoic acid, 2-hydroxy-2-methylpropanoic acid, 3-methylbutanoic acid, 3, 3-dimethylacrylic acid, cyclohexane carboxylic acid, p-dodecahydrophenic acid, 2-ethylhexanoic acid and umbelliferone were identified. Fractional distillation of the oily liquid produced some saturated terpenes and cycloparaffins. Paramethane and α-alkyl decalin were identified.

Raw oil shale and the three kerogen concentrates were exhaustively oxidized with alkaline potassium permanganate. Samples containing 1 g. of organic carbon were oxidized with excess hot alkaline permanganate for 100 hrs. The rate of reaction was determined using the amount of permanganate reduced in a given interval of time. Carbon was determined in gases evolved, steam volatile acids, oxalic acid, non-volatile non-oxalic acids and the residue. After 100 hrs. 92 to 100 per cent of the carbon was converted to carbon dioxide and oxalic acid. From 1 to 6 per cent was converted to non-volatile non-oxalic acids. From zero to 5 per cent remained in the residue. Exhaustive oxidation with alkaline permanganate converted the kerogen to carbon dioxide and oxalic acid.

In order to obtain intermediate oxidation products, the flotation concentrate was oxidized with alkaline permanganate in steps. A sample containing 100 g. of organic carbon was allowed to react with 100 g. of potassium permanganate. After all the permanganate was reduced, the kerogen was filtered. The kerogen was then oxidized with another 100 g. of potassium permanganate. Eight steps were required. Oxidation occurred rapidly in the first four steps requiring only 30 min. of total reaction time. Eleven hours were required to oxidize the remaining portion. After the final step, the filtrates were acidified and the precipitated acids were filtered. The precipitated acids were extracted with ether and ethanol. The acid filtrate was evaporated and a black liquid separated. The liquid was extracted with ether and ethanol. The ether-alcohol soluble fraction of the precipitated acids was a light brown waxy semisolid and represented 3.8 per cent of the carbon. The ether-alcohol insoluble fraction of the precipitated acids was a light brown resinous solid and represented 36.6 per cent of the carbon. The ether soluble fraction from the acid filtrate was a light brown viscous liquid and represented 6.6 per cent of the carbon. The alcohol soluble fraction of the acid filtrate was a dark brown to black viscous liquid and represented 30.4 per cent of the carbon.

Raw oil shale was oxidized in two steps by alkaline permanganate. Raw oil shale was reacted with six parts hot alkaline permanganate. After reaction the solid was filtered. The solid was then reacted with two parts of hot alkaline permanganate and filtered. The combined filtrates were acidified, filtered and dried, removing volatile acids. The non-volatile acids represented 57.8 per cent of the original carbon. The non-volatile acids were converted to n-butyl esters and fractionated by distillation. The solid residue and 20 distillation fractions were analyzed. Dicarboxylic acid esters (C_2-C_8) were identified in the first 10 fractions by mass spectrometry, X-ray diffraction and infrared spectrometry. Dicarboxylic acids (C_2-C_7) were also identified by partition of the non-volatile acids on silicic acid columns. Individual acids were not identified in fractions 10 to 20. Dicarboxylic acids of the alkane series were not detected. These fractions were composed of diacids of different series. The molecular weight increased from 305 to 480. The oxygen to carbon ratio remained constant while the hydrogen to carbon ratio decreased, indicating that the higher molecular weight fractions contained increasingly more cyclic materials. Because a large portion of the nonvolatile acids were not identified by the above procedures, an attempt was made to convert the acids to hydrocarbons. The n-butyl esters were reduced to alcohols with lithium aluminum hydride in ether solution. The alcohols were converted to iodides with potassium iodide and phosphorus pentoxide in 85 per cent phosphoric acid. The iodides were converted to hydrocarbons by zinc and hydrogen chloride gas. The yield of hydrocarbons was 15 per cent of the original oxidation product. Acids converted to low molecular weight alkanes were lost due to volatility. The resulting material was separated into several fractions by distillation, solvent extraction and partition chromatography. The hydrocarbon fractions were analyzed by mass spectrometry, X-ray diffraction and infrared spectrometry. The major hydrocarbons produced were cyclic and heterocyclic alkanes. The cyclic alkanes contained one to six rings. Isoalkanes, n-alkanes (C_{16}-C_{36}) and aromatic compounds were also produced. The aromatic compounds consisted primarily of indanes and tetralins. The oxidation product from the two step oxidation of raw oil shale with alkaline permanganate consisted of diacids composed of the following types; 59 percent n-alkane (C_2-C_8), 2 per cent n-alkane (C_{16}-C_{36}) and iso-alkane, 0.14 per cent cycloalkane, 6 per cent aromatic compounds and 19 per cent heterocyclic compounds.

Stefanovic et al. (56) attempted to oxidize Green River oil shale with permanganate in acetone solution. The authors claim that permanganate in acetone solution is a specific reagent for the oxidation of double bonds. Green River oil shale was resistant to oxidation indicating a low number of double bonds.

Hoering and Abelson (30) oxidized a kerogen concentrate with chromic acid. The kerogen concentrate was prepared by extracting crushed Green River oil shale with a mixture of benzene and methanol followed by reaction with hydrochloric and hydrofluoric acids to remove carbonate and silicate minerals. The kerogen concentrate was oxidized with chromic acid in 3 M sulfuric acid for six hrs. The reaction mixture was covered with heptane which extracted the fatty acids produced during the oxidation. The authors noted from experiments with C^{14} tagged palmitic acid that not all of the acid could be extracted from the kerogen residue. The reaction mixture was analyzed for n-carboxylic acids only. The heptane was evaporated from the acids. The acids were converted to methyl esters with boron trifluoride in methanol. The esters were exposed to a urea-decane clathrate. Straight chain esters were allowed to enter the clathrate excluding branched and cyclic compounds. The solid clathrate was filtered and then destroyed with water. The esters liberated from the urea adduct were further purified on a silica-gel column. The esters were eluted with benzene. The purified esters were then analyzed by gas chromatography using a 100 foot capillary column. The acids isolated represented only 0.05 per cent of the original organic carbon. Compounds identified were n-carboxylic acids (C_{14}-C_{30}). There was a predominance of acids with an even number of carbon atoms over acids with an odd number of carbon atoms.

Burlingame and coworkers (8, 10, 11, 38) oxidized a kerogen concentrate with chromic acid. The kerogen concentrate was prepared by extracting pulverized Green River oil shale with a four to one mixture of benzene and methanol, followed by reaction with a one to one mixture of concentrated hydrochloric and hydrofluoric acids and exhaustive extraction with the mixture of benzene and methanol. A sample of 25 g. of the kerogen concentrate was oxidized with 3 M chromic acid in sulfuric acid for 3 hrs. The kerogen residue was filtered. The residue and filtrate were extracted with heptane followed by ether. The respective extracts were combined and the acids separated from neutral compounds. The residue was oxidized for an additional 6 hrs. and extractions repeated. The residue was oxidized an additional 15 hrs. then an additional 24 hrs. with the extractions repeated after each step. No organic material remained in the final residue. Only 3.6 per cent of the kerogen concentrate was recovered as oxidation products. The total amount of acids recovered increased with each step. The acids were converted to methyl esters with boron tribluoride in methanol. The esters were subjected to urea clathration to separate straight chain esters from branched and cyclic esters. Each fraction was analyzed using gas chromatography with low resolution mass spectrometry. Each fraction was also analyzed by high resolution mass spectrometry. The range of products isolated was the same for each step. The ether fractions contained lighter weight and more polar acids than the heptane fractions. The major products identified were isoprenoid carboxylic acids (C_5-C_7, C_9-C_{12}, C_{14}-C_{17}, C_{19}-C_{22}, C_{24}, C_{25}) and n-carboxylic acids (C_5-C_{36}). Dicarboxylic acids (C_4-C_{25}) and methyl keto carboxylic acids (C_4-C_{20}) were identified as minor constituents. The following acids represented traces and were detected by high resolution mass spectrometry only; cyclic acids (C_5-C_{28}), aromatic acids (C_{10}-C_{19}), tetracyclic acids (C_{18}-C_{32}) and pentacyclic acids (C_{26}-C_{34}).

Simoneit and Burlingame (48) analyzed the neutral fraction from the above reaction. The neutral fraction represented only 0.08 per cent of the kerogen concentrate. Ketones composed 90 per cent of the neutral fraction. The neutral fraction was analyzed by gas chromatography coupled with low resolution mass spectrometry, high resolution mass spectrometry, ^{13}C-nuclear magnetic resonance, and infrared spectrometry. Three isoprenoid ketones (C_{13}, C_{18}, C_{23}) were the major constituents and there was evidence for three triterpanones (C_{30}). The three isoprenoid ketones represent the highest oxidation of isoprenoid chains 13, 18 and 23 carbons in length. These ketones fill the gaps left by the missing C_{13}, C_{18} and C_{23} isoprenoid acids.

Djuricic and coworkers (15, 16) oxidized a kerogen concentrate with alkaline potassium permanganate. The kerogen concentrate was prepared by extraction of crushed Green River oil shale with a four to one mixture of benzene and methanol, followed by reaction with a one to one mixture of concentrated hydrochloric and hydrofluoric acid to remove carbonate and silicate minerals. The sample was then exhaustively extracted with the benzene-methanol mixture. Five grams of the kerogen concentrate was oxidized in 16 steps with 1.25 g. of potassium permanganate per step at a maximum temperature of 80°. After each step the solid material was filtered. The final residue contained no organic matter. The filtrates from the first 15 steps were combined and extracted with methylene chloride. The filtrates were acidified. The precipitated acids were filtered. The acid filtrate was then extracted with methylene chloride and ether. Almost 70 per cent of the organic matter was recovered as oxidation products. The precipitated acids constituted the largest fraction containing 46.2 per cent of the original organic material. The acids were converted to methyl esters with ethereal diazomethane. The esters were then analyzed with a gas chromatograph coupled to a mass spectrograph and computer. The major products were n-carboxylic acids (C_8-C_{29}), n-dicarboxylic acids (C_4-C_{17}) and isoprenoid carboxylic acids (C_9, C_{12}, C_{14}-C_{17}, C_{19}-C_{22}). Dicarboxylic acids were in a higher relative concentration than monocarboxylic acids. With the exception of methyl keto acids, the major oxidation products in this study were essentially the same as found by Burlingame and coworkers (10, 11, 38). However, oxidation products in this study were recovered in a much higher yield.

Young et al. (64, 65) oxidized a kerogen concentrate with alkaline potassium permanganate. The kerogen concentrate was prepared by reacting crushed Green River oil shale with dilute hydrochloric acid followed by extraction with a four to one mixture of benzene and methanol. Silicate minerals were not removed. Stepwise oxidation was performed in a manner similar to that performed by Djuricic et al. (15, 16) described earlier in this review. A sample of 10 g. of the concentrate was oxidized with 25 ml. portions of 0.08 M potassium permanganate. After all the permanganate was reduced in each step, the aqueous phase was separated from the solid residue by centrifugation. The residue was then oxidized with a fresh portion of permanganate. The solid residue showed 0.83 per cent carbon after 28 steps. The silicate mineral structure was not destroyed. The aqueous layers were combined and acidified with hydrochloric acid. The precipitated acids were a lustrous dark brown when dried. The acid filtrate was extracted with diethyl ether. The precipitated acids were analyzed by nuclear magnetic resonance. The results indicated that only aliphatic protons were present. The precipitated acids were converted to methyl esters by boron trifluoride in methanol. The esters were analyzed by gas chromatography. The major oxidation products were n-carboxylic acids (C_4-C_{31}), dicarboxylic acids (C_{12}-C_{18}) and branched or cyclic carboxylic acids (C_{12}-C_{20}). The oxidation products were essentially the same as found by Djuricic et al., however, there was no dominance of dicarboxylic acids as found by Djuricic.

Wen and Yen (58) electrolytically oxidized and reduced the kerogen concentrate prepared by Young et al. (64, 65) and electrolytically oxidized a bioleached oil shale. The bioleached shale was prepared by exposing the shale to a sulfur oxidizing bacteria, Thiobaccillus. The acid produced by this bacteria dissolved the carbonate minerals. Silicate minerals were not removed from the bioleached shale. The oxidations were carried out in an H-cell. The anode and cathode compartments were separated by a glass frit. The anode electrode was copper or platinum gauze having an area of 12.5 $cm.^2$. The cathode electrode was a lead sheet. A typical reaction was the oxidation of 1.0 g. of bioleached oil shale in 3 M sodium hydroxide for 40 hrs. at a current density of 0.01 amp./cm.^{2}. After completion of the reaction the residue was filtered. The filtrate was acidified with hydrochloric acid. The precipitated acids were converted to methyl esters with boron trifluoride in methanol and analyzed by gas chromatography. The acid filtrate was extracted with carbon tetrachloride and the extract was anlayzed by gas chromatography. Analysis of the solid residue indicated that 76.3 per cent of the organic material in the bioleached oil shale had been converted to soluble products. Similar products were produced by the kerogen concentrate and the bioleached oil shale. The major oxidation products were n-carboxylic acids (C_{10}-C_{22}), n-dicarboxylic acids (C_6-C_{11}) and branched carboxylic acids (no range given). Several compounds were separated in the carbon tetrachloride fraction. Primary n-alcohols (C_{14}-C_{20}) were identified. The acids obtained were essentially the same as those obtained by oxidation with alkaline permanganate.

Electrolytic reduction was performed in a three neck 250 ml. flask. The central neck was fitted with a thermometer. An aluminim sheet having an area of 12 cm.^{2} was sealed into one of the side necks and was used as the cathode. A carbon rod was used as the anode and was inserted in the other neck. A sample of 1 g. of the kerogen concentrate was dissolved in 100 ml. of ethylenediamine containing 1.4 g. of lithium chloride. The reaction vessel was cooled to -35°. The solution was electrolyzed for 30 hrs. at a current density of 0.05 amps/cm.^{2}. After reaction the solid was separated by centrifugation and washing. The residue was extracted with heptane and a four to one mixture of benzene and methanol. The heptane extract was analyzed by gas chromatography. The liquid layer from the reaction was extracted with heptane and chloroform. The extracts were analyzed by gas chromatography. The benzene-methanol extract consisted of an orange-brown semisolid and constituted 6.4 per cent of the kerogen concentrate. The heptane extract obtained from the residue accounted for 3.7 per cent of the kerogen concentrate. This extract contained n-alkanes (C_{19}-C_{32}). The heptane and chloroform extracts obtained from the liquid layer resulted in a group of peaks in the gas chromatogram. Compounds identified were n-alkanes (C_{20}-C_{22}).

Schmidt-Collerus and Prien (45, 46) analyzed a kerogen concentrate with micro-pyrochromatography and mass spectrometry. The kerogen concentrate was prepared by extraction of Green River oil shale with several solvents of increasing polarity over a period of several weeks. The shale was then leached with acetic acid to remove carbonate minerals and the series of extractions was repeated. The kerogen was separated from the remaining mineral matrix by density gradient separation or acid leaching (assumed hydrofluoric acid). A portion of the kerogen concentrate was then pyrolyzed. The pyrolysis products were directly injected into a gas chromatograph coupled to a mass spectrograph or collected in a condenser. The material collected by the condenser was separated into major fractions. The fractions were then analyzed by gas chromatography with detection by mass spectrometry. The major products observed were n-alkanes (C_{10}-C_{34}), branched alkanes (C_{10}-C_{36}), alkyl cyclohexanes (C_{16}-C_{19}), alkyldecalins (C_{15}-C_{18}), alkyl hexahydrophanathrenes (C_{15}-C_{18}), alkyl benzenes (C_{14}-C_{18}), alkyl napthalenes (C_{13}, C_{14}) and alkyl phenanthrenes (C_{15}-C_{18}).

F. Proposed Structural Models of Kerogen

Several of the above workers proposed models for the structure of kerogen based on the results of their investigations. Yen (62) reviewed the proposed models for the structure of Green River kerogen.

Burlingame and co-workers (8, 11) based their model for the structure of kerogen (Fig. 1) on the results of their chromic acid oxidations. Only 3.6 per cent of the organic material was recovered as oxidation products, consisting of isoprenoid and n-alkyl carboxylic acids. The model consisted of isoprenoid and paraffinic structures attached to a kerogen nucleus by ester, ether and carbon-carbon linkages. No attempt was made to define the kerogen nucleus.

Djuricic et al. (15) based their model for the structure of kerogen (Fig. 2) on the results of their alkaline permanganate oxidations. Since 70 per cent of the organic material was recovered as n-carboxylic acids, isoprenoid carboxylic acids, and predominantly n-dicarboxylic acids, the model consisted of a network of polymethylene bridges with isoprenoid and n-aliphatic chains attached through an undefined linkage. Although not defined, the linkage was of a type susceptible to permanganate oxidation or alkaline hydrolysis. Possibilities for linkages included any functional group as well as quarternary carbons.

Schmidt-Collerus and Prien (45, 46) based their model for the structure of kerogen (Fig. 3) on the results of their micro-pyrochromatography and mass spectrometry experiments. In this model, subunits of the kerogen polymer consisted of alkyl substituted decalins and tetralins connected through n-aliphatic, isoprenoid and ether

Figure 1. Model of Green River kerogen proposed by Burlingame and co-workers (8, 11)

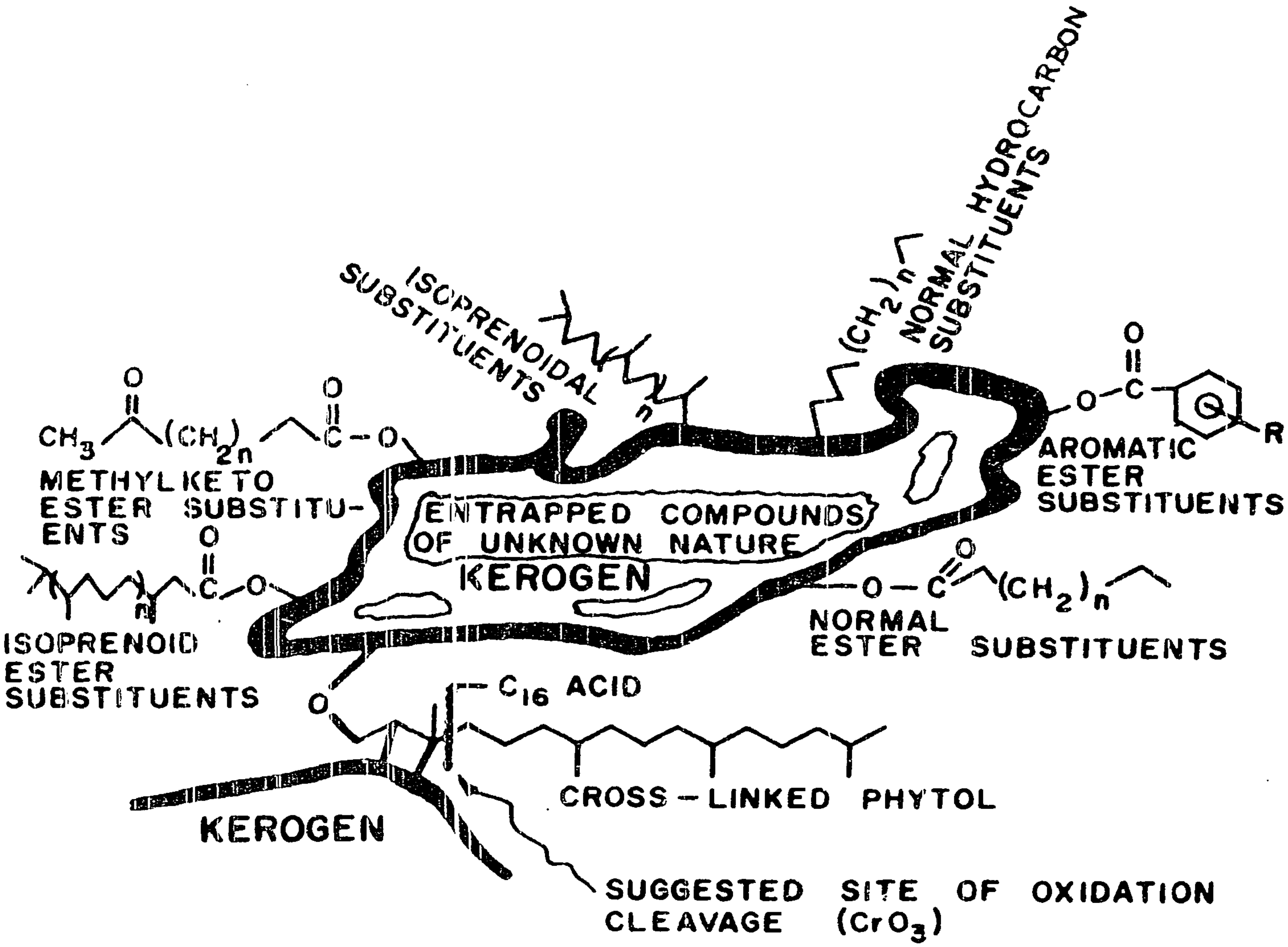

ISOPRENOIDAL SUBSTITUENTS
n
$(CH_2)_n$
NORMAL HYDROCARBON SUBSTITUENTS
CH_3 O (CH$_2$)$_n$ O C O
METHYLKETO ESTER SUBSTITUENTS
O C O
AROMATIC ESTER SUBSTITUENTS
R
ENTRAPPED COMPOUNDS OF UNKNOWN NATURE
KEROGEN
n O C O
ISOPRENOID ESTER SUBSTITUENTS
O C O (CH$_2$)$_n$
NORMAL ESTER SUBSTITUENTS
O
C_{16} ACID
CROSS-LINKED PHYTOL
KEROGEN
SUGGESTED SITE OF OXIDATION CLEAVAGE (CrO_3)

Figure 2. Model of Green River kerogen proposed by Djuricic et al. (15)

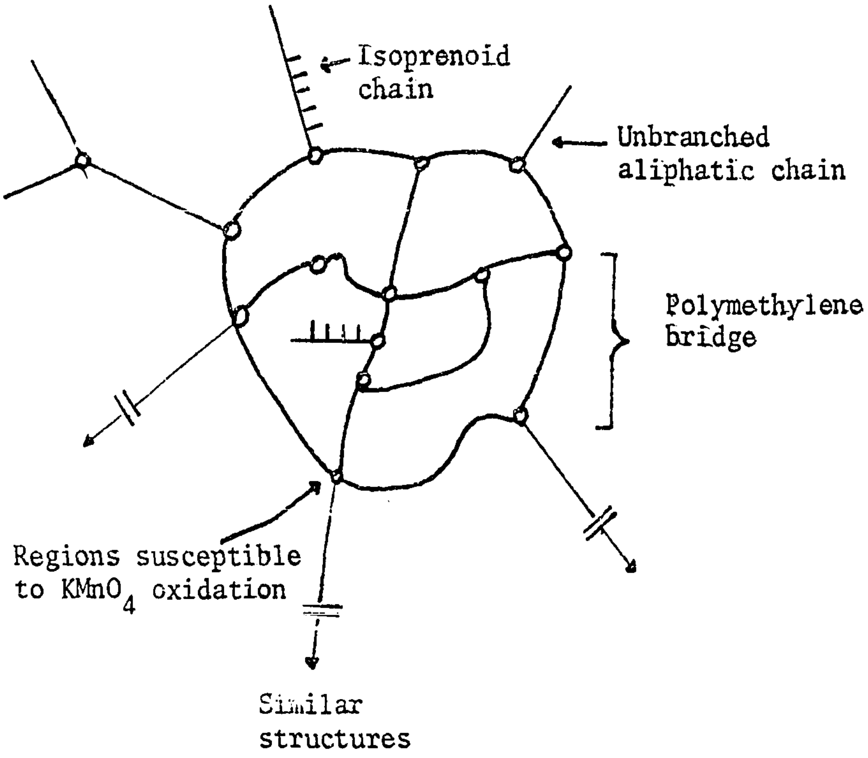
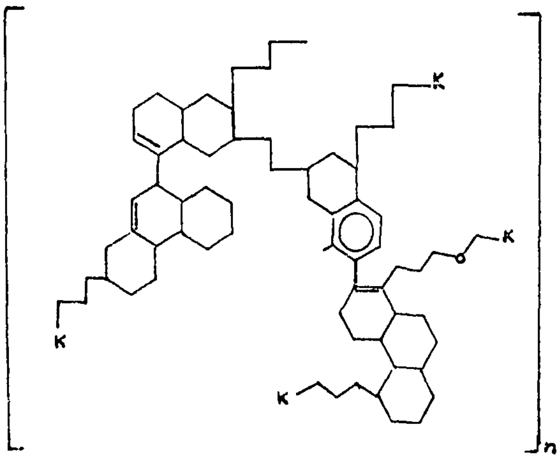

Isoprenoid chain
Unbranched aliphatic chain
Polymethylene bridge
Regions susceptible to $KMnO_4$ oxidation
Similar structures

Figure 3. Model of Green River kerogen proposed by Schmidt-Collerus and Prien (45, 46)

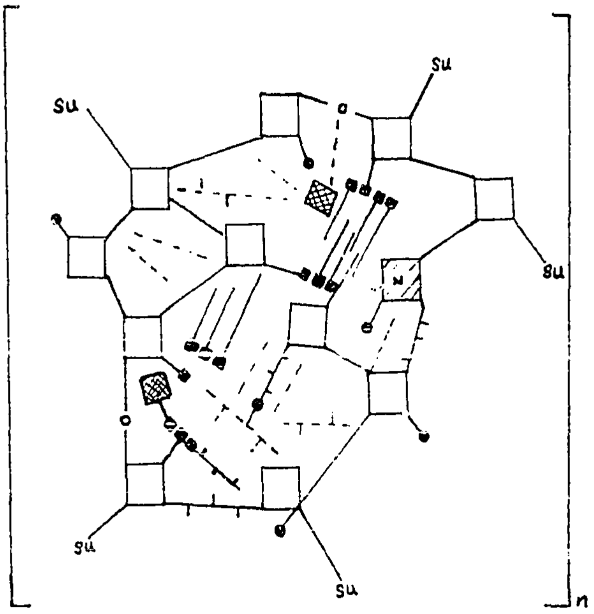
a. General structure of subunits

b. Structure of kerogen

a



b



☐ Matrix Subunit (nucleus)

☐-● Acid Matrix Subunit

▨ N-hetero Matrix Subunit (nucleus)

▩-● Entrapped Acidic Subunit

▩… Entrapped Neutral Subunit

—⊥— Alkane Matrix Bridges (normal + branched)

—o— Ether Matrix Bridges

—⊥—┬● Me-terminal Matrix Alkanes (normal + branched

⊥—┐● Entrapped Aliphatic Acids (normal + branched)

⊥ – – ┌ Entrapped Alkanes (normal + branched)

SU Other Matrix Subunits

linkages. Components entrapped by the kerogen matrix were also indicated.

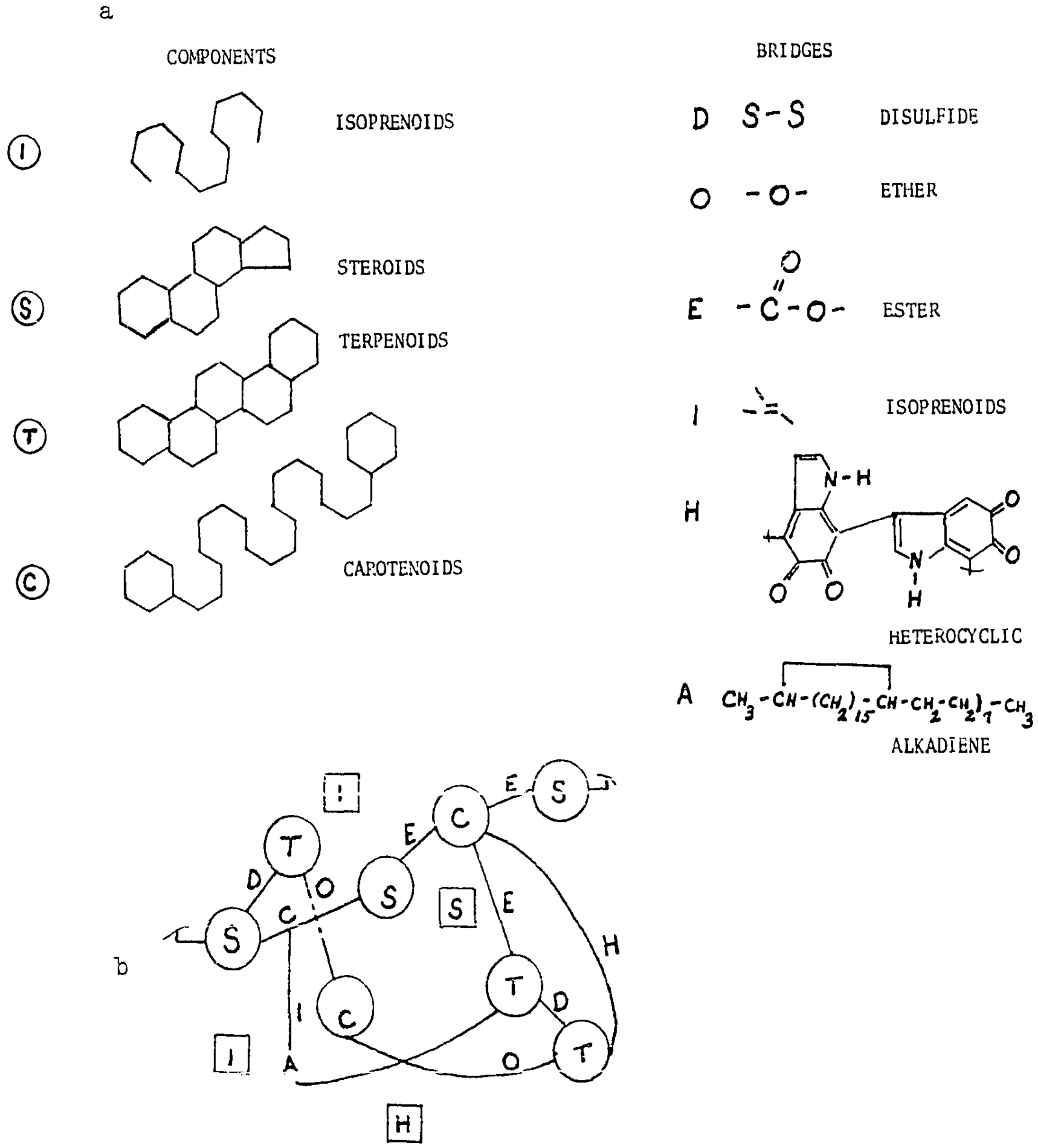
Yen (60,61) and Young et al. (64,65) based their model for the structure of kerogen (Fig. 4) on the results of their alkaline permanganate oxidations and X-ray diffraction studies. This model of kerogen was a multi-polymer. Manomers consisted of multifunctional components and difunctional bridges. Major components were isoprenoids, steroids, terpenoids and cartenoids. Bridges consisted of disulfides, ethers, esters, isoprenoid, heterocyclic and n-alkyl substituents. Components were linked by bridges to form a matrix containing entrapped components and bridges.

The Burlingame model is of limited use since only 3.6 per cent of the kerogen was recovered. Djuricic obtained in higher yield the same oxidation products as Burlingame. The Djuricic model is just an extension of the Burlingame model. The Schmidt-Collerus and Prien model is drastically different from the Djuricic model. The Schmidt-Collerus and Prien model is largely cyclic and contains a definite aromatic content. A drawback of this model is that the model is based on pyrolysis. It is known that the content of pyrolysis products is not the same as the original material. For example, isoprenoids will form naphthenics and aromatic compounds by ring closure and dehydrogenation (62). The Yen model is also not in good agreement with the Djuricic model. The Yen model contains a large number of naphthenic components. The Djuricic model could be accommodated by the Yen model if ring structures were destroyed by alkaline permanganate before paraffinic and isoprenoid structures were attacked. Robinson et al. (42,44) and Robinson and

Figure 4. Model of Green River kerogen proposed by Yen (60,61) and Young et al. (64,65)

a. Components and bridges

b. Structure of the kerogen


a
COMPONENTS
I
ISOPRENOIDS
S
STEROIDS
TERPENOIDS
T
C
CAROTENOIDS
BRIDGES
D
S-S
DISULFIDE
O
-O-
ETHER
E
-C-O-
ESTER
I
ISOPRENOIDS
H
N-H
N
H
HETEROCYCLIC
A
CH3-CH-(CH2)15-CH-CH2-CH2)7-CH3
ALKADIENE
b
I
T
D
O
C
S
E
C
E
S
S
E
H
I
C
T
D
A
O
T
I
H

Lawlor (43), however, did identify cyclic structures as a result of oxidation with alkaline permanganate.

G. Purpose

The purpose of this dissertation is to further characterize the structure of Green River oil shale by oxidizing a kerogen concentrate with perchloric acid. Work is described in which the oxidation products from the reaction of a kerogen concentrate with perchloric acid are analyzed. A model for the structure of kerogen is presented based on the results of the analyses. Perchloric acid was chosen as the oxidizing agent for two reasons. First, the reduction potential of perchloric acid can be varied by changing the concentration of the acid. In this manner, stepwise oxidation of oil shale kerogen can be performed by varying the reduction potential of the oxidizing agent. In previous experiments, stepwise oxidation of kerogen was effected by varying either the amount of oxidizing agent or the time of reaction. Second, a different oxidizing agent may well alter the nature of the oxidation products and give new insight into the structure of the kerogen oxidized.

H. Perchloric Acid as an Oxidizing Agent

As an oxidizing agent, perchloric acid is unique. When cold or dilute, perchloric acid is a non-oxidizing acid. When hot and concentrated, perchloric acid is one of the most powerful oxidizing agents known.

Smith (52) demonstrated that the apparent reduction potential of perchloric acid rises slowly as the boiling point and concentration increase. At boiling points below 130°, iron was dissolved by perchloric acid to form iron (II) perchlorate and hydrogen gas. Iron (II) was oxidized to iron (III) by boiling 50 per cent perchloric acid; the reduction potential was estimated to be 0.8-0.85 volts. Vanadyl ion was slowly oxidized to vanadate by boiling 57.5 per cent perchloric acid (150°); the reduction potential was estimated to be 1.3-1.4 volts. Vanadyl was readily oxidized to vanadate by boiling 60 per cent perchloric acid; the reduction potential was estimated to be 1.45-1.5 volts.

Commercial perchloric acid is 72.5 per cent perchloric acid. It is prepared by distilling the perchloric acid-water azeotrope. The boiling, concentrated acid (202°) has an estimated reduction potential of 2.0 volts. The perchloric acid-water azeotrope corresponds closely in composition to perchloric acid dihydrate, $HClO_4 \cdot 2H_2O$. Perchloric acid monohydrate has also been prepared. The monohydrate has a melting point of 49.9° and may be safely stored for an extended period of time. Anhydrous perchloric acid is a heavy oily liquid which causes explosions when brought into contact with most organic material. Anhydrous perchloric acid undergoes slow decomposition on standing, producing decomposition products which ultimately explode. The anhydrous acid is not easily prepared. The anhydrous acid may be the active oxidizing agent when perchloric acid is used with sulfuric acid.

Smith (53) used perchloric acid alone, and in combination with nitric, periodic and sulfuric acids, for the safe oxidation and dissolution of organic materials. Martinie and Shilt (36) showed that hot concentrated perchloric acid alone completely converts most organic materials to carbon dioxide. The notable exceptions being nitrogen heterocyclics such as pyridine and phenanthroline.

II. PREPARATION OF KEROGEN CONCENTRATE

A. Introduction

The ultimate purpose of the research described in this dissertation is to contribute to the knowledge of the structure of the kerogen in Green River oil shale. In my M.S. thesis (37), the oxidation of Green River oil shale with perchloric acid was described. The reaction of the raw oil shale with the perchloric acid involved the oxidation of the inorganic matrix and the bitumen as well as the kerogen material. Because of the calcium derived from the shale, calcium salts of carboxylic acids were precipitated during the work up procedures causing some complications in the subsequent analysis of the oxidation products. In the oxidations described in this dissertation, most of the inorganic matrix and bitumen were removed from the oil shale.

Hubbard et al. (31) separated the organic materials in Green River oil shale from the inorganic minerals by employing a flotation technique. The raw oil shale was leached with acetic acid to remove carbonate minerals. The carbonate free shale was finely ground and centrifuged with mixtures of carbon tetrachloride and benzene having densities of 1.4 to 1.2 g./ml. In this manner the low density organic material was separated from the high density pyrite and silicate minerals. This technique, however, does not afford a satisfactory separation. Ash in kerogen concentrates prepared by this technique ranged from 14 to 28 per cent.

Robinson et al. (44) used the above flotation technique, attrition grinding and reaction with hydrochloric and hydrofluoric acids to prepare kerogen concentrates. The attrited concentrate was prepared by grinding a thick paste of carbonate free oil shale and cetane with water to remove most of the silicate minerals. A satisfactory separation was not attained as the resulting kerogen concentrate contained 15 per cent ash. The third kerogen concentrate was prepared by reacting raw oil shale with concentrated hydrochloric acid and concentrated hydrofluoric acid to remove both carbonate and silicate minerals respectively. Pyrite was not removed by this method. The resulting kerogen concentrate contained 5.2 per cent ash.

Burlingame and co-workers (8, 10, 11, 38, 48) and Djuricic and co-workers (15, 16) prepared a kerogen concentrate by reacting raw oil shale with a one to one mixture of concentrated hydrochloric acid and concentrated hydrofluoric acid to remove carbonate and silicate minerals. The shale was also exhaustively extracted with a four to one mixture of benzene and methanol to remove a large portion of the bitumen. Pyrite was not removed by this method. The kerogen concentrate prepared by Djuricic and co-workers contained 23.8 per cent ash.

Wen and Yen (58) and Young et al. (64,65) prepared a bioleached oil shale. The oil shale was used as a medium for the growth of a sulfur oxidizing bacteria, Thiobaccillus. The bacteria oxidized the pyrite sulfur to sulfuric acid. Carbonate minerals were then dissolved. Silicate minerals were not removed by this method.

In the present work treatment with a one to one mixture of hydrochloric and hydrofluroic acids was chosen to remove the mineral matrix. This method removes the largest portion of the mineral matrix. By choosing the hydrochloric and hydrofluoric acid method, a comparison can be made between the results reported in this dissertation and the results reported by Burlingame and co-workers (8, 10, 11, 38, 48) and Djuricic and co-workers (15, 16).

B. Experimental Work and Results

The sample used in this dissertation was the same sample used in my thesis for the M.S. degree (37). The sample was obtained from the Marathon Oil Company of Littleton, Colorado.

A 786.7-g. sample of raw oil shale was placed in a 4-l. plastic beaker. To the beaker was added 500 ml. of concentrated hydrochloric acid and 500 ml. of concentrated hydrofluoric acid. Vigorous reaction resulted upon the addition of the hydrofluoric acid. An attempt was made to stir the reaction mixture but the amount of solid material was too large for effective stirring. The material remaining after this reaction was divided into 12 equal portions for filtration. Only a 9-cm. Buchner funnel made of plastic was available and this necessitated the use of small fractions of the sample. The material was filtered into a 4-l. flask which had been coated with mineral oil and contained a saturated solution of boric acid. The filtered material was placed in a 2-l. plastic beaker and 250 ml. of concentrated hydrochloric acid and 250 ml. of concentrated hydrofluoric acid were added. The mixture was stirred for 24 hrs. The mixture was filtered in the manner described above until no precipate occurred in the washings upon the addition of silver nitrate. Approximately 3 l. of wash water was required. The filtered material was extracted in a Soxhlet extractor with acetone for 10 days. The initial washings were dark brown and the final acetone washings were colorless. After extraction the 12 samples were combined and dried. The weight of the kerogen concentrate was 319.0 g. This was 40.55 per cent of the original sample.

Upon reaction of a portion of the sample prepared above with boiling perchloric acid, the reaction vessel was highly etched; indicating the incomplete removal of fluroide from the sample. A salt of a fluorsilicate probably remained in the sample. In order to remove the fluoride, a 117.1-g. sample of the kerogen concentrate was placed in a 4-l. beaker and 2 l. of 6 M HCl were added. The solution was heated slowly until the volume had been reduced to 500 ml. The solid was filtered. The solid was returned to the 4-l. beaker and 1 l. of water was added. The mixture was heated until the volume was reduced to 500 ml. The solid was filtered and washed with 20 l. of water. The solid was again returned to the 4-l. beaker and 1 l. of water was added. The mixture was heated until the volume was reduced to 500 ml. The solid was filtered and washed with 20 l. of water until no precipitate formed in the washings upon addition of silver nitrate. The sample was dried and found to weigh 34.1 g. This corresponded to 11.8 per cent of the original raw oil shale. The sample was passed through a #16 sieve. This kerogen concentrate reacted violently with boiling concentrated perchloric acid but the reaction vessel was not etched.

The kerogen concentrate was dark brown. A sample of the kerogen concentrate was submitted to Chemalytics Inc. for elemental analysis. The results were 70.36 per cent carbon, 9.11 per cent hydrogen, 2.36 per cent nitrogen and 5.18 per cent sulfur. A sample of the kerogen concentrate was ashed and found to contain 6.12 per cent ash. The ash was red. The arc emission spectrum of the kerogen concentrate and the ash was obtained using an ARL spectrograph. In the spectrum of the ash, emission lines resulting from iron were strongest. Strong lines resulting from calcium and magnesium were also present. Very weak lines were observed for aluminum and titanium. Lines due to cyanogen were the only other lines present. Only cyanogen lines were observed in the spectrum of the kerogen concentrate. The kerogen concentrate was observed under a dissecting microscope supplied by Dr. D. L. Biggs of the Department of Earth Sciences at Iowa State University. Under the microscope, the kerogen concentrate appeared as massive brown particles. Small yellow metallic crystals were dispersed throughout the kerogen concentrate. However, a few of the particles of kerogen concentrate appeared to contain almost 50 per cent of the yellow crystals. The kerogen concentrate was analyzed with an X-ray diffraction instrument designed specifically to determine pyrite in coal. This analysis was done by Mr. Jim Benson of the Ames Laboratory at Iowa State University. Pyrite was found in a concentration of 2.7 per cent. No other minerals were observed as a result of the X-ray diffraction analysis.

III. A STUDY OF THE REACTION OF THE KEROGEN CONCENTRATE WITH PERCHLORIC ACID OF VARYING CONCENTRATION AND BOILING POINT

A. Introduction

Work described in my M.S. thesis (37) involved the oxidation of Green River oil shale with perchloric acid. The oil shale was oxidized with perchloric acid of varying concentration and boiling temperature. The carbon dioxide evolved was used as in index of oxidation. The extent of oxidation was followed also by the color changes of the aqueous phase, the percentage of the undissolved material, the color changes of the undissolved material and the weight of the acetone-soluble fraction in the undissolved material. As a result of that work, the following conclusions were drawn: 1) at boiling points less than 150°, carbonate minerals were dissolved to produce carbon dioxide, 2) at boiling points of 150° to 165°, some organic material was oxidized and the silicate minerals were not dissolved, 3) at boiling points of 165° to 190°, organic material was oxidized and the silicate minerals were dissolved, and 4) at boiling points of 190° to 204°, the organic material was completely oxidized to carbon dioxide.

Some of the above work was repeated on the kerogen concentrate prepared as described in Section II. In as much as the kerogen concentrate was prepared from the same oil shale used in the preceding work, correlations were possible between the findings of the two studies.

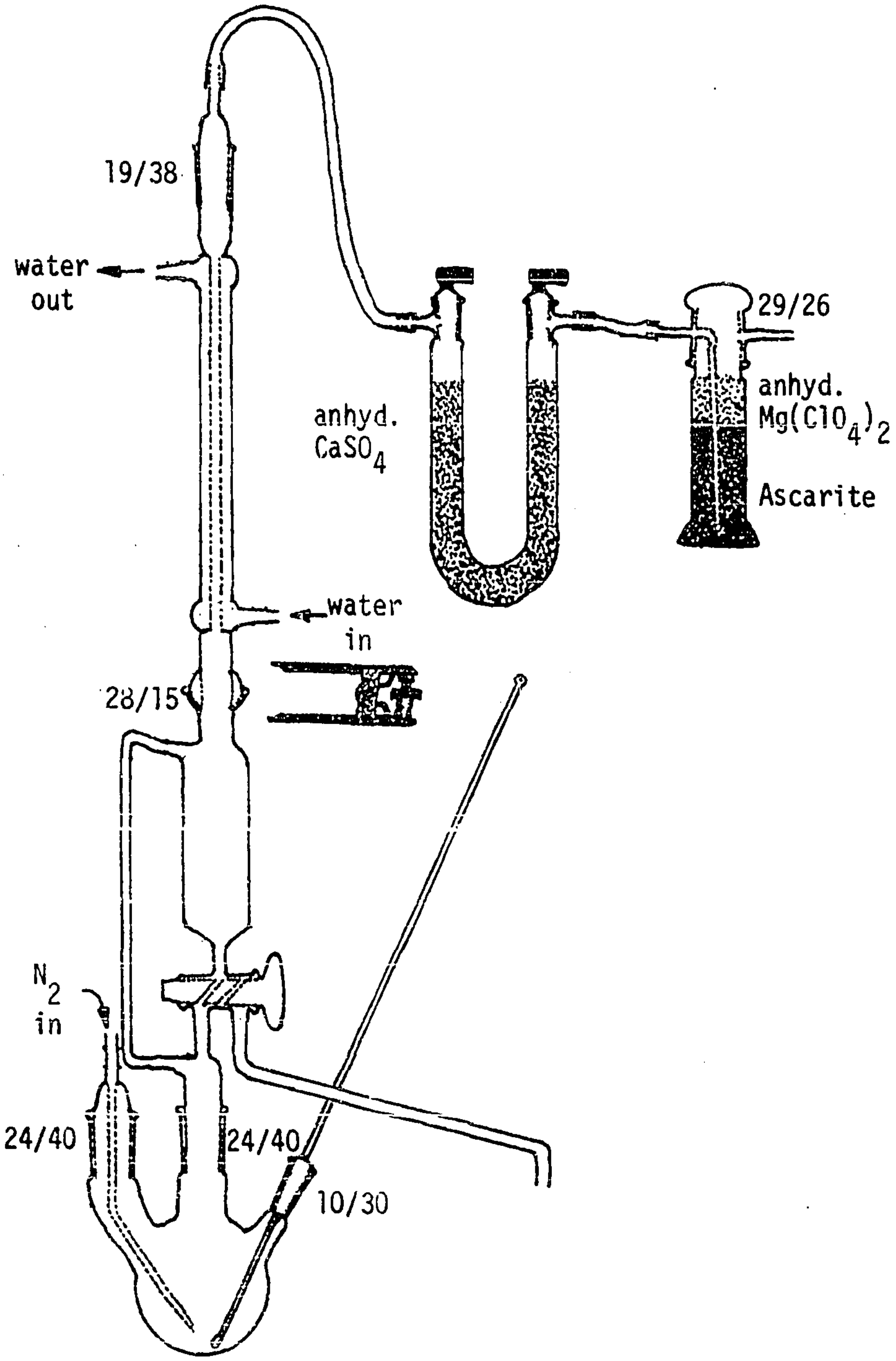
B. Apparatus

The apparatus (Fig. 5) used for the controlled potential oxidation of oil shale has been described in my M.S. thesis (37). The reaction vessel was a 250-ml., round-bottom flask with two 24/40 ground glass openings and a 10/30 ground glass, thermometer side arm. The mercury bulb of the 250°-thermometer entering the flask was completely immersed in the reaction mixture. The air condenser was supported by the central 24/40 ground glass opening. The water cooled condenser was supported by the air condenser through a 28/15 ball-and-socket ground glass joint. All ground glass joints were sealed with Teflon fillers except the ball-and-socket joint which was sealed with 50 per cent perchloric acid. The stopcock was made of Teflon.

The concentration and boiling point of the perchloric acid during a reaction was held constant by positioning the stopcock to return the reflux condensate to the reaction vessel. Because the vapor phase of perchloric acid contains a higher percentage of water than the liquid phase, the boiling point and concentration of the perchloric acid could be increased by positioning the stopcock to remove reflux condensate from the system. Thus, any desired concentration and consequent boiling point and oxidizing power could be obtained and maintained.

For the determination of the carbon dioxide produced during the attack on the kerogen concentrate, nitrogen was bubbled through the reaction mixture. This flow of gas agitated the mixture and swept the carbon dioxide from the reaction vessel. The water cooled condenser was connected by Tygon tubing to a "U" shaped drying tube filled with

Figure 5. Modified Bethge apparatus used for the controlled potential oxidation of the kerogen concentrate


19/38
water out
water in
28/15
N_2 in
24/40
24/40
10/30
anhyd. $CaSO_4$
29/26
anhyd. $Mg(ClO_4)_2$
Ascarite

anhydrous calcium sulfate. The drying tube was connected by Tygon tubing to a weighed Turner absorption bulb. The Turner absorption bulb was packed with Ascarite (sodium hydroxide absorbed on asbestos) and anhydrous magnesium perchlorate. Carbon dioxide was removed by the Ascarite and the water produced during this absorption was retained in the vessel by the anhydrous magnesium perchlorate.

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O$$

The weight of the bulb was thus a measure of the carbon dioxide absorbed. A second absorption bulb was used as a counterpoise during the work to cancel the effect of absorption of water on the large exterior surface of the bulb. A double pan balance was used to weigh the Turner absorption bulb.

All reactions with perchloric acid were carried out behind an explosion shield.

C. Experimental Work

Several samples of kerogen concentrate were reacted with perchloric acid of varying concentration and boiling point. The sample of kerogen concentrate was given the designation of "KC." The designation KC was then followed by the boiling point of the perchloric acid solution used to oxidize a particular sample. A lower case letter immediately following the boiling point indicated that more than one reaction was run at that temperature employing different experimental conditions. Thus, the designation, KC-202b, would represent an oxidation of the kerogen concentrate with perchloric acid having a boiling point of 202° and with experimental conditions different from KC-202a or KC-202c.

The following procedure was employed for each reaction KC-110 through KC-190. Perchloric acid was added to the Bethge apparatus and the boiling point adjusted to the desired temperature. By varying the initial amount of perchloric acid added, a final volume of approximately 50 ml. of solution remained in the Bethge apparatus after the adjustment of the boiling point. The perchloric acid solution was cooled and three 1.00-ml. aliquots of the solution were pipetted into conical flasks. The aliquots were titrated with standard 0.25 N sodium hydroxide. A weighed 1-g. sample of the kerogen concentrate was added to the Bethge apparatus. The reaction system was purged with nitrogen for 30 min. A weighed Turner absorption bulb was placed in the system. The reaction vessel was heated. The stable reaction temperature was noted at the beginning and at the end of the reaction. The reaction proceeded for 1.5 hrs. at which time heat was removed. The system was purged with nitrogen for 30 min. The Turner absorption bulb was removed and weighed. The total carbon collected as carbon dioxide for each reaction was calculated and expressed as a percentage of the sample. The reaction mixture was filtered. The aqueous phase, given the designation KC-°C-P, was saved. The solid phase, given the designation KC-°C-S was dried and weighed. The percentage of undissolved material was calculated.

Four experiments, KC-202a through KC-202d, were performed in an attempt to determine the total carbon in the kerogen concentrate. In each experiment, 50 ml. of concentrated perchloric acid was added to the Bethge apparatus and the boiling point checked at 202°. Three 1.00-ml.

aliquots of the perchloric acid solution were pipetted into conical flasks. The aliquots were titrated with standard 0.25 N sodium hydroxide. After the sample of kerogen concentrate was added to the Bethge apparatus, the system was purged with nitrogen for 30 min. A weighed Turner absorption bulb was placed in the system. The reaction vessel was heated. After the reaction was completed, the system was purged with nitrogen for 30 min. The Turner absorption bulb was removed and weighed. The total carbon collected as carbon dioxide was calculated and expressed as a percentage of the sample. The first experiment, KC-202a, was the reaction of a 0.1-g. sample of the kerogen concentrate for 1.5 hrs. After the reaction was completed the reaction mixture was filtered. The aqueous phase (KC-202a-P) was saved. The solid phase (KC-202a-S) was dried and weighed. The percentage of undissolved material was calculated. The second and third experiments, KC-202b and KC-202c, were the reaction of 0.1-g. samples of the kerogen concentrate. A few mg. of potassium dichromate was added to the reaction mixture. After a reaction time of 25 min. the mixture turned orange indicating the complete oxidation of organic material. The fourth experiment, KC-202d, was the reaction of a 0.1-g. sample of the kerogen concentrate for 30 min. After completion of the reaction, the reaction mixture was filtered. The aqueous phase (KC-202d-P) was saved. The solid material (KC-202d-S) was dried and weighed. The percentage of undissolved material was calculated.

A fifth experiment, KC-202e, was also performed with concentrated perchloric acid. A weighed 1-g. sample of the kerogen concentrate was added to 50 ml. of concentrated perchloric acid (b.p. 202°) in a 500-ml. conical flask. The flask was stoppered and the contents were stirred for 19.5 hrs. The mixture was filtered. The aqueous phase (KC-202e-P) was saved. The solid material (KC-202e-S) was dried and weighed. The percentage undissolved material was calculated.

D. Results and Discussion

The results for each experiment described, KC-110 through KC-202e appear in Table 1.

The graph of the concentration of perchloric acid versus the boiling point of perchloric acid (Fig. 6) is similar to the corresponding plot for raw oil shale reported in my M.S. thesis (37). The data agrees with that reported by Smith (53). Non-linearity of the curve around 170° and 200° was claimed by Smith (53) to be the result of formation of the tri- and dihydrates of perchloric acid. The data obtained in the present work does not indicate the presence of other hydrates proposed by Smith (52).

The data for the amount of carbon converted to carbon dioxide as a function of boiling point and concentration of perchloric acid was plotted (Figs. 7 and 8). Below boiling points of 150° and concentrations of 8.0 N perchloric acid, an insignificant amount of carbon dioxide was produced. Carbon dioxide was not expected to be produced because carbonate minerals were not present in the sample and perchloric acid has little oxidizing ability below a boiling point of 150°. As the boiling point and concentration of perchloric acid increased, the amount of carbon dioxide produced rose almost linearly. At a boiling point of 190° and a concentration of 10.7 N perchloric acid, the total carbon collected as carbon dioxide was 50 per cent of the sample.

Table 1. Results obtained from the reaction of the kerogen concentrate with perchloric acid at varying concentration and boiling point

Sample Number	Sample Weight (g.)	Normality $HClO_4$	Boiling Point $HClO_4$ (°C)	Reaction Temp. (°C)	Reaction Time (hr.)	Total Carbon Collected (percentage of sample)	Undissolved Material (percentage of sample)
KC-110	1.0260	2.20	110	104	1.5	0.26	102.7
KC-120	1.0189	4.61	120	114	1.5	0.31	104.0
KC-130	0.9924	6.21	130	125	1.5	0.47	101.5
KC-141	1.0225	7.02	141	132	1.5	0.92	101.3
KC-150	1.0124	7.99	150	142	1.5	1.96	99.0
KC-161	1.0250	8.97	161	155	1.5	8.28	77.42
KC-169	1.0095	9.53	169	167-6	1.5	21.00	21.77
KC-170	0.9914	9.60	170	168-6	1.5	24.38	13.48
KC-180	0.9838	10.18	180	176-2	1.5	39.78	1.88
KC-190	1.0004	10.72	190	184-8	1.5	50.32	2.27
KC-202a	0.0898	11.97	202	200-1	1.5	300.	0.29
KC-202b	0.0964	11.88	202	200	0.5	101.5	-
KC-202c	0.0959	11.89	202	201	0.5	86.34	-
KC-202d	0.1020	11.89	202	200	0.5	69.73	0.00
KC-202e	0.9898	11.89	202	25	19.5	-	99.8

Figure 6. Boiling point of perchloric acid versus concentration of perchloric acid

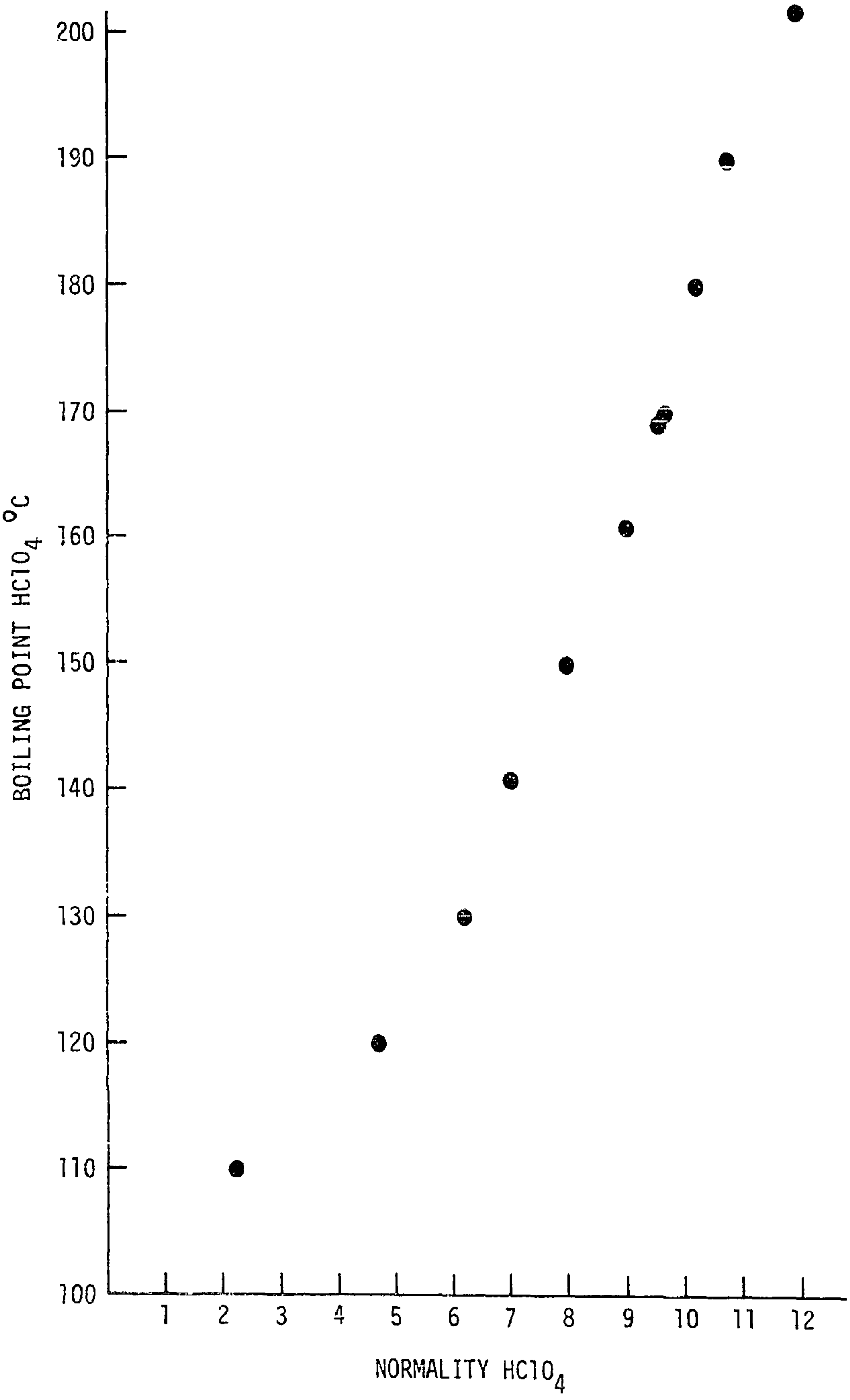

BOILING POINT $HClO_4$ °C
200
190
180
170
160
150
140
130
120
110
100
1
2
3
4
5
6
7
8
9
10
11
12
NORMALITY $HClO_4$

Figure 7. Total carbon collected versus the boiling point of perchloric acid

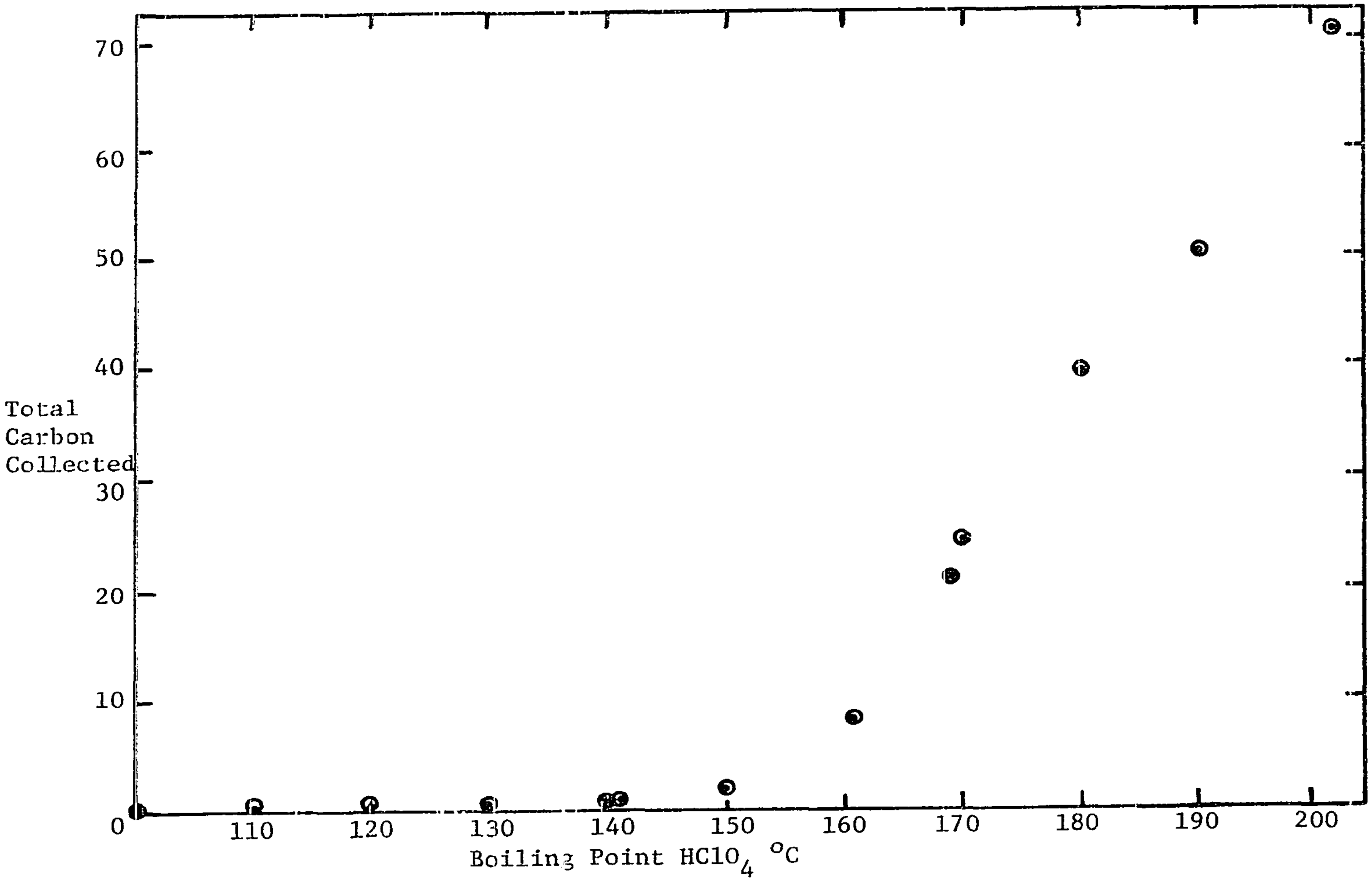
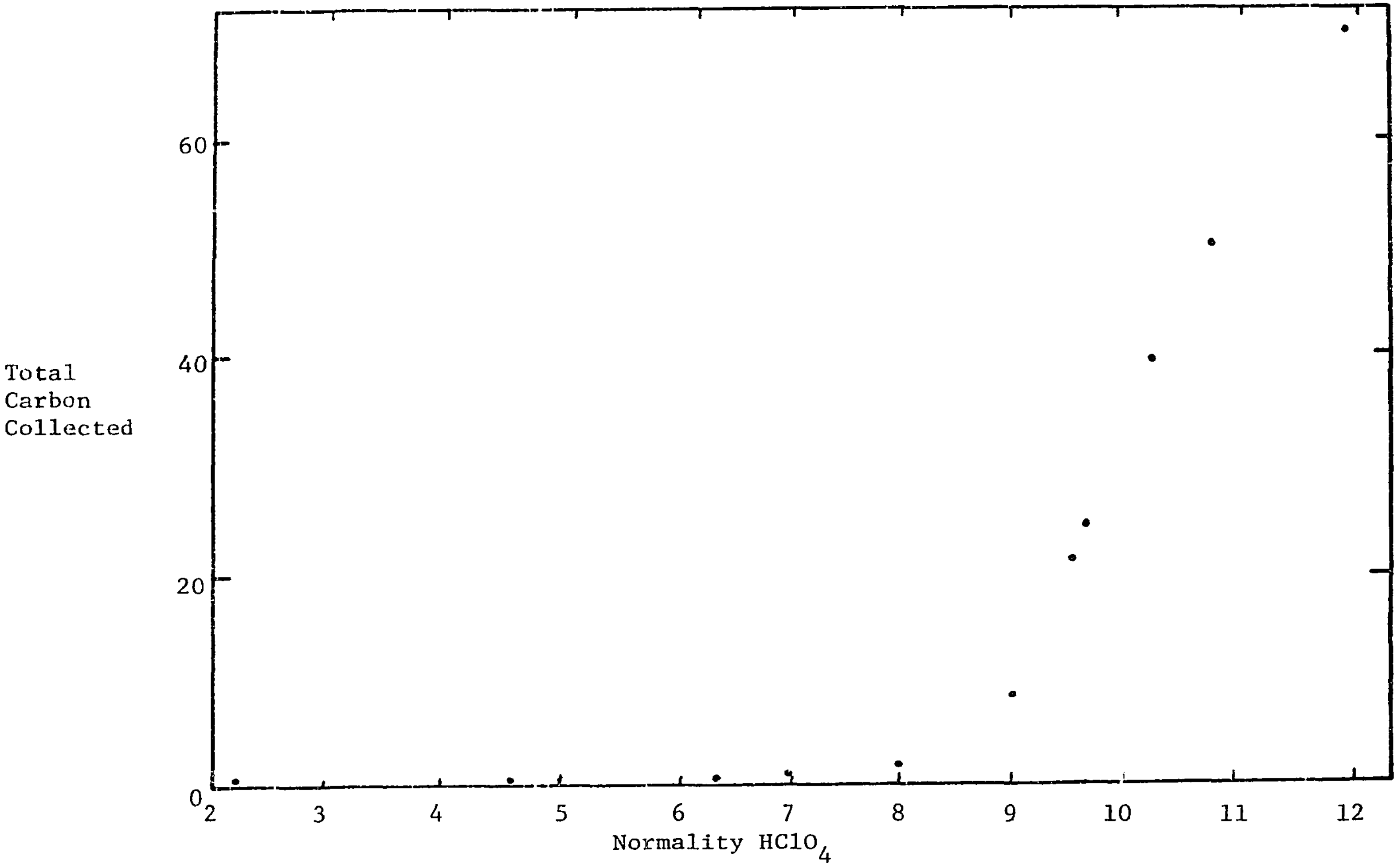

Total Carbon Collected
70
60
50
40
30
20
10
0
110
120
130
140
150
160
170
180
190
200
Boiling Point $HClO_4$ °C

Figure 8. Total carbon collected versus the concentration of perchloric acid


Total
Carbon
Collected
60
40
20
0
2
3
4
5
6
7
8
9
10
11
12
Normality $HClO_4$

The results for the determination of total carbon by reaction of the kerogen concentrate with perchloric acid were not reproducible. Only the value for KC-202d, 69.73 per cent carbon, was in the same range as the value 70.36 per cent carbon obtained by Chemalytics, Inc. Possible interferences for the determination of carbon using this reaction are discussed in Section IV. Because concentrated perchloric acid oxidizes most organic compounds completely (36), the value for total carbon obtained by Chemalytics, Inc. was plotted in Figs. 7 and 8 at the boiling point (202°) and normality (11.89 N) of concentrated perchloric acid.

A concern of the present work was to study the effect of the structure of the silicate minerals on the oxidation of the organic material in the shale. This was done by comparing the results for the oxidation of raw oil shale (described in my M.S. thesis) (37) with the results for the oxidation of the kerogen concentrate. Below a boiling point of 190°, the shapes of the curves of total carbon collected versus boiling point of perchloric acid for the raw oil shale and kerogen concentrate were identical. Below a boiling point of 150° there was a straight line portion with essentially zero slope on both curves. Above a boiling point of 150°, the production of carbon dioxide rose linearly with the boiling point to 190°. At a boiling point of 190° the organic material in the raw oil shale was dissolved and separated from the silicate minerals; and the silicate minerals were converted to silica. Thus, the presence of silicate minerals had no effect on the oxidation of the organic material contained in the shale.

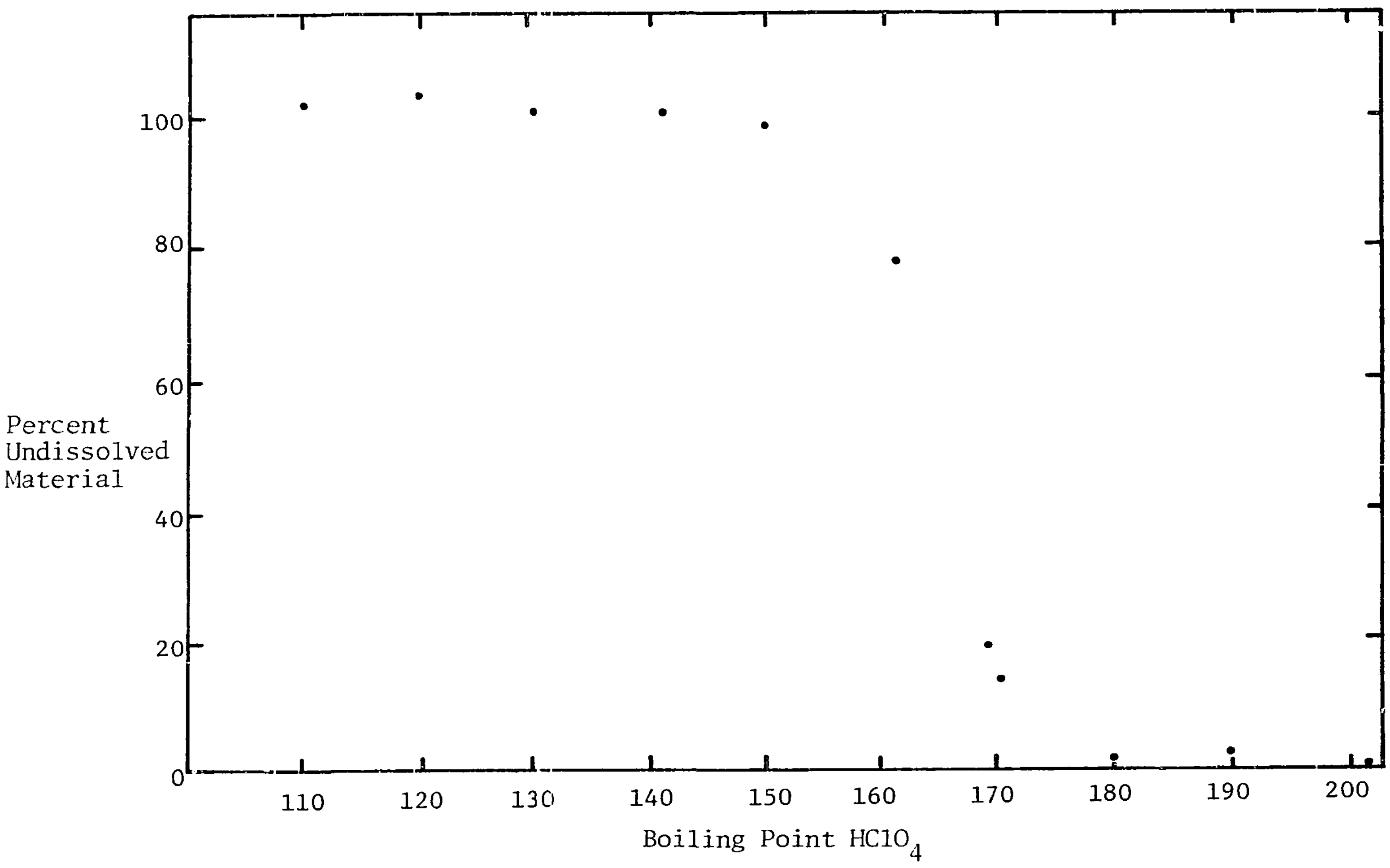
The color of the aqueous phase (KC-°C-P) changed drastically with change in boiling point and concentration of perchloric acid. As the boiling point increased, the color intensity rose to a maximum and then faded. The color of KC-110-P through KC-150-P was yellow. KC-161-P was orange. Maximum color intensity occurred in KC-169-P and KC-170-P which were dark orange to brown. Color intensity decreased in KC-180-P, which was dark orange, and KC-190-P which was the same color as KC-161-P. KC-202a-P and KC-202d-P were colorless. These color changes corresponded with the color changes of the aqueous phase for the reaction of perchloric acid with raw oil shale (37).

The aqueous phase (KC-°C-P) was observed to fluoresce. Changes in the intensity of fluorescence followed the same pattern as changes in the intensity of color. The color of fluorescence was light blue in all solutions. KC-202a-P and KC-202d-P were non-fluorescent.

The graph (Fig. 9) of percentage of undissolved material versus boiling point is a smooth "S"-shaped curve. At low boiling points the solid material recovered weighed more than the original sample. This was probably caused by the absorption of some perchloric acid which was not removed by washing with water. Dissolution of the solid material occurred simultaneously with the increase in the production of carbon dioxide and with the increase in the intensity of the color in the aqueous phase. Inasmuch as no silicate minerals were present, the amount of undissolved material at high boiling points of perchloric acid was zero.

The color of the undissolved material (KC-¼C-S) changed slightly. KC-110-S through KC-150-S were the same brown color as the

Figure 9. Percentage of undissolved material versus boiling point of perchloric acid


Percent
Undissolved
Material
100
80
60
40
20
0
110
120
130
140
150
160
170
180
190
200
Boiling Point $HClO_4$

kerogen concentrate. KC-161-S through KC-190-S were brown, but much darker.

E. Conclusions

The following conclusions were drawn concerning the reaction of the kerogen concentrate with perchloric acid. At boiling points less than 150°, little or no reaction occurred between the kerogen and perchloric acid. Some residual bitumen was dissolved by the hot perchloric acid. A small amount of oxidation may have occurred at 150°. At boiling points between 150° and 170°, the kerogen was dissolved and some oxidation of the kerogen to carbon dioxide occurred. At boiling points between 170° and 202°, the dissolved kerogen was oxidized to carbon dioxide. At a boiling point of 202°, the dissolved kerogen was completely oxidized to carbon dioxide.

Because the oxidation of organic matter to carbon dioxide and the dissolution of the solid material occurred at the same boiling point and concentration of perchloric acid for both the raw oil shale and the kerogen concentrate, the conclusion was drawn that the silicate mineral structure has no effect on the oxidation of organic material. Young et al. (64, 65) drew the same conclusion by comparing the results obtained when carbonate-free oil shale was oxidized with alkaline permanganate with the results obtained by Djuricic et al. (15). Djuricic used alkaline permanganate to oxidize a kerogen concentrate prepared by treatment with hydrochloric and hydrofluoric acids.

F. Proposal

As a result of the above work the following research proposal was made. The dissolution of the kerogen as a function of the boiling point of perchloric acid resulted in an "S"-shaped curve with a sharp break (Fig. 9). This parameter could be used as an indicator for the reaction of model compounds with perchloric acid of varying boiling points. Insight into the type of linkages holding the kerogen together could be made by comparing the results for the dissolution of kerogen to the results obtained for the dissolution of model polymers. The type of polymers investigated should include different types of linkages, for example: polyethelene to study aliphatic carbon-carbon bonds, polystyrene to study aromatic carbon-carbon bonds, polyester to study ester groups, nylon to study amide groups, and crown compounds to study ether groups.

IV. INTERFERENCES WITH THE MEASUREMENT OF CARBON DIOXIDE PRODUCED IN THE REACTION OF THE KEROGEN CONCENTRATE WITH HOT CONCENTRATED PERCHLORIC ACID

A. Introduction

The results for the determination of the total carbon in kerogen by reaction with, hot, concentrated perchloric acid were not reproducible and were always high (See Table 1, KC-202a-d). Some material, which was absorbed on Ascarite, other than carbon dioxide was produced during the reaction.

Smith (52) has observed that chlorine gas was produced when concentrated perchloric acid was boiled. Chlorine gas exhibits acidic properties by disproportionating in base to from chloride and hypochlorite.

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O$$

Chlorine would not be removed from the system by either the water condenser or the calcium sulfate drying tube. Chlorine could then be absorbed by the Turner absorption bulb and cause high results for the determination of carbon.

The kerogen concentrate contained 5.18 per cent sulfur (Section II). What happened to the sulfur during the reaction was not known. Sulfur could be oxidized to several states. Organic or pyrite sulfur could be oxidized to elemental sulfur, sulfur dioxide, sulfite, or sulfate. Several compounds containing chlorine, such as $SOCl$, SO_2Cl_2 or SCl_2

could also be produced. Of the above compounds, sulfur dioxide and the chlorine compounds are possible interferences. Perchloric acid should oxidize sulfur completely to sulfate. If all of the sulfur in the kerogen concentrate were converted to SO_2Cl_2, an absolute error of only 5.19 per cent would result in the measurement of carbon.

B. Experimental Work and Results

Several experiments were performed in which 50 ml. of concentrated perchloric acid was placed in the Bethge apparatus. The system was purged with nitrogen for 30 min. The Turner absorption bulb was placed in the system and the perchloric acid was boiled for 30 min. The system was purged with nitrogen for 30 min. and the Turner absorption bulb was removed and weighed. For calculation purposes, the increase in weight of the Turner absorption bulb was assumed to be due to the absorption of carbon dioxide from a 0.1-g. sample of the kerogen concentrate. The carbon collected was then calculated. The absolute error for total carbon collected was not reproducible and ranged from 36.3 per cent to 100.4 per cent of the kerogen concentrate. This interference more than accounts for the error in the results for KC-202a through KC-202d.

A similar experiment was performed using perchloric acid having a boiling point of 190°. The solution was boiled for 1.5 hrs. The resulting absolute error in the carbon collected for KC-190 was 0.14 per cent of the sample.

A sample of pyrite derived from an Iowa coal vein was obtained from Dr. D. L. Biggs of the Earth Science department at Iowa State University. The pyrite was crushed. A 0.7-g. sample of pyrite and 50 ml. of concentrated perchloric acid were added to the Bethge apparatus. The mixture was heated for 1 hr. after which the solution was slightly yellow. The undissolved material was crystalline and white. The mixture was filtered. The pH of a portion of the filtrate was adjusted to 1.2 with 50 per cent sodium hydroxide. A precipitate of barium sulfate formed upon the addition of 2 ml. of 0.2 M barium nitrate. Because the sample was impure pyrite no attempt was made to quantitate the results. A portion of the sulfur was oxidized to sulfate by hot concentrated perchloric acid.

V. SEPARATION OF OXIDATION PRODUCTS

A. Introduction

One of the problems with the analysis of oxidation products resulting from the reaction of the kerogen concentrate with perchloric acid is the presence of perchloric acid. The presence of perchloric acid poses several problems. For example, an organic solvent containing perchloric acid cannot be heated to evaporate the solvent as this would result in the oxidation of the solvent; organic acids can not be esterified in the presence of perchloric acid as this would result in the formation of explosive perchloric acid esters. To analyze the oxidation products, prior separation of the oxidation products from perchloric acid was necessary. Direct extraction of the oxidation products from the perchloric acid solution, with organic solvents, cannot be employed because of the high solubility of perchloric acid in most organic solvents (37). XAD resins have been shown to remove trace organic compounds from aqueous solution (34).

In the present work the use of XAD resins was investigated as a possible means of separating soluble oxidation products from perchloric acid. The XAD resins were rejected because of the resins inability to absorb enough oxidation products for subsequent analysis. Removal of perchloric acid from insoluble oxidation products was effected by washing the solid with water. The perchloric acid-free oxidation products were then separated into neutral, acidic, polar and non-polar fractions.

B. Experimental Work and Results

1. Designation of samples

Several samples of kerogen concentrate were reacted with perchloric acid of varying concentration and boiling point (Sec. III). The sample of kerogen concentrate was given the designation of "KC." The designation, KC, was followed by the boiling point of the perchloric acid solution used to oxidize a particular sample. A lower case letter immediately following the boiling point indicated that more than one reaction was run at that temperature employing different experimental conditions. Thus, the designation, KC-202b, would represent an oxidation of the kerogen concentrate with perchloric acid having a boiling point of 202° and with experimental conditions different from KC-202a or Kc-202c.

2. Preliminary study

A preliminary study was made, using KC-170, to develop a separation scheme yielding oxidation products which were free of perchloric acid. A large concentration of oxidation products was expected in KC-170 because of the intensity of the color in the aqueous phase. Thus, KC-170 was chosen for the preliminary study.

After reaction with perchloric acid, KC-170 was filtered. The brown solid phase (KC-170-S) was dried and weighed. The brown aqueous phase (KC-170-P) was passed through a column of XAD-2 resin 2 cm. in diameter and 11 cm. in length. Some brown solid material which either passed through the original filtration or precipitated on standing was filtered by the column. The color of the resin became orange. The column was overloaded by KC-170-P as evidenced by the passage of orange liquid in the column effluent. The column was washed with 1 l. of water. The initial washing was orange; the final washing was light yellow. The water washing (KC-170-P1) was saved. The column was then washed with 100 ml. of 0.05 N sodium hydroxide. The brown solid material which had been filtered on top of the column dissolved. The sample eluted by sodium hydroxide (KC-170-P2) was almost black. The column was then washed with 100 ml. of diethyl ether. The ether eluent (KC-170-P3) was yellow in color. KC-170-P2 was acidified with concentrated hydrochloric acid to pH 1. The brown solid reprecipitated. The solution and solid was extracted with two 50 ml. portions of heptane. KC-170-P2 was then extracted with two 50 ml. portions of methyl isobutyl ketone (MIBK). The volume of the colorless heptane extract (KC-170-P4) and the brown MIBK extract (KC-170-P5) were reduced to 5 ml. The extracts were transferred to a weighed 25-ml. flask, evaporated to dryness and weighed. The solid remaining in KC-170-P2 was filtered and washed with water. The solid was washed with methanol until the washings were colorless. The methanol washings (KC-170-P6) were brown. The solid was then redissolved with 0.05 N sodium hydroxide. The sodium hydroxide solution (KC-170-P7) was orange in color.

KC-170-S was washed with 500 ml. of water to insure removal of perchloric acid. KC-170-S was then washed with 0.05 N sodium hydroxide until the washings were colorless. KC-170-S was then washed with water to remove sodium hydroxide. KC-170-S was dried and weighed to determine the weight of the sodium hydroxide-soluble fraction. The sodium hydroxide washings were acidified to pH 1 with concentrated sulfuric acid. A brown precipitate formed. The brown precipitate was filtered. The filtrate (KC-170-S1) was pale yellow. The precipitate was washed with heptane. The heptane washings (KC-170-S2) were colorless. The precipitate was then washed with methanol until the washings were colorless. The methanol washings (KC-170-S3) were brown. The precipitate was redissolved in 0.05 N sodium hydroxide (KC-170-S4).

A flow chart of KC-170 appears in Fig. 10. Results for KC-170 appear in Table 2.

3. Separation scheme

Samples KC-110 through KC-190, except KC-170, were treated in the following manner. KC-°C was filtered. The aqueous phase (KC-°C-P) was retained. The undissolved material (KC-°C-S) was dried and weighed. KC-°C-S was washed with 0.05 N sodium hydroxide until the washings were colorless. KC-°C-S was dried and weighed to determine the weight of the sodium hydroxide-soluble fraction. The sodium hydroxide washings were acidified to pH 1 with concentrated sulfuric acid. A brown precipitate formed. The precipitate was filtered. The filtrate (KC-°C-S1) was retained. The precipitate was washed with heptane into a weighed 25-ml. flask. The heptane washings (KC-°C-S2) were evaporated to dryness with a flow of nitrogen and weighed. The precipitate was then washed with methanol into a weighed 25-ml. flask until the washings were colorless. The methanol washings (KC-°C-S3) were evaporated to dryness with a flow of nitrogen and weighed. The remaining precipitate was redissolved with 0.05 N sodium hydroxide. The sodium hydroxide solution (KC-°C-S4) was

Figure 10. Flow chart of fractionation of KC-170

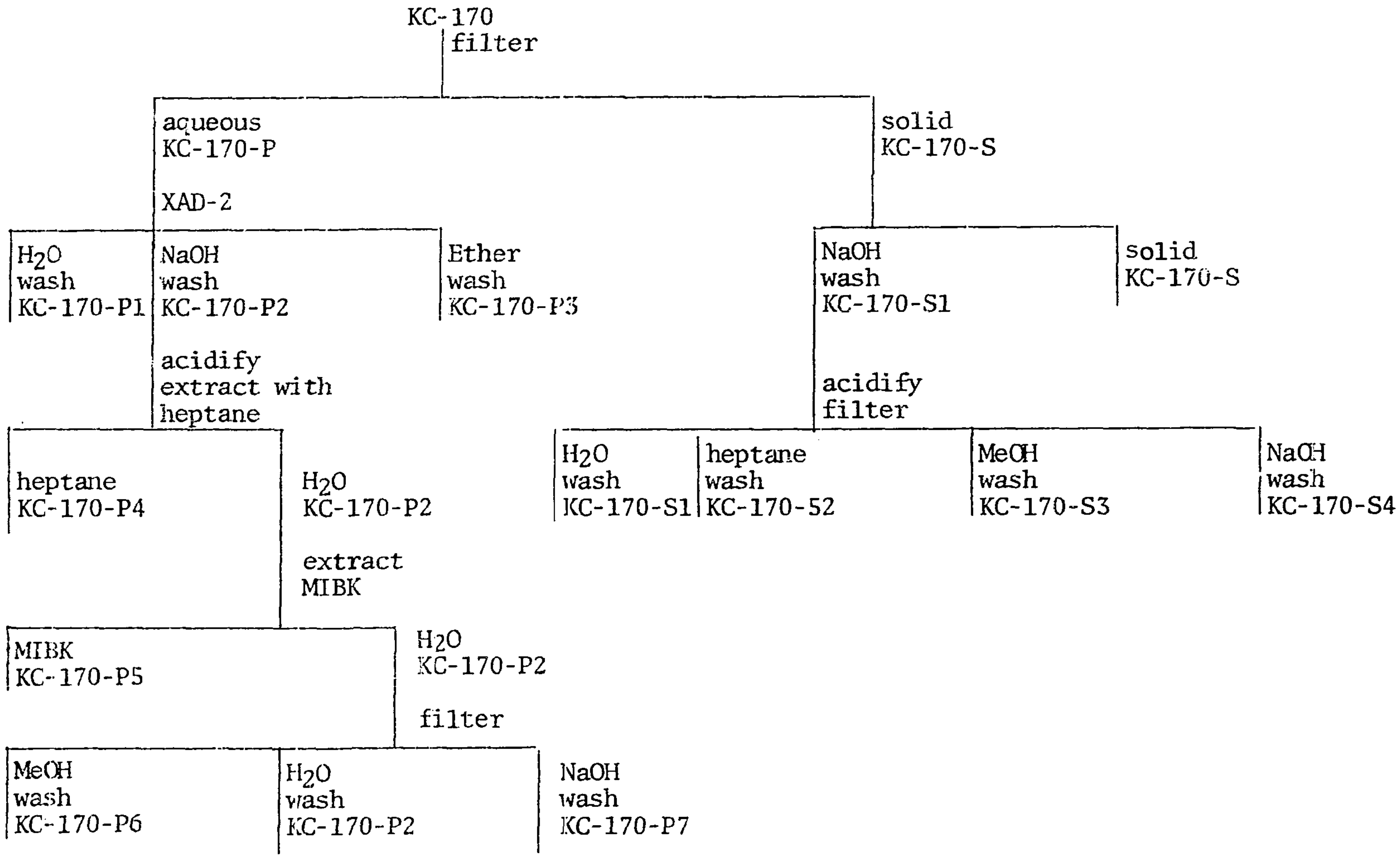

KC-170
filter
aqueous
KC-170-P
XAD-2
solid
KC-170-S
H_2O
wash
KC-170-P1
NaOH
wash
KC-170-P2
Ether
wash
KC-170-P3
acidify
extract with
heptane
NaOH
wash
KC-170-S1
solid
KC-170-S
acidify
filter
heptane
KC-170-P4
H_2O
KC-170-P2
extract
MIBK
H_2O
wash
KC-170-S1
heptane
wash
KC-170-52
MeOH
wash
KC-170-S3
NaOH
wash
KC-170-S4
MIBK
KC-170-P5
H_2O
KC-170-P2
filter
MeOH
wash
KC-170-P6
H_2O
wash
KC-170-P2
NaOH
wash
KC-170-P7

Table 2. Results obtained for the fractionation of sample KC-170

Sample Weight (g.)	Boiling Point $HClO_4$ (°C)	Acidic Fraction of Solid (percentage of sample)	Weight S1, S2, S3 & S4 (mg.)	Weight P4 (mg.)	Weight P5 (mg.)	Carbon Collected as CO_2 (percentage of sample)	Weight Undissolved Solid KC-170-S (mg.)
0.9914	170	7.19	71.3	0.2	98.6	13.48	35.9

retained. KC-°C-S was extracted with heptane in a soxhlet extractor for 8 hrs. KC-°C-S was dried and weighed to determine the weight of the heptane soluble fraction (KC-°C-S5).

Upon standing, KC-130-P through KC-180-P developed a precipitate. The precipitate was filtered. The filtrate (KC-°C-P) was retained. The solid (KC-°C-PS) was washed with heptane into a weighed 25-ml. flask. The heptane washings (KC-°C-PS1) were evaporated to dryness and weighed. The precipitate was washed with methanol into a weighed 25-ml. flask until the washings were colorless. The methanol washings (KC-°C-PS2) were evaporated to dryness and weighed. The precipitate was washed with 0.05 N sodium hydroxide. The precipitate was completely dissolved by the sodium hydroxide. The sodium hydroxide washings (KC-°C-PS3) were retained.

A flow chart for KC-°C appears in Fig. 11. Results for KC-°C appear in Tables 3 and 4.

C. Discussion

Some of the results for KC-°C have been plotted in Fig. 12. This figure gives an indication of the type of material recovered from the reaction of perchloric acid with the kerogen concentrate. The insoluble solid consisted of unreacted kerogen and inorganic minerals which still remain in the concentrate. The soluble solid consisted of solid organic oxidation products which had been solubilized by organic solvents or an aqueous sodium hydroxide solution. Carbon collected as carbon dioxide was the carbon in the sample oxidized completely to carbon dioxide. The total sample recovered represented the sum of the insoluble solid,

Figure 11. Flow chart of fractionation of oxidation products

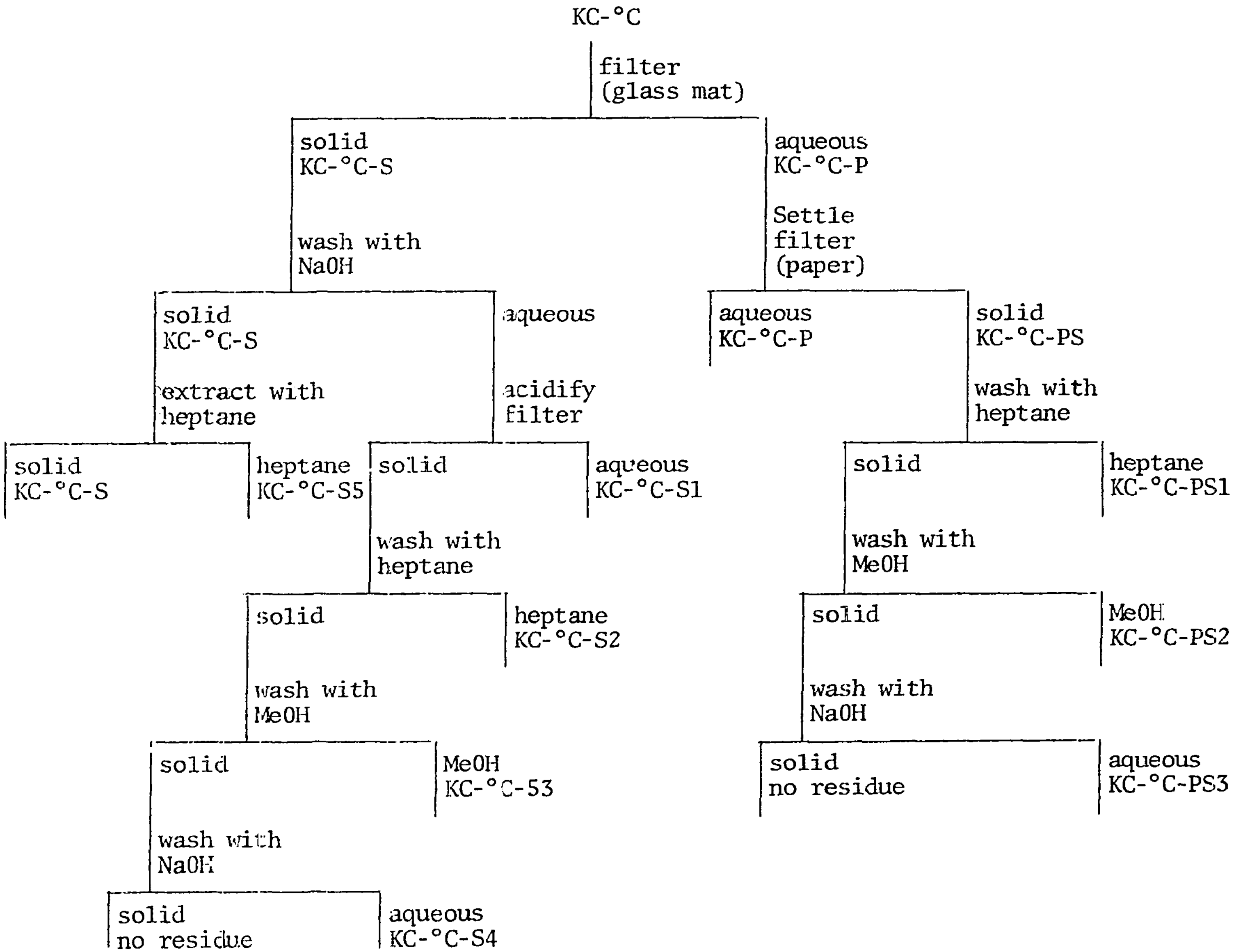

KC-°C
filter
(glass mat)
solid
KC-°C-S
wash with
NaOH
aqueous
KC-°C-P
Settle
filter
(paper)
solid
KC-°C-S
extract with
heptane
aqueous
acidify
filter
aqueous
KC-°C-P
solid
KC-°C-PS
wash with
heptane
solid
KC-°C-S
heptane
KC-°C-S5
solid
wash with
heptane
aqueous
KC-°C-S1
solid
wash with
MeOH
heptane
KC-°C-PS1
solid
wash with
MeOH
heptane
KC-°C-S2
solid
wash with
NaOH
MeOH
KC-°C-PS2
solid
wash with
NaOH
MeOH
KC-°C-53
solid
no residue
aqueous
KC-°C-PS3
solid
no residue
aqueous
KC-°C-S4

Table 3. Results for the fractionation of the oxidation products

Sample Number	Sample Weight (g.)	Weight S1, S2, S3 & S4 (mg.)	Weight S2 (mg.)	Weight S3 (mg.)	Weight S4 (mg.)	Weight S5 (mg.)	Weight PS1 (mg.)	Weight PS2 (mg.)	Weight Insoluble Solid, S (g.)
KC-110	1.0260	11.4	0.0	5.0	6.4				1.0423
KC-120	1.0189	30.0	0.0	3.0	27.0	13.9			1.0297
KC-130	0.9924	44.1	0.0	2.6	41.5	7.3	1.1	4.6	0.9634
KC-141	1.0225	47.1	0.0	3.7	43.4	10.4	1.1	22.9	0.9886
KC-150	1.0124	50.7	0.0	26.8	23.9	42.9	1.2	8.9	0.9518
KC-161	1.0250	111.3	0.6	71.1	40.2	0.6	1.1	139.3	0.6823
KC-169	1.0095	164.8	0.0	63.0	101.8	16.6	0.9	78.6	0.0550
KC-180	0.9838	8.4	0.0	8.8	-	4.9	0.8	27.1	0.0101
KC-190	1.0004	5.4	0.6	6.0	-	0.1			0.0174

Table 4. Results for the fractionation of the oxidation products as a percentage of the sample

Sample Number	Boiling Point $HClO_4$ (°C)	Carbon Collected as CO_2 (percentage of sample)	S1, S2, S3 & S4 PS1 & PS2 (percentage of sample)	Insoluble Solid (percentage of sample)	Total Material Recovered (percentage of sample)
KC-110	110	0.26	1.1	101.6	103.8
KC-120	120	0.31	2.9	101.1	104.4
KC-130	130	0.47	5.0	97.1	102.6
KC-141	141	0.92	7.0	96.7	104.6
KC-150	150	1.96	6.0	94.0	102.0
KC-161	161	8.28	24.6	67.4	100.3
KC-169	169	21.00	24.2	5.5	50.7
KC-180	180	39.78	3.7	1.0	44.5
KC-190	190	50.32	0.5	1.7	52.6

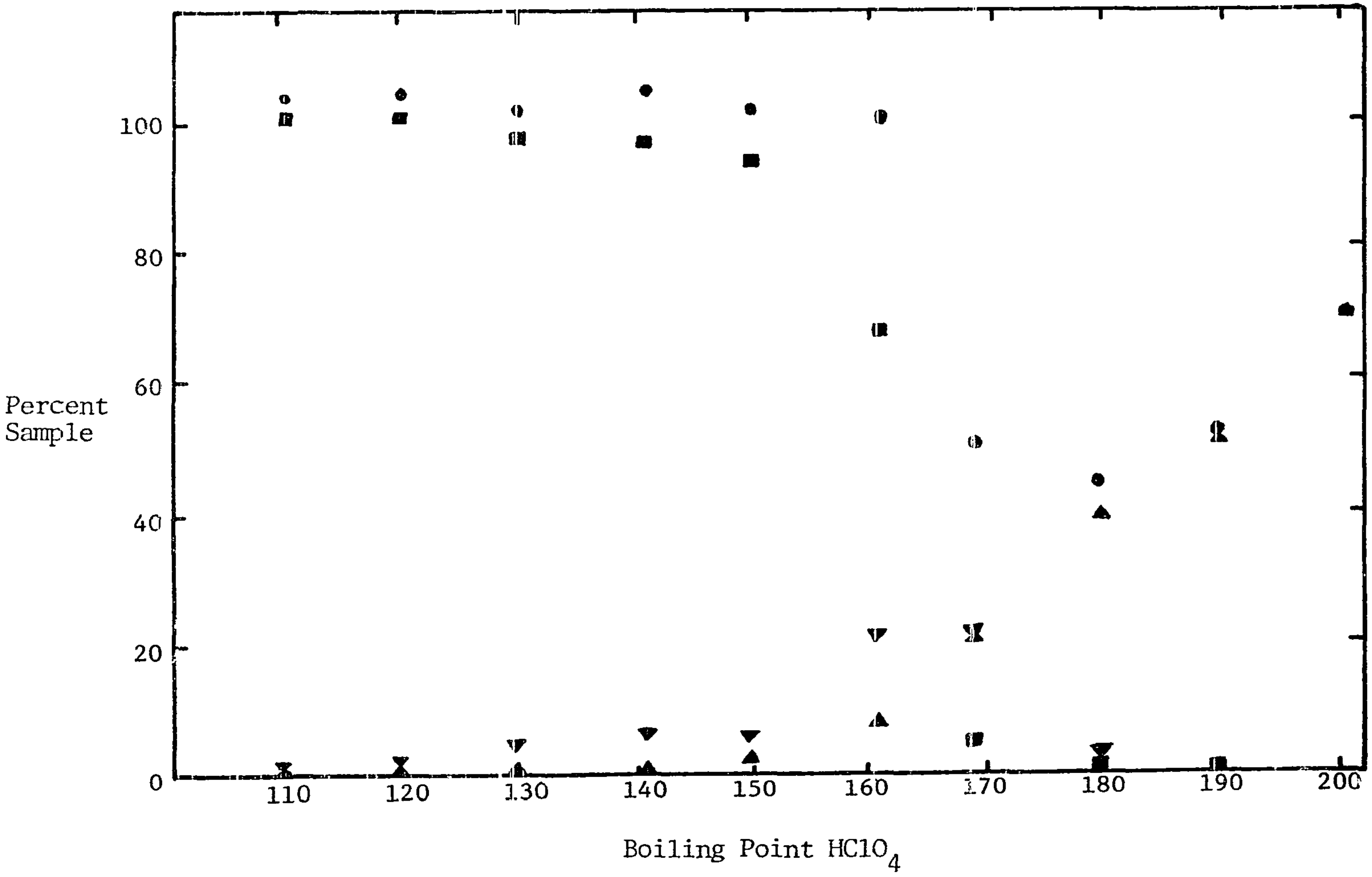
Figure 12. Oxidation products recovered versus boiling point of perchloric acid

▲ Carbon collected as carbon dioxide

◧ Insoluble solid

▼ Soluble solid

◐ Total sample recovered


Percent Sample
0
20
40
60
80
100
110
120
130
140
150
160
170
180
190
200
Boiling Point $HClO_4$

soluble solid and carbon collected as carbon dioxide. The total sample recovered did not include any material volatilized as a neutral gas or solubilized in the perchloric acid solution. Materials in the perchloric acid solution included organic oxidation products and inorganic minerals dissolved by perchloric acid.

At boiling points below 150°, little reaction took place. Most of the sample was recovered as insoluble solid. At a boiling point of 161°, some reaction had taken place; however, most of the sample was recovered indicating only a small amount of the sample was in the aqueous phase. At a boiling point of 169°, the insoluble solid had dropped to less than 6 per cent of the sample. The production of carbon dioxide had increased and the amount of sample recovered as soluble solid was maximum. However, only 50 per cent of the sample was recovered, indicating that a large portion of the sample was in the aqueous phase. At boiling points of 180° and 190°, the total amount of insoluble solid and soluble solid had dropped to less than 5 per cent of the sample. The production of carbon dioxide increased with increasing temperature. At a boiling point of 202°, all of the sample recovered was recovered as carbon dioxide. Since few organic materials are resistant to oxidation to carbon dioxide by boiling concentrated perchloric acid (61), there was little or no organic material present in the aqueous phase. The 30 per cent of the sample that remained in solution or was volatilized as a neutral gas consisted of the inorganic minerals and the hydrogen, oxygen, nitrogen and sulfur of the organic kerogen. The minimum in the curve for the total sample recovered occurred at 169° and 180° and should correspond to the aqueous phases which contain the highest amount of soluble organic oxidation products. The aqueous phases from the reactions at 169° and 180° were the aqueous phases which had the highest color intensity and the highest fluorescent intensity. The largest amount of recoverable organic oxidation products were obtained from reactions at 161°, 169°, and 170°.

The oxidation products isolated consisted of three types. The first type was the acidic fraction isolated from the undissolved material. The resulting solid acids were divided into three fractions. Any non-polar acids, such as long chain fatty acids were dissolved by heptane (KC-°C-S2). There was no evidence that any material was extracted by heptane. Polar acids were then extracted with methanol (KC-°C-S3). The remaining acids were redissolved in 0.05 N sodium hydroxide (KC-°C-S4). Both KC-°C-S3 and KC-°C-S4 were dark brown in color. The polar fractions of KC-180 and KC-190 were lighter in color than the polar fractions of the other reactions.

The second type of oxidation product was the solid material which settled out of the aqueous phase. This material either passed through the original filtration or precipitated from the aqueous phase upon standing or dilution with water. Experiments with KC-170 indicated that this material was acidic. This material was filtered and divided into three fractions described above. There was some evidence for a non-polar, heptane soluble material (KC-°C-PS1). The non-polar fraction was very small and colorless. The methanol soluble material (KC-°C-PS2) and sodium hydroxide soluble material (KC-°C-PS3) were dark brown in color. This material appeared to be the same as the S3 and S4 fractions isolated above.

The third type of material isolated was the neutral, non-polar fraction of the undissolved material. This heptane soluble fraction (KC-°C-S5) should have contained any low molecular weight neutral compounds or weakly acidic compounds, possibly long chain fatty acids. Very little material was extracted by heptane.

All of the fractions isolated were fluorescent. Most of the oxidation products isolated were represented by the S3, S4, PS2, and PS3 fractions. The PS2 and PS3 fractions appeared to be very similar to the S3 and S4 fractions. The material consisted of dark brown acids which were insoluble in heptane and aqueous acid. The acids were slightly soluble in water. Some of the acids were soluble in methanol. All of the acids were soluble in sodium hydroxide. The solubility characteristics were similar to humic acids. The acids were probably high molecular weight and polyfunctional. Robinson and co-workers (41, 42, 43, 44) have reported similar types of acids as a result of the oxidation of Green River oil shale with alkaline permanganate. Robinson and co-workers (41, 43, 44) concluded that these acids were high molecular weight, polyfunctional, and primarily cyclic and heterocyclic. Most of the acids were di- and tri-nuclear cyclic compounds.

VI. ANALYSIS OF OXIDATION PRODUCTS

A. Introduction

The oxidation products which were separated into neutral, acidic, polar and non-polar fractions were characterized by potentiometric titration with base, proton magnetic resonance spectra, infrared spectra, mass spectra, X-ray excited optical luminescence and gas chromatography. The S3, PS2, S5, and PS1 fractions were analyzed. The S3 fraction was composed of methanol-soluble acids derived from the undissolved material. The PS2 fraction was composed of methanol-soluble acids derived from the solid material which formed in the aqueous phase. The S5 fraction was composed of heptane-soluble neutral components derived from the undissolved material. The PS1 fraction was composed of heptane-soluble acids derived from the solid material which formed in the aqueous phase.

B. Titrations

Several of the S3 and PS2 fractions, for which there was sufficient material, were titrated with sodium hydroxide to determine the equivalent weight. A carbonate-free standard 0.01 N sodium hydroxide solution was prepared from 50 per cent sodium hydroxide. Water, which had been boiled, was used to dilute the sodium hydroxide solution. The standard solution was stored under nitrogen. A 10-mg. sample of the oxidation product was weighed and dissolved in 4 to 6 ml. of dimethylsulfoxide. The sample was diluted to 20 ml. with water. Nitrogen was bubbled through the solution for 5 min. The dissolved acids did not reprecipitate.

The sample was then titrated under nitrogen with the standard 0.01 N sodium hydroxide solution. The titrant was delivered from a 5-ml. buret which could be read to ±0.005 ml. The end-point was determined potentiometrically using a combination glass and saturated calomel electrode. The pH meter stabilized within seconds after the addition of an aliquot of the titrant. The titration curve was smooth and had only one break. The buffer region was not particularly flat.

The results for the titrations appear in Table 5. An example of a titration curve appears in Fig. 13. The equivalent weight of the acids extracted from the solid phase (S3) was higher than the acids derived from the aqueous phase (PS2). There was a trend for the equivalent weight to decrease as the boiling point of perchloric acid increased. The shape of the titration curve in the buffer region indicated a wide range of pK_a values for the acids.

C. Proton Magnetic Resonance Spectra

Several attempts were made to determine the proton magnetic resonance (PMR) spectra of the S3 and PS2 fractions. A variety of solvents were used including D_6-acetone, D_6-dimethylsulfoxide and D_4-methanol. The PMR spectra was recorded on a Varian A-60 spectrometer. However, only signals due to solvents were observed.

D. Infrared Spectra

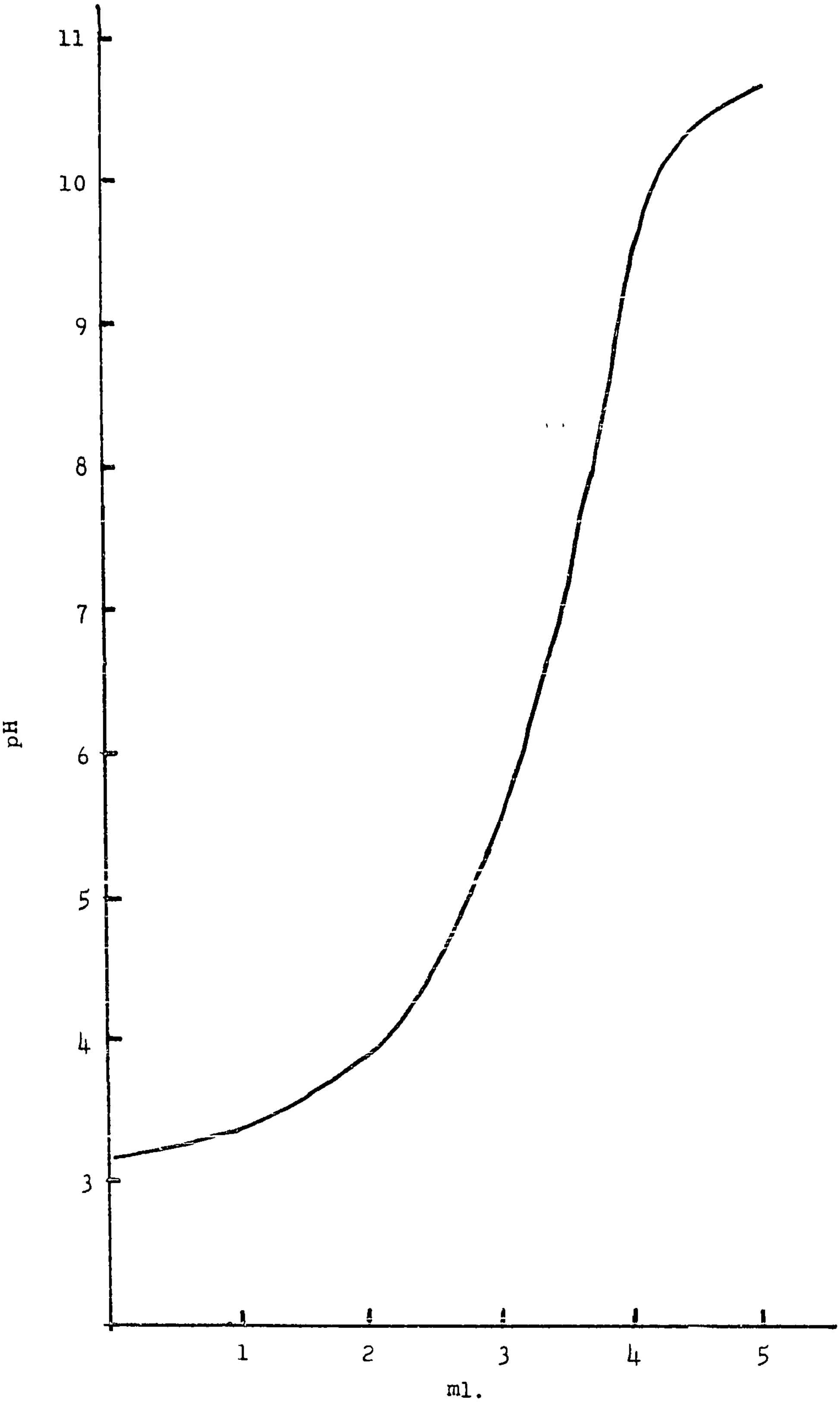
The infrared (IR) spectra was recorded for all S3 and PS2 fractions. A portion of the fraction was dissolved in methanol. A few drops of the

Table 5. Results of the potentiometric titrations of selected PS2 and S3 fractions

Sample	Equivalent Weight (g./eq.)
KC-161-S3	373
KC-169-S3	293
KC-161-PS2	236
KC-169-PS2	183

Figure 13. Titration of KC-169-S3 with standard sodium hydroxide

Sample weight	8.0 mg.
N NaOH	0.0117 N
End-point	3.74 ml.
Equivalent weight	183 g./eq.


11
10
9
8
7
6
5
4
3
pH
1
2
3
4
5
ml.

solution were placed on a sodium chloride plate. The methanol was evaporated under a stream of nitrogen to form a thin film of the product. The spectra was recorded on a Beckman IR 4350 spectrophotometer. A spectra of methanol was also recorded.

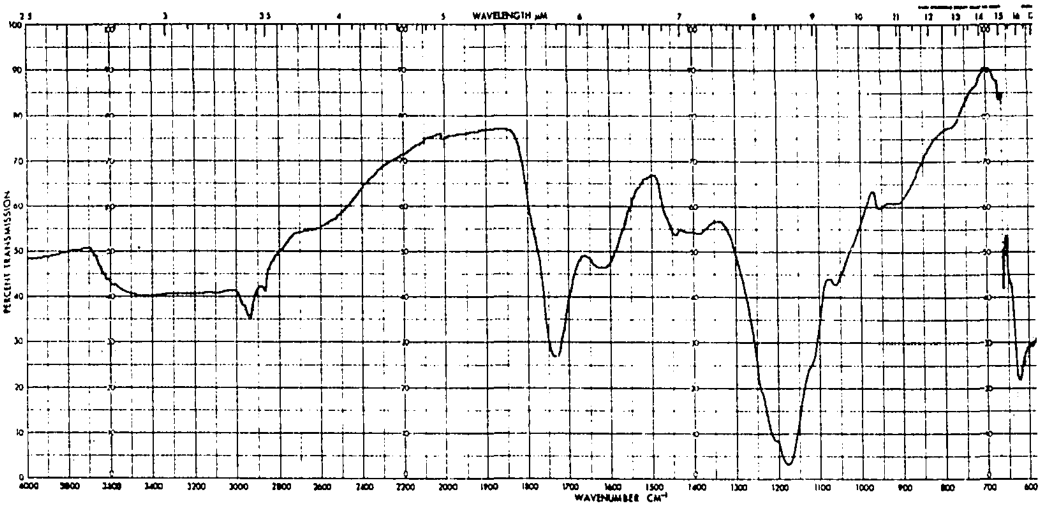
Some of the IR spectra appear in Fig. 14. Band assignments appear in Table 6. No distinct methanol peaks were observed in the spectra of the oxidation products. The peaks observed in the IR spectra of the oxidation products were generally broad and not well defined. The spectra were typical of aliphatic carboxylic acids. The broad band covering the region from 2500 cm.$^{-1}$ to 3600 cm.$^{-1}$ and the band from 900 cm.$^{-1}$ to 950 cm.$^{-1}$ were characteristic of carboxylic acids. The band from 1700 cm.$^{-1}$ to 1750 cm.$^{-1}$ was in the range of the carbonyl stretch of carboxylic acids and ketones. The band from 1600 cm.$^{-1}$ to 1650 cm.$^{-1}$ was in the range of carboxylate ions and aldehydes. The broad band occurring from 1100 cm.$^{-1}$ to 1300 cm.$^{-1}$ was at a lower wave number than the characteristic range for carboxylic acids (1210 cm.$^{-1}$ - 1320 cm.$^{-1}$). However, the C-O stretching band is subject to change in environment which may account for the shift to lower wave number (47). This band was in the range for the C-O stretch for ethers. The band from 1350 cm.$^{-1}$ to 1450 cm.$^{-1}$ was characteristic of carboxylic acids and methylene groups. The bands at 2800 cm.$^{-1}$ to 2850 cm.$^{-1}$ and 2900 cm.$^{-1}$ to 2950 cm.$^{-1}$ were characteristic of methylene groups. The band from 2950 cm.$^{-1}$ to 3000 cm.$^{-1}$ did not appear in all the spectra, but was characteristic of the asymmetrical stretching of methyl groups. The corresponding band for the symmetrical stretch of methyl groups (2850 cm.$^{-1}$ to 2900 cm.$^{-1}$) did not appear in any of the spectra.

Figure 14. Representative infrared spectra of fractions of the oxidation products

a. KC-161-S3

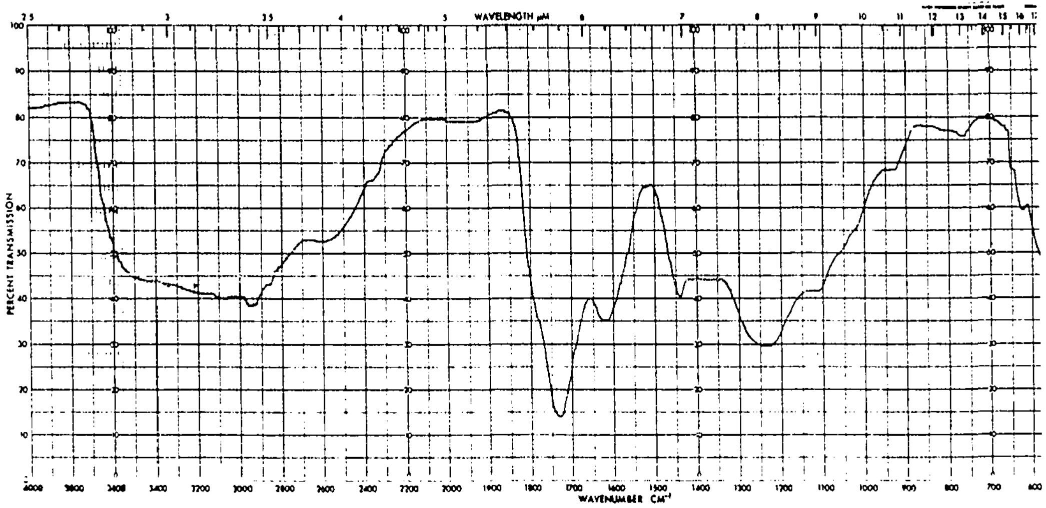
b. KC-169-PS2

c. KC-190-S3



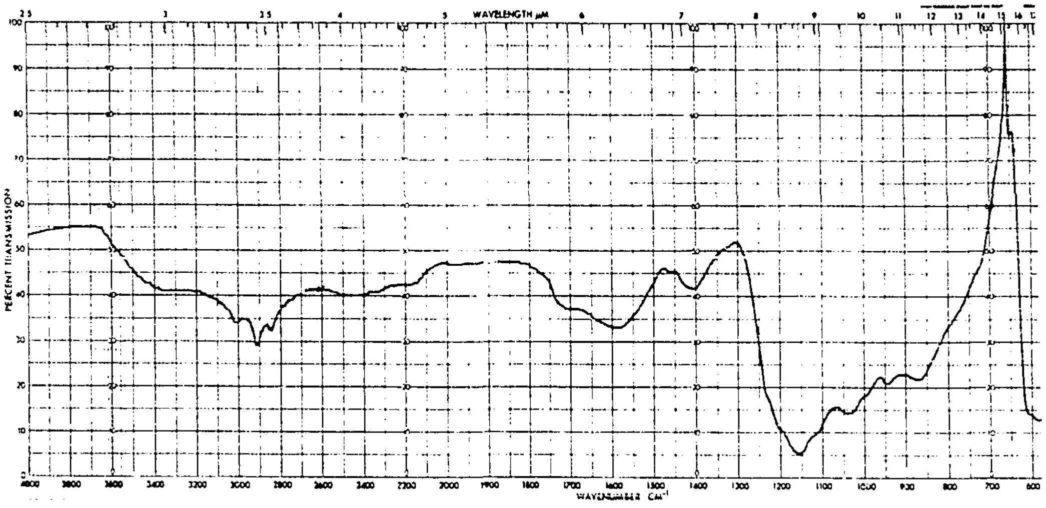
a

WAVELENGTH μM
2.5 3 3.5 4 5 6 7 8 9 10 11 12 13 14 15 16
PERCENT TRANSMISSION
0 10 20 30 40 50 60 70 80 90 100
WAVENUMBER CM⁻¹
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600



b

WAVELENGTH μM
2.5 3 3.5 4 5 6 7 8 9 10 11 12 13 14 15 16
PERCENT TRANSMISSION
10 20 30 40 50 60 70 80 90 100
WAVENUMBER CM⁻¹
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600



c

WAVELENGTH μM
2.5 3 3.5 4 5 6 7 8 9 10 11 12 13 14 15 16
PERCENT TRANSMISSION
0 10 20 30 40 50 60 70 80 90 100
WAVENUMBER CM⁻¹
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600

Table 6. Infrared band assignments[a]

Spectral Band (cm^{-1})	Transition
900-950	OH out of plane bend
1100-1300	C-O stretching
1350-1450	CH_2 bend, COH in plane bend
1600-1650	C = O stretch
1700-1750	C = O stretch
2800-2850	CH_2 symmetrical stretch
2900-2950	CH_2 assymmetrical stretch
2950-3000	CH_3 assymmetrical stretch
3000-3020	aromatic CH stretch
2500-3600	OH stretch

[a] Band assignments were made from Silverstein, Bassler and Morrill (47).

However, because most of the peaks in this region were small and broad the methyl stretching bands may be hidden under the methylene stretching bands. The band from 3000 cm.$^{-1}$ to 3020 cm.$^{-1}$, characteristic of the C-H stretch in aromatic compounds, appeared only in the spectra of KC-190-S3.

E. Mass Spectrometry

Mass spectra were recorded for all the PS2 and S3 samples. The mass spectra were recorded using a Finnigan 4000 GC-MS-data system.[1] The mass spectra of KC-170-S3 was recorded using an AEI MS 190. Since samples were non-volatile, a subambient programmable direct insertion probe was used. Ion currents were not observed until the probe had been heated to a temperature of 260°. A spectrum was obtained and useful information was derived.

The highest mass observed for each fraction is recorded in Table 7. The highest mass observed was generally higher than the corresponding average equivalent weight. Because of the high temperatures used it was concluded that the peaks observed were breakdown products of each fraction and not molecular ions. This indicated that the oxidation products contained more than one replaceable hydrogen atom per molecule.

The spectra of all the fractions were very similar. The spectra of KC-169-S3 and KC-169-PS2 are shown in Figs. 15 and 16. The spectra were typical of alkyl carboxylic acids with several series of peaks at intervals of 14 mass units, corresponding to a difference of

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[1] Support for the funding of the Finnegan 4000 came from NSF.

Table 7. Maximum mass unit observed in the mass spectrum of the S3 and PS2 fractions

Sample	Mass (m/e)
KC-130-S3	447
KC-130-PS2	313
KC-141-S3	447
KC-141-PS2	446
KC-150-PS2	303
KC-161-S3	282
KC-161-PS2	370
KC-169-S3	322
KC-169-PS2	303
KC-170-S3	428
KC-180-S3	303
KC-180-PS2	286
KC-190-S3	304

Figure 15. Mass spectrum of KC-169-S3

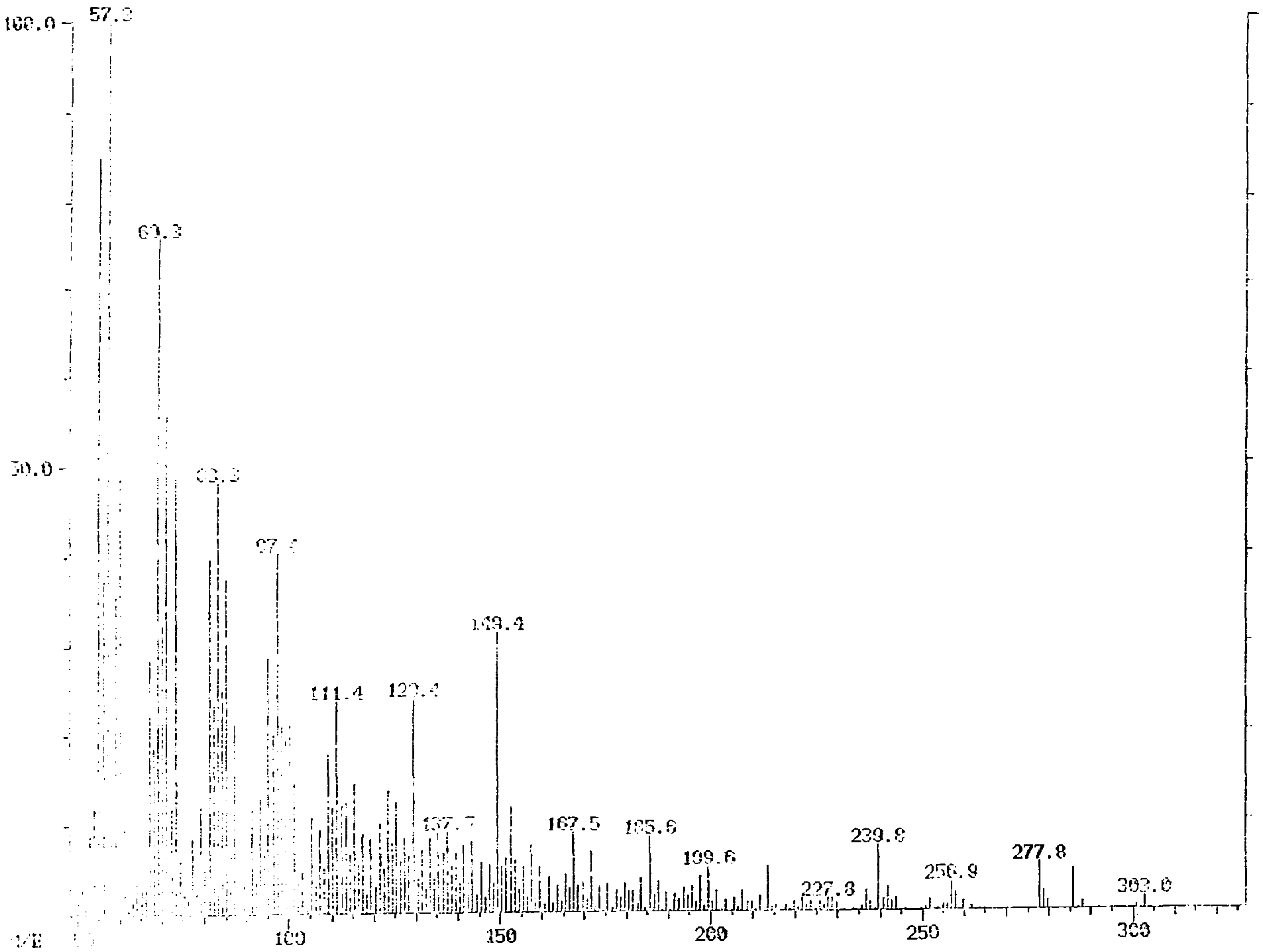
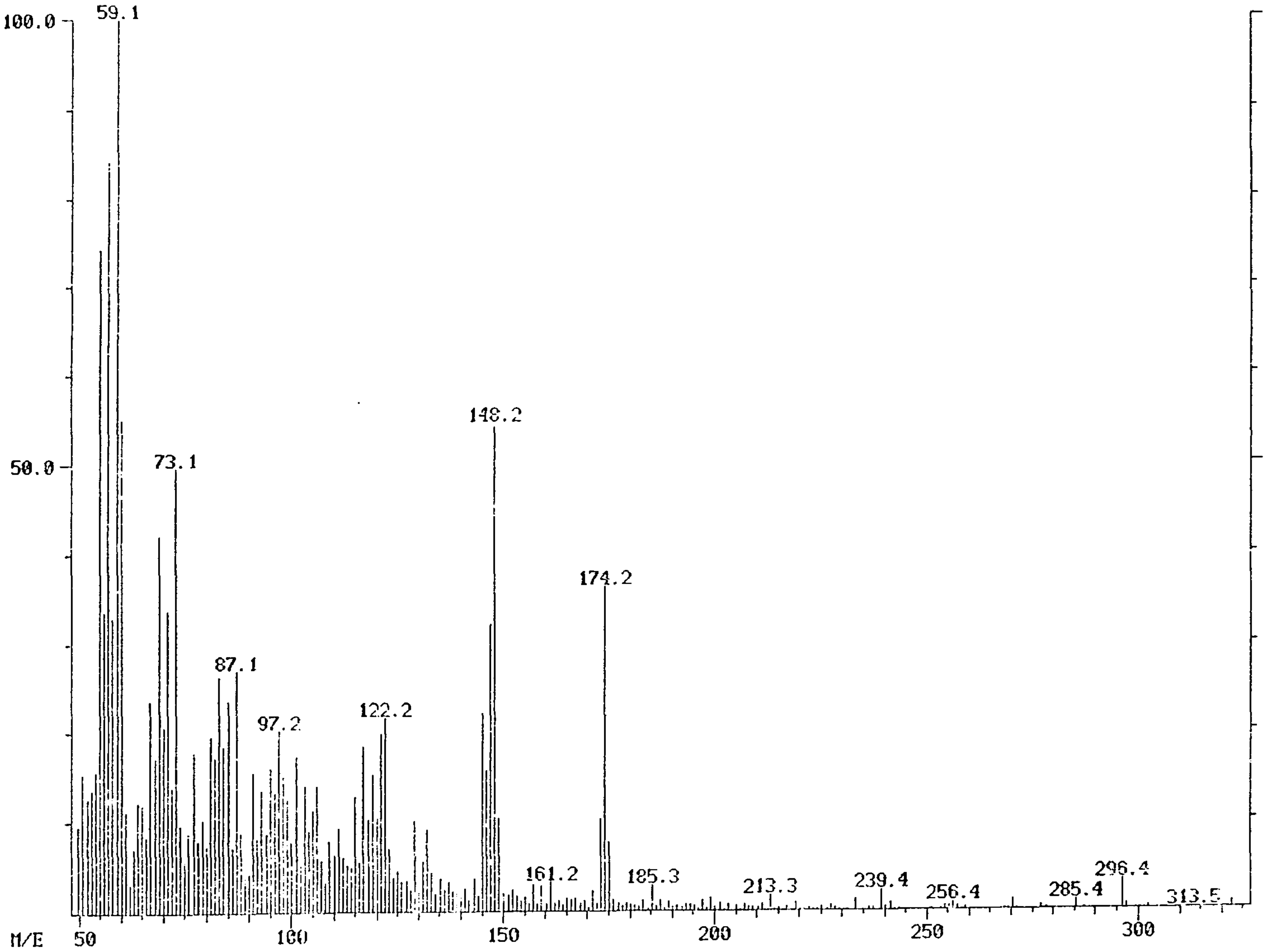
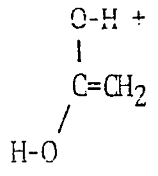

100.0
50.0
57.3
69.3
83.3
97.4
111.4
129.4
137.7
149.4
167.5
185.6
199.6
227.3
239.8
256.9
277.8
303.0
M/E
100
150
200
250
300

Figure 16. Mass spectrum of KC-169-PS2

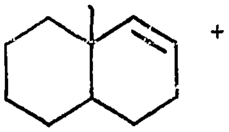

100.0
50.0
59.1
73.1
87.1
97.2
122.2
148.2
161.2
174.2
185.3
213.3
239.4
256.4
285.4
296.4
313.5
M/E
50
100
150
200
250
300

CH_2,methylene. The series of peaks represented by 57, 71, 85, 99, 115, 127, 141, 155, 169, and 183 mass units corresponded to the breakdown of a saturated alkane; the ions causing the peaks had the general formula $C_nH_{2n+1}^+$. A second series of peaks represented by 55, 83, 97, 111, 125, 139, 153 and 167 mass units was the typical breakdown of an alkane with one degree of unsaturation; the ions causing the peaks had the general formula $C_nH_{2n-1}^+$. A third series of peaks represented by 67, 81, 95, 109, 123, 137, 151, 165, 179, 193 and 207 mass units corresponded to the breakdown pattern of an alkane with two degrees of unsaturation; the ions causing the peaks had the general formula $C_nH_{2n-3}^+$. A fourth series typical of fatty acids was represented by masses at 59, 73, 87, 101, 115, 129, 143, 157, 171, 185, 199, 213 and 227 mass units; the ions causing the peaks had the general formula $C_nH_{2n}COOH^+$. A peak at mass unit 60 was characteristic of aliphatic carboxylic acids; the ion causing the peak had the structure:



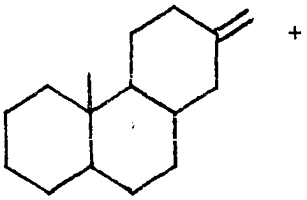
m/e 60

Characteristic peaks for alkyl substituted benzenes, 65, 77 and 91 mass units were present but the intensities were low. In KC-180-S3, KC-180-PS2 and KC-190-S3 the intensity of the peaks at masses 65, 77 and 91 were a little higher. The large peak at mass 149 could be explained as being caused by the ion:



m/e 149

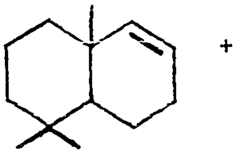
This ion is characteristic of steranes and steroidal structures (8). However, steranes also show a large characteristic ion at mass 217:



m/e 217

This ion was present in most of the spectra but the intensity was low. The most common high masses which occurred were 239, 256, 277 and 303. No explanation of these masses is offered in this dissertation.

The mass spectrum of KC-170-S3, which was made on the AEI MS 190, was somewhat different from the above spectra. The same series described above were present; however, the mass spectrum of KC-170-S3 displayed prominent peaks at masses 149, 191, 203 and 217. The presence of large peaks at 149 and 217 was indicative of the presence of the steroid structure. Peaks at 191 and 203 indicated the presence of the terpanoid structure. Terpanes exhibit a strong peak at mass 191 due to the presence of the ion:



me/ 191

Some terpanes exhibit a strong peak at mass 203 due to the addition of one carbon to the ion for mass 191 (22).

As a result of the mass spectra, several types of compounds were indicated in the oxidation products. The series $C_nH_{2n+1}^+$ and $C_nH_{2n}COOH^+$ were evidence for the presence of long chain alkyl groups. This was not conclusive evidence that long chain fatty acids were present as both the alkyl and the carboxyalkyl group could have been attached to some other nucleus. The series of peaks corresponding to one degree of unsaturation, $C_nH_{2n-1}^+$, was the most prominent series in the spectra. As the mass increased the series corresponding to two degrees of unsaturation, $C_nH_{2n-3}^+$, became more prominent. This was strong evidence for the presence of ring structures. This series of peaks could have resulted from the presence of either rings or double bonds. From a chemical standpoint, the presence of double bonds was highly unlikely. Double bonds were probably destroyed during the preparation of the sample. Double bonds could have been produced on the direct insertion probe as a result of the heating process. There was evidence for the presence of steroid and terpanoid structures. There was some evidence for the presence of aromatic compounds.

F. X-ray Excited Optical Luminescence

KC-160-S5, KC-190-S5 and a sample prepared by Soxhlet extraction of the kerogen concentrate with heptane were analyzed by X-ray excited optical luminescence (XEOL). KC-160-S5 and the sample extracted from the unreacted concentrate gave a blue fluorescence when excited by ultraviolet light. KC-190-S5 also gave a blue fluorescence but the intensity was very low.

The instrument used for the analysis was built at Iowa State University. For analysis by XEOL, the sample, dissolved in heptane, was placed in a sample holder and cooled to 77°K. Excitation by X-rays resulted in fluorescence. The fluorescence was recorded as a function of wavelength. XEOL has two advantages over conventional fluorescence analysis. Narrow emission bands are observed instead of broad fluorescent bands and the use of X-rays eliminates error caused by stray light from the excitation source reaching the detector.

The results of XEOL analysis for KC-160-S5 and the sample extracted from the kerogen concentrate showed two fluorescent bands at 325 nm. and 340 nm. No fluorescent bands were observed for KC-190-S5. The two peaks at 325 nm. and 340 nm. were exactly the same as the corresponding spectra for napthalenes and biphenyls. This indicated the presence of similar compounds in the oil shale. The disappearence of these two peaks in the spectrum of KC-190-S5 coincided with the appearance of aromatic hydrogens in the infrared spectrum of KC-190-S3. It must be noted that the fluorescence observed in all oxidation products could result from trace concentrations of aromatic compounds.

G. Gas Chromatography

Several of the S5 and all of the PS1 fractions were esterified and analyzed by gas chromatography.

Each fraction was evaporated to dryness under a stream of nitrogen. Five ml. of a solution of methanol containing 14 per cent boron trifluoride was added to each fraction and boiled for 5 min. on a hot plate. The esters were extracted with two 5-ml. portions of pentane. The volume of the pentane extracts was reduced to 2 ml. under a stream of nitrogen. The pentane extract was then analyzed on a Hewlett-Packard 5700A gas chromatograph. A 6-ft., 1/8 in. column packed with 3 per cent OV-1 on Chromosorb W was used. The column was temperature programmed from 150° to 250°. A flame ionization detector was used. Mixtures of standard methyl esters, containing the esters of fatty acids C_8-C_{22} were also chromatographed.

The pentane extracts of KC-169-S5 and KC-169-PS1 were chromatographed on a Finnegan 4000 GC-MS-data system. Column conditions were identical to those described above. Mass spectra were recorded for the major peaks in each chromatogram.

The chromatograms of the PS1 fractions were essentially identical. The chromatograms of the S5 fractions were more complex; however, the major peaks were the same as the peaks in the chromatograms of the PS1 fractions.

The chromatograms of KC-169-S5 and KC-169-PS1 obtained using the Finnegan 4000 are shown in Figs. 17 and 18. Each of the numbered peaks in Figs. 17 and 18 is listed in Table 8 with the identity of the peak or a characteristic of the mass spectrum corresponding to the peak. The analysis of the mass spectra of the various peaks in the chromatograms proved an interesting problem. Because the sample size was very small, the ion current from the background was often several times larger than the ion current of the peaks. The large number of overlapping peaks also contributed to the large ion currents from the background. For

Figure 17. Gas chromatogram of esterified KC-169-S5

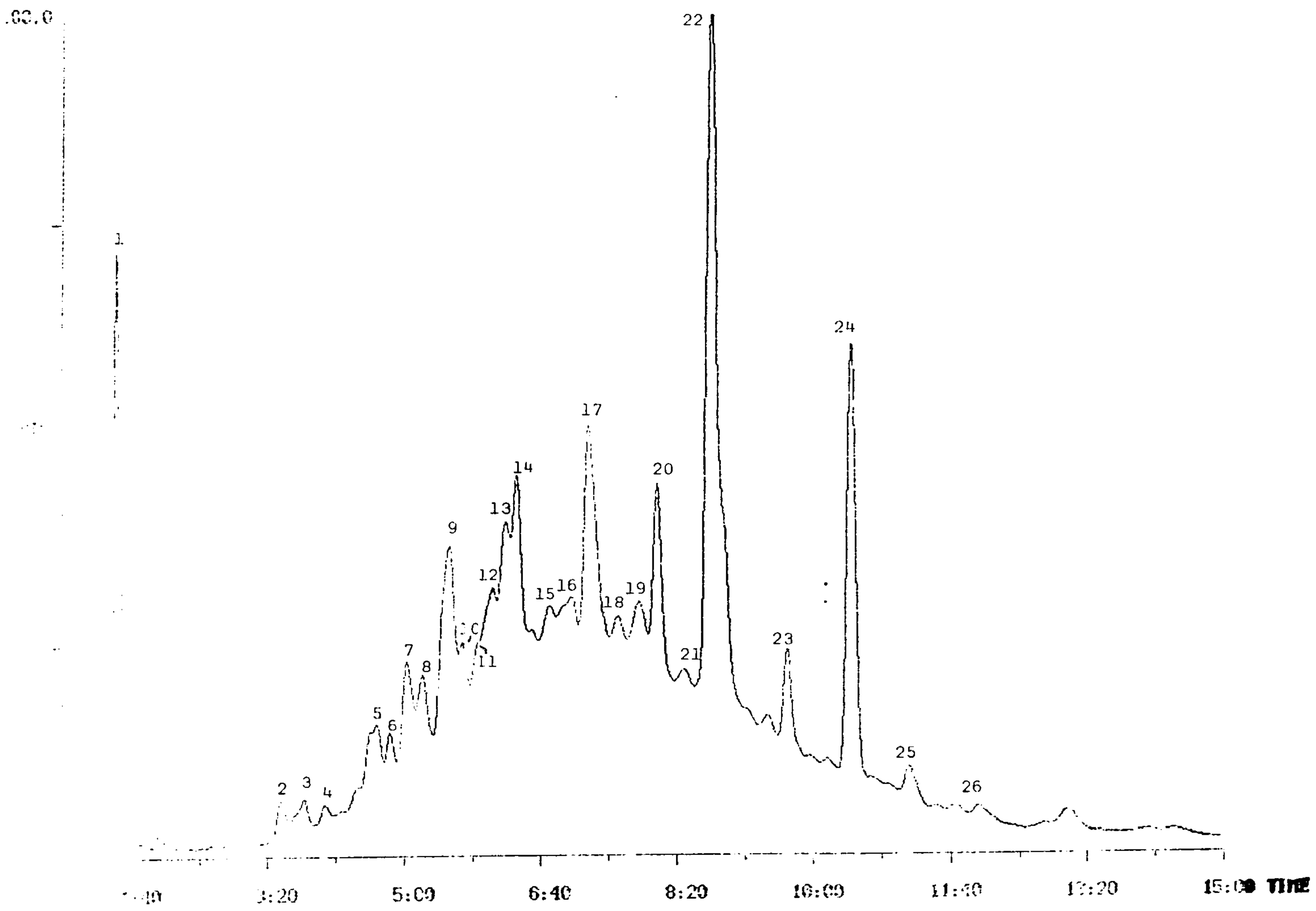

100.0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
1:40
3:20
5:00
6:40
8:20
10:00
11:40
13:20
15:00 TIME

Figure 18. Gas chromatogram of esterified KC-169-PS1

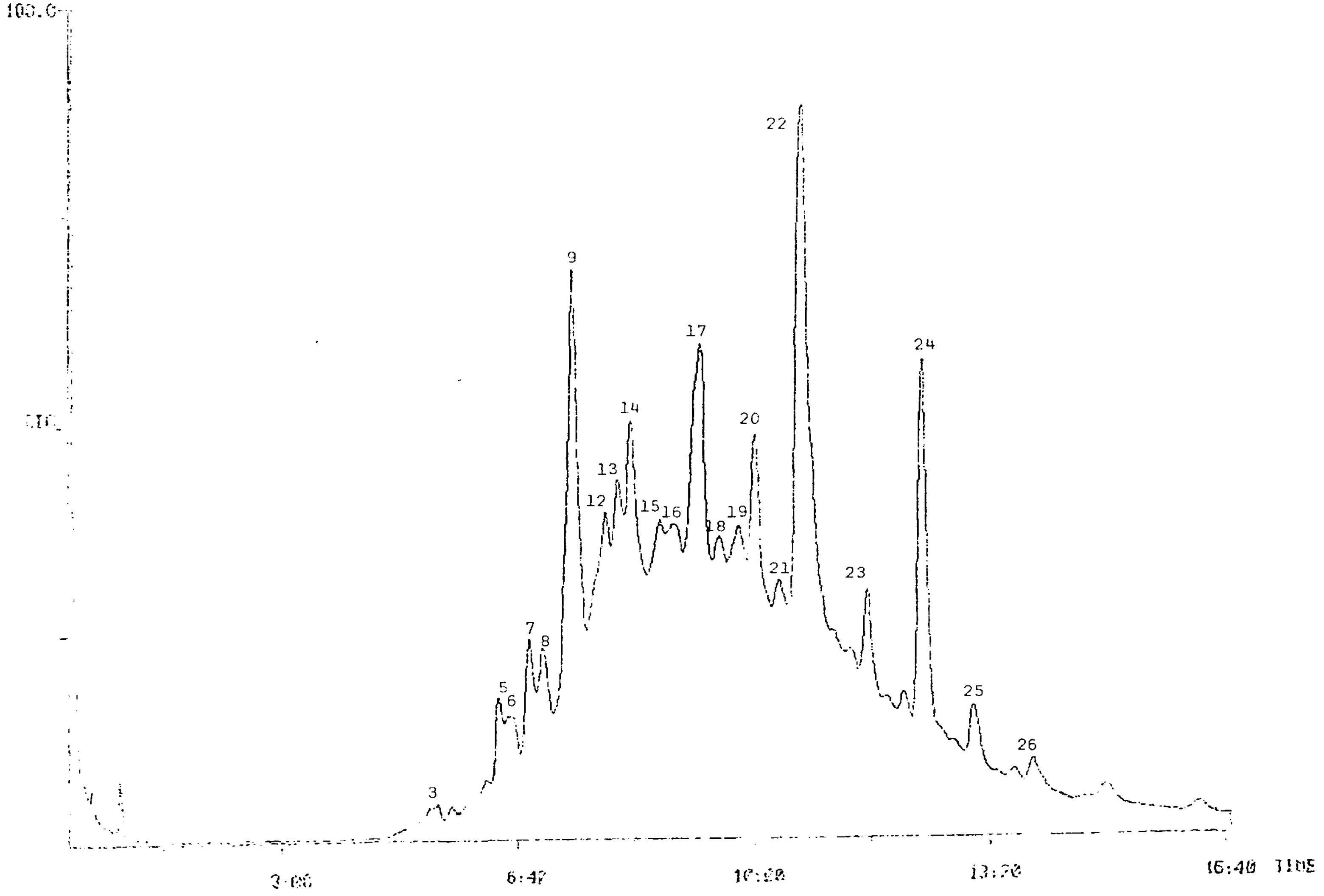

100.0
TIC
3
5
6
7
8
9
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
3:20
6:40
10:00
13:20
16:40 TIME

Table 8. Identification of peaks in the gas chromatograms of KC-169-S5 and KC-169-PSI

Peak number	Identification
1	dimethyl phthalate
2	substituted dimenthyl phthalate
3	methyl tetradecanoate
4	saturated C_{15} methyl ester phenanthrene
5	methyl pentadecanoate $C_{18}H_{38}$
6	unsaturated alkyl group
7	a methyl phenanthrene
8	a methyl phenanthrene
9	methyl hexadecanoate $C_{19}H_{40}$
10	unsaturated alkyl group
11	saturated alkyl group
12	unsaturated alkyl group
13	methyl heptadecanoate a dimethyl phenanthrene
14	$C_{20}H_{42}$
15	a dimethyl phenanthrene
16	saturated alkyl group
17	methyl octadecanoate $C_{21}H_{44}$
18	saturated alkyl group
19	saturated alkyl group
20	$C_{22}H_{46}$
21	saturated alkyl group
22	aromatic
	$C_{23}H_{48}$
	Saturated C_{19} methyl ester

Table 8. (continued)

Peak number	Identification
23	$C_{24}H_{50}$
24	aromatic $C_{25}H_{52}$
25	$C_{26}H_{54}$
26	$C_{27}H_{56}$

example, the mass spectra of peaks 11 through 15 appeared identical upon casual observation; however, close inspection of the mass spectra revealed the presence of several different kinds of compounds. Unresolved peaks also posed a problem. For example peaks 9 and 22 appear to contain unresolved shoulders. Close examination of the mass spectra indicated the presence of two different compounds in these peaks. The presence of two compounds in the same peak has been indicated in Table 8.

Methyl esters of n-carboxylic acids (C_{14}-C_{18}) were identified from mass spectral analysis and retention times. Based on retention times the methyl esters of n-carboxylic acids C_{19} and C_{20} were expected in peaks 20 and 22 respectively; however, evidence for these compounds was not found in the mass spectra. The methyl esters of two other saturated carboxylic acids C_{15} and C_{19} were also observed. The dimethyl ester of phthalic acid was identified in KC-169-S5. A series of alkanes (C_{18}-C_{24}) were identified. Phenanthrene, two methyl phenanthrenes and two dimethyl phenanthrenes were identified.

If long chain carboxylic acids existed only in the PS1 and S5 fractions, then this type of acid represented only a small portion of the total oxidation product; approximately 0.1 per cent of the original sample. This recovery of long chain acids is similar to the recoveries of long chain acids obtained by Hoering and Abelson (30), 0.05 per cent of original organic carbon; and Burlingame and co-workers (8, 10, 11) who recovered only 3.6 per cent of the original sample as oxidation products. Both of these studies employed chromic acid oxidation and no other oxidation products were isolated. The results of the present study are in contrast with the work of Djuricic and co-workers (15, 16) and

Young et al. (64, 65) who found 70 per cent long chain acids as a result of alkaline permanganate oxidations. The identification of phthalic acid clearly indicated the presence in the oil shale of fused ring systems of which at least a portion is aromatic. The hydrocarbons identified were probably remnants of the original bitumen.

VII. PROPOSALS

A. Introduction

As a result of the work described in this dissertation several statements can be made concerning the reaction of the kerogen concentrate with perchloric acid and the nature of the kerogen of Green River oil shale.

The amount of soluble oxidation products obtained from the reaction of the kerogen concentrate with perchloric acid varied with the boiling point of the perchloric acid. The largest amount of soluble oxidation products were obtained from reactions with perchloric acid having boiling points of 160° to 170°. However, the nature of the soluble oxidation products obtained, changed very little. The exception being the relative increase in aromatic content as the boiling point increased.

The major oxidation product was a mixture of brown, high molecular weight, carboxylic acids. Analysis by infrared spectometry and mass spectrometry showed that these acids consisted primarily of aliphatic materials containing both saturated carbon chains and cyclic compounds with one to two rings. Infrared analysis also indicated the presence of ether groups. Steroid and terpanoid structures were indicated by mass spectral analysis. Aromatic material containing two aromatic rings were identified by X-ray excited optical luminescence in very low relative concentration. Long chain fatty acids $(C_{14}\text{-}C_{18})$ were identified by gas chromatography, also in low relative concentration. Sulfur and nitrogen are also contained in the organic material.

Of previous workers, only Robinson and co-workers (41, 42, 43, 44) reported similar oxidation products as a result of oxidation with alkaline permanganate. Robinson reported the presence of high molecular weight, brown acids which he concluded were cyclic. The major oxidation products, however, were normal dicarboxylic acids (C_2-C_8). Robinson did not report the presence of n-carboxylic acids or of aromatic materials. Burlingame and co-workers (8, 10, 11) recovered only 3.6 per cent of the original material as oxidation products as a result of oxidation with chromic acid. The major oxidation products were long chain n-carboxylic acids, isoprenoid acids and n-dicarboxylic acids. The production of long chain acids was similar to the production of long chain acids in the present work; however, no other organic material was recovered in the chromic acid oxidations. The results of the present dissertation are in direct contrast to the results of Djuricic and co-workers (15, 16) who reported 70 per cent of the organic material converted to long chain acids.

B. Proposed Method of Oxidation

The author proposes that the attack of perchloric acid on kerogen was surface oriented and random. That is, the kerogen was not clipped at the site of a particular functional group; rather a surface site was attacked by perchloric acid and the attack continued from one carbon to the next. Soluble oxidation products from this kind of attack would be high molecular weight resulting from undercutting the kerogen material. Low molecular weight materials, in the process of being oxidized, would be converted to carbon dioxide sooner than high molecular weight materials. Several experimental results support this hypothesis. First, the type of oxidation product isolated did not vary with increasing oxidation potential, only the amount of oxidation product varied. Thus, with increasing oxidizing ability only the overall rate of reaction was affected. Second, only high molecular weight materials were isolated in high yield. Third, very little saturated long chain carboxylic acids were isolated and identified. However, ions caused by long chain alkyl groups were prominent in the mass spectra of the major oxidation products. Ions of long chain carboxyalkyl groups were also prominent. This indicated that the long chain groups were not clipped from the kerogen nucleus by perchloric acid but that oxidation was occurring along the carbon chain.

C. Proposed Structural Model

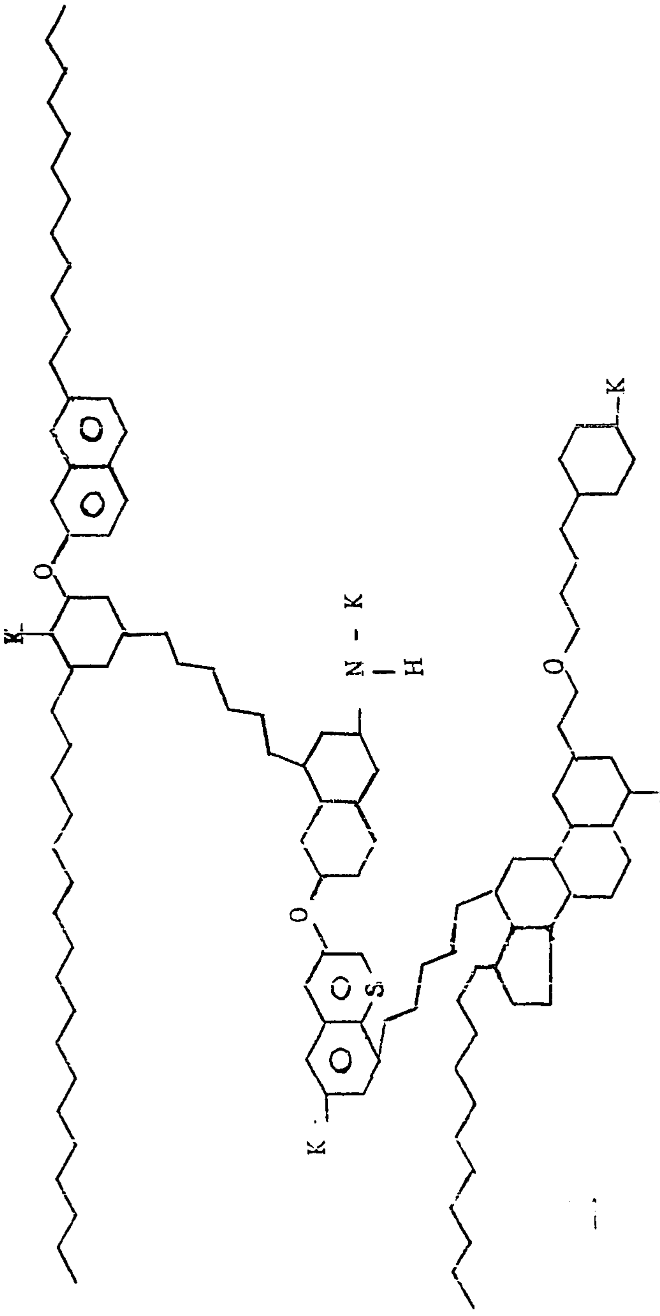
Organic molecules can be represented by structural models. The structure of simple molecules can be ascertained by physical and chemical measurements. The structure of larger and more complex materials is not so easily determined. Several structures have been proposed for the kerogen of Green River oil shale based on the results of individual analyses (Sec. I, F). However, any one study can not and does not encompass all of the properties of the kerogen. Therefore, no one of the proposed models represents the actual structure of the kerogen. However, the structure may well be approximated by continuous modification of and interrelation among the proposed models. A model is proposed here based on the results of the present work.

Based on the results of the work described in this dissertation, the kerogen of Green River oil shale is a three dimensional polymer composed primarily of aliphatic material. The kerogen contains both long chain and cyclic saturated material. The long chain material can be branched. The cyclic material contains one to two rings, sterane, and terpane structures. The kerogen contains a small amount of aromatic material containing two conjugated rings. Ether oxygen accounts for some linkages between the kerogen units. Both sulfur and nitrogen exist in the organic material in some form. Sulfur and nitrogen probably exist in heterocyclics or in functional groups such as amines and sulfides. This model is depicted in Fig. 19.

The model presented here is consistent with the model proposed by Yen (60,61) and Young et al. (64,65) (Fig. 4). The Yen model is based on results of a wide range of measurements. The present model can easily be converted to the Yen model by the addition of some of the additional information used by Yen in developing his model. The major difference in the two models is the lack of aromatic material contained in the Yen model. The present work clearly indicates the presence of aromatic material in Green River oil shale. In this regard, the present model is similar to the Schmidt-Collerus and Prien model (45, 46) (Fig. 3) which also contains a definite aromatic content.

Figure 19. Proposed model for the structure of the kerogen of Green River oil shale

K indicates kerogen matrix


K
O
N - K
H
O
S
K
O
K
K

VIII. SUMMARY

A short history of interest in the Green River oil shale has been presented. The nature of the Green River oil shale has been reviewed. An extensive review of investigations concerned with the characterization of the kerogen of Green River oil shale has been made. Results of these investigations have led several workers to propose models for the organic kerogen. All of the models have presented the kerogen as a three dimensional aliphatic polymer.

It has been proposed to obtain further insight into the nature of Green River kerogen by oxidizing the kerogen with perchloric acid under conditions which permit selection and control of the oxidizing power (reduction potential) applied.

A so called "kerogen concentrate" of Green River oil shale has been prepared by reacting the raw oil shale with a one-to-one mixture of concentrated hydrochloric and concentrated hydrofluoric acids to remove carbonate and silicate minerals respectively. A portion of the soluble organic material, bitumen, has been removed by exhaustive extraction with acetone. The resulting kerogen concentrate has been shown to contain 2.4 per cent pyrite as determined by X-ray diffraction. The kerogen concentrate has been found to contain 70.36 per cent carbon, 9.11 per cent hydrogen, 5.18 per cent sulfur, 2.36 per cent nitrogen and 6.12 per cent ash. Iron, calcium, magnesium, aluminum and titanium have been identified in the ash by arc emission analysis.

The reaction of the kerogen concentrate with perchloric acid of varying boiling point and concentration has been studied with reference to

1) the percentage of carbon converted to carbon dioxide, 2) the color and fluorescence of the aqueous phase and 3) the amount of undissolved material. A modified Bethge apparatus has been used to maintain a constant concentration of boiling perchloric acid.

At boiling points below 150°, little or no reaction has been found to occur between the kerogen concentrate and the boiling perchloric acid. At boiling points between 150° and 170°, the boiling perchloric acid has been found to dissolve the kerogen and to begin oxidation of the dissolved kerogen. At boiling points between 170° and 202°, the boiling perchloric acid has been found to oxidize the dissolved kerogen. At a boiling point of 202°, the boiling perchloric acid has been found to completely oxidize the kerogen to carbon dioxide.

The results of the oxidation of the kerogen concentrate with perchloric acid has been compared to the results of the oxidation of the raw oil shale with perchloric acid. It has been determined that the silicate mineral structure has no effect on the oxidation of the organic material contained in the shale.

The dissolution of the kerogen as a function of the boiling point of perchloric acid has been observed to result in a "S"-shaped curve with a sharp break between 160° and 170°. It has been proposed that this parameter be used as an indicator for oxidation of model compounds with perchloric acid to obtain information concerning the linkages holding the kerogen together. Polyethylene, polystyrene, polyester, nylon and crown compounds have been proposed as model compounds.

The results for the determination of the total carbon by the measurement of carbon dioxide produced from the reaction of the kerogen concentrate with hot concentrated perchloric acid has been found not to be reproducible and always high. It has been demonstrated that boiling concentrated perchloric acid produced a blank which more than accounted for the error in the measurement.

Solid materials resulting from the reaction of the kerogen concentrate with perchloric acid have been separated from perchloric acid by washing with water. Soluble organic oxidation products have been isolated from the solid. The oxidation products have been separated into heptane-soluble acids, methanol-soluble acids, sodium hydroxide-soluble acids and heptane-soluble neutral compounds. Most of the oxidation products have been isolated in the methanol- and sodium hydroxide-soluble acidic fractions. The major oxidation products have been shown to be dark brown, highly polar acids.

The methanol-soluble acids have been analyzed by potentiometric titration with base. Equivalent weights of acids have been shown to range from 183 g./eq. to 373 g./eq.

The methanol-soluble acids have been analyzed by infrared spectrometry. The spectra have shown that the material consisted primarily of aliphatic carboxylic acids, that ether groups were present, and that aromatic compounds were resistant to oxidation by perchloric acid as the aromatic carbon-hydrogen stretch appeared only in the sample resulting from oxidation at 190° indicating a concentration of the aromatic material in that sample.

The methanol-soluble acids have been analyzed by mass spectrometry. The analyses have shown that the material consisted of aliphatic carboxylic acids composed of both long chain and cyclic material. The cyclic material has been shown to contain one to two rings. Steroid and terpanoid structures have also been indicated.

The heptane-soluble neutral fractions have been analyzed by X-ray excited optical luminescence. The analyses have indicated the presence of aromatic material containing two aromatic rings.

The heptane-soluble acidic fractions and the heptane-soluble neutral fractions have been esterified with boron trifluoride in methanol and analyzed by gas chromatography. n-Carboxylic acids (C_{14}-C_{18}) have been identified.

A method for the process of oxidation of the kerogen of Green River oil shale with perchloric acid has been proposed. The method has been shown to be consistent with the results of the present work.

A model for the kerogen of Green River oil shale has been proposed based on the results of the present work. The model consisted of a three dimensional polymer composed of saturated long chain and cyclic materials.

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