

CONSTITUTION OF HYDROCARBON-LIKE MATERIALS DERIVED FROM
KEROGEN OXIDATION PRODUCTS

W. E. Robinson and D. L. Lawlor

Laramie Petroleum Research Center
U. S. Department of the Interior
Bureau of Mines
Laramie, Wyoming

Oxidation is one method of converting the insoluble organic material (commonly called kerogen) present in oil shale to soluble degradation products for constitutional studies. The amount of degradation and the molecular weight of the products depend upon the extent of oxidation and severity of the reaction conditions. A variety of oxidants can be used to accomplish this degradation, but some are more suitable than others.

In a previous study (6), organic material from Colorado oil shale was oxidized to high-molecular-weight acids by a boiling solution of alkaline potassium permanganate under controlled conditions, and to carbon dioxide and oxalic acid by exhaustive oxidation for 100 hours. By choosing different ratios of $KMnO_4$ to kerogen, large or small amounts of intermediate acids were obtained. However, it was not possible to obtain complete conversion to intermediate acids without simultaneously producing carbon dioxide and oxalic acid. In general, small yields of final oxidation products were associated with large yields of high-molecular-weight intermediate acids and vice versa.

In another report (5), the nature of the organic acids that were obtained by oxidizing raw oil shale from the Mahogany-zone beds of the Green River formation near Rifle, Colo., was studied. The oil shale assayed approximately 66 gallons of oil per ton of shale and contained about 34% kerogen. An oxidation product was prepared by treating each part of organic carbon present in the kerogen with eight parts of $KMnO_4$. The organic acids obtained were converted to n-butyl esters, fractionated by distillation, and identified, where possible, by mass and infrared spectra of the esters and by X-ray diffraction of selected derivatives. A total of 59% of the organic acids in the oxidation product was identified as C_2 to C_8 difunctional acids of the alkane series. The remaining 41% of the organic acids were not identified by this method because of their complex nature. Identification or classification of this material would contribute to the knowledge of the structure of kerogen and might suggest new commercial uses for oil shale.

In this study by the Federal Bureau of Mines, characterization of the remaining 41% of the organic acids in this oxidation product was accomplished by reducing the carboxyl groups of the acids through a series of reactions. The resulting hydrocarbon-like materials were amenable to fractionation and characterization. Some of the usual methods of decarboxylation were tried, but extensive thermal degradation resulted.

The oxidation product also contained n-paraffinic, isoparaffinic, aromatic, naphthenic, and heterocyclic acids. The naphthenic and heterocyclic acids predominated, which suggested that the structure of Colorado kerogen is mainly alicyclic and heterocyclic, with smaller amounts of straight-chain and aromatic structures.

EXPERIMENTAL PROCEDURE

Preparation of Organic Acids. Kerogen oxidation products were prepared from raw oil shale using a method described in earlier reports (5,6). The raw oil shale was oxidized in two steps by an aqueous solution of alkaline $KMnO_4$. The first step was treatment of 1 part of organic carbon of the kerogen with 6 parts of $KMnO_4$, 1.6

parts of KOH and 34 parts of water at 70° to 90° C. until the KMnO_4 was reduced. The treatment was repeated in the second step except that only 2 parts of KMnO_4 were used. The alkaline solution was separated from the shale residue, acidified with 1 to 1 sulfuric acid and evaporated to dryness. Nonvolatile organic acids were extracted from this dried product using methyl ethyl ketone. Based upon total carbon, the kerogen was oxidized to 58% nonvolatile acids, 15% carbon dioxide, a trace of volatile acids, and 27% remained unoxidized.

Preparation of n-Butyl Esters. The nonvolatile organic acids were converted to n-butyl esters by reacting 250 grams (0.8 mole) of the acids with 1275 ml. (14 mole) of n-butyl alcohol and 25 ml. (0.5 mole) of concentrated sulfuric acid under reflux conditions for about 100 hours. Water was removed by using an enlarged Dean-Stark tube mounted above the reaction flask. After completion of the reaction, the n-butyl alcohol was removed by distillation. The resulting product was dissolved in ether, was washed free of acid with a solution of sodium carbonate, and finally was dried over anhydrous sodium sulfate and recovered.

Preparation of Alcohols. All the recovered n-butyl esters were reduced to alcohols in the following manner (1): The esters were treated with a total of 61 grams (1.6 mole) of LiAlH_4 in 2500 ml. (23.6 mole) of anhydrous ether in five different batches. An ether solution of the esters was added slowly to an ether solution of LiAlH_4 , then refluxed 4 to 5 hours. Excess hydride was decomposed by cautiously adding water to the reaction mixture. After gas stopped evolving, the complex was treated with 10% sulfuric acid and the reduced product was recovered from the ethereal layer.

Preparation of Iodides. The alcohols were converted to iodides by reacting the alcohols with 115 grams (0.8 mole) of P_2O_5 , 216 ml. (3.2 mole) of 85% H_3PO_4 and 530 grams (3.2 mole) of KI (7). After the reaction mixture was heated at 100° to 120° C. for 3 to 5 hours, the iodides were extracted with ether. The ether solution was washed with sodium thiosulfate and sodium chloride solutions, dried over anhydrous sodium sulfate, and the ether was distilled from the iodides.

Reduction of Iodides. The resulting iodides were reduced with zinc and hydrogen chloride gas (2). Zinc dust was added over a period of 2 hours to a warm glacial acetic acid solution of the iodides, which was constantly stirred. The reaction mixture was stirred and heated at 90° to 95° C. for an additional 24 hours and was saturated with dry HCl gas every 4 hours. A trap, submerged in a dry ice and acetone bath, was connected to the exit gas tube to condense any hydrocarbons with low boiling points formed during the reduction. After completion of the reaction, the mixture was diluted with water, and the product was extracted with ether. After the ether solution was washed free of acid, it was dried over anhydrous sodium sulfate, and the ether was partly distilled from the product.

Fractionation of the Reduced Product. The product and a small quantity of ether were placed in a spinning band distillation column and distilled at atmospheric pressure (580 mm. mercury) up to a head temperature of 70° C. (pot temperature of 175° C.). After the reduced product cooled to room temperature, the distillation was continued at 1 mm. mercury pressure with a head temperature up to 130° C. and a pot temperature of 200° C.

A flow diagram of the fractionation of the distillate and distillation residue is shown in figure 1. The distillate and residue fractions were dissolved in a 40 to 1 volume ratio of pentane, allowed to stand overnight at 0° C., and then filtered. The insoluble material was washed with a small quantity of cold pentane, freed of solvent, and weighed. The pentane-soluble material was fractionated on pretreated columns of alumina (25 to 1 weight ratio of Alcoa XF-21 alumina) using pentane, benzene and a 10% methanol-90% benzene mixture as eluting solvents. The benzene-eluted material, referred to as nonpolar resins, and the benzene-methanol eluted resins, referred to as polar resins, were freed of solvent and weighed.

Wax was separated by dissolving the pentane-eluted fraction (oil plus wax) in a 40 to 1 volume ratio of methyl ethyl ketone (MEK), allowing it to stand at -5°C . for 1 hour. The wax was filtered from the MEK-soluble oil, freed of solvent, and weighed. Urea adducts were prepared by reacting each gram of wax with 21 ml. of a saturated solution of urea in methanol. Excess urea, 1.5 grams per gram of wax, and 6 or 7 drops of benzene, were added. This mixture was stirred at room temperature for 24 hours. The adduct and nonadduct waxes were separated by filtration; the adduct was then decomposed with hot water and extracted with ether. Both fractions were freed of solvent by distillation. Wax was not separated from the distillate fraction.

The distillate oil, the wax fraction, and the distillation residue oil were fractionated by a method similar to that reported by Mair, Marculartis and Rossini (3). Each fraction was placed on a pretreated column of silica gel (25 grams of Davidson analytical grade silica gel to 1 gram of sample) and eluted successively with 2,2,4-trimethyl pentane, benzene, and 2-propanol. The fractions were freed of solvent, weighed and identified as paraffin oil, aromatic oil, and polar oil respectively. The paraffin oil from the distillation residue was adducted with urea by the same technique used for waxes. The aromatic oil from the distillation residue was further fractionated on a pretreated column of alumina using a 25-to-1 ratio of alumina to sample. Eluting materials were a mixture of iso-octenes, benzene, and 2-propanol.

Reduction with Hydriodic Acid. The wax and paraffin oil fractions were completely reduced by concentrated hydriodic acid. Samples of 0.1 to 0.5 gram were reduced by sealing them in glass ampoules with 15 ml. of concentrated hydriodic acid (sp. gr. 1.9) and heating at 175°C . for 24 hours. The treated samples were dissolved in benzene and washed free of iodine with a solution of sodium thiosulfate. The benzene solution was washed with water and finally dried over anhydrous sodium carbonate. Benzene was distilled from the reduced product at reduced pressure.

Physical and Chemical Properties. The elemental composition and functional groups of the fractions were determined by macro methods at the Bureau's laboratory and by micro methods at a commercial laboratory, using conventional methods. Carbon and hydrogen were determined by combustion, nitrogen by the Kjeldahl or Dumas methods, sulfur by ignition in a Parr oxygen bomb, oxygen by difference or by the Unterzaucher direct method, saponification equivalents by hydrolysis and hydroxyl groups by acetylation. Molecular weights were determined from mass spectra and by the rise-in-boiling-point method using benzene as solvent. Infrared and mass spectra, as well as X-ray diffraction, were used to characterize the various fractions.

RESULTS AND DISCUSSION

The total yield of reduced product from 250 grams of kerogen acids amounted to 36 grams after removal of all solvents, or approximately 15 weight percent. The theoretical yield, based on data from a previous study (5), was 198 grams or 79 weight percent. However, approximately 50% of the oxidation product consisted of difunctional acids containing 2 to 4 carbon atoms per molecule. The reduction method used in this study converted these acids to gases that were not recovered in the reduced product. Because of this loss, the overall yield of reduced product was 36% of the theoretical. Typical yields were: esters - 95%, alcohols - 75%, iodides - 95%, and hydrocarbons 50%. Losses were probably due to handling rather than to unreactivity of the components. However, the possibility of fractionation occurring did exist and some unreactive parts of the oxidation product may have been eliminated from the reduced material. Vacuum distillation of the reduced product resulted in a yield of 8.5% distillate and 91.5% distillation residue.

Composition of the Distillate Fraction. In addition to the solvents used, the distillate obtained by atmospheric distillation contained trace amounts of pentanes, hexanes, hexenes, and cyclohexanes. The distillate obtained by vacuum distillation (8.5% of the total reduced product) was fractionated by the method described earlier

and shown in figure 1. Nearly equal amounts of five fractions were obtained, namely paraffin oil, aromatic oil, polar oil, nonpolar resins, and polar resins.

Mass spectra analysis of the paraffin oil fraction showed that it consisted of isoparaffins and cycloparaffins, with the latter predominating. The cyclic part contained 1 to 5 rings per molecule with dinuclear material constituting the largest single type material. The major components of the aromatic fraction were benzenes, indanes/tetralins and naphthalenes.

Infrared analysis of the nonpolar resins, polar resins, and polar oil indicated that these fractions were predominantly cyclic because absorption in the 13.7 and 13.9 micron region was very weak. They also appeared highly saturated as shown by strong absorption in the 3.45 and 6.84 micron regions. The presence of considerable terminal CH₃ groups was suggested by medium to strong absorption in the 7.3 micron region. Absorption in the aromatic region was weak. There was indication of the presence of OH groups and other oxygen functionals; however, the strong absorption in the 5.70, 5.78, and 5.95 micron region may be due to C=O groups of unreduced esters.

Composition of the Distillation Residue. The amount of each of the various fractions from the distillation residue, which represented 91.5% of the reduced product, is shown in table 1. The major fractions consisted of resins and paraffin oil, while wax, aromatic oil, polar oil, and pentane-insoluble material were present in smaller amounts. Molecular weights ranged from about 300 to 1200.

Table 1. Distribution and Molecular Weights of the Distillation Residue Fractions

	Percentage of Total Distillation Residue	Percentage of Total Reduced Product	Molecular Weights
Pentane-insoluble material	3.0	2.7	1220
Resins			
Nonpolar resins	11.9	10.9	530
Polar resins	25.9	23.7	800
Wax			
Urea adduct	3.0	2.7	405
Urea nonadduct	10.4	9.5	400
Oil			
Paraffin oil adduct	1.5	1.4	310
Paraffin oil nonadduct	30.5	27.9	410
Aromatic oil (iso-octene eluted)	9.5	8.7	270
Aromatic oil (benzene eluted)	0.3	0.3	340
Aromatic oil (2-propanol eluted)	0.3	0.3	345
Polar oil	<u>3.7</u>	<u>3.4</u>	-
Total	100.0	91.5 ^a	

^aThe remaining 8.5% consisted of the vacuum distillate fraction.

Ultimate analyses shown in table 2 indicated that the recovered fractions contained appreciable amounts of oxygen. It was necessary to determine the nature of

this oxygen and to eliminate the oxygen from portions of the fractions by HI reduction, so that mass spectra data for ring analysis and carbon chain length would have meaning.

Table 2. Elemental Analyses of Distillation Residue Fractions

	C	H	O	N	S	Atomic H/C
Wax						
Urea adduct	83.6	14.2	1.8 ^a	0.2	0.2	2.04
Urea nonadduct	82.9	11.1	5.4 ^a	0.2	0.4	1.61
Oil						
Adduct paraffin	84.2	14.3	1.2 ^a	0.2	0.1	2.04
Nonadduct paraffin	81.1	11.1	7.6 ^b	0.0	0.2	1.64
Mono/di-aromatic	86.2	11.2	-	2.6 ^c	-	1.56
Resins						
Nonpolar	78.9	10.1	9.4 ^b	0.4	1.2	1.54
Polar	70.2	9.6	19.1 ^b	1.0	0.1	1.64

^aDirect oxygen (Unterzaucher).

^bOxygen was determined by difference.

^cTotal oxygen, nitrogen, and sulfur determined by difference.

An estimate of the type and amount of oxygen functional groups for various fractions was obtained by analyses for hydroxyl, ester, and alkoxy oxygen. Other ether, carbonyl and unaccounted for oxygen was determined by difference. As this difference value was large in all cases, infrared analyses was used to indicate the most likely type oxygen present.

Mass spectra data reported for the oil and wax fractions were obtained from the HI-reduced material. By contrast, infrared spectra was determined on the oil, wax, and resin fractions before reduction with hydriodic acid; also the aromatic oil was not reduced with HI.

Adduct Wax. Based on mass spectra data, this fraction, which represented 2.7% of the total reduced product, contained mostly isoparaffins and normal paraffins with smaller amounts of cycloparaffins (table 3). Isoparaffins appeared to predominate over normal paraffins; the normal paraffins ranged from C₁₃ to C₃₆ carbon chains with an average chain length of C₂₆. (Average carbon chain length of this wax, determined by X-ray diffraction, was 28.) These data showed the presence of long carbon chains, which suggested that the original oxidation product contained a small amount of fatty acids.

Ultimate analyses (table 2) showed that the adduct wax was highly saturated with hydrogen and contained 1.3% oxygen. Infrared analyses of the fraction before reduction with HI, shown in table 4, confirmed the presence of a predominance of chain structures. The average molecular weight of the adduct wax before reduction with HI was 405.

Nonadduct Wax. By contrast, the nonadduct wax fraction, which represented 9.5% of the total reduced product, contained predominantly cyclic structures and only a small amount of normal paraffins and isoparaffins (table 3). The cyclic portion

consisted of aromatic and naphthenic rings with a predominance of the naphthenic rings. The number of rings per molecule ranged from 1 to 6 with an average of 2 to 3 rings per molecule.

Table 3. Constitution of the HI-reduced Wax and Paraffin Oil Fractions Obtained from the Distillation Residue

	Average Composition, mole % ^a			
	Wax		Paraffin Oil	
	Adduct	Nonadduct	Adduct	Nonadduct
n-Paraffins	27	4 ^b	84	6 ^b
Isoparaffins	66	-	7	-
Naphthenes				
Mono and noncondensed naphthenes	3	11	-	18
Condensed naphthenes				
2 rings	1	19	1	22
3 rings	1	14	2	13
4 rings	1	5	2	3
5 rings	1	19	2	7
6 rings	-	6	2	6
Aromatics	-	22	3	25
Total	100	100	100	100

^aDetermined from mass spectra.

^bTotal normal and isoparaffins.

Oxygen functional groups were determined by the methods described earlier and the results are shown in table 5. The fraction contained 5.4% oxygen (table 2), which appeared to be mostly in the form of ether or carbonyl oxygen with smaller amounts of ester, but no hydroxyl oxygen. Infrared spectra before reduction with HI, shown in table 4, indicated medium to weak absorption for ester, ketone, alcohol, and anhydride oxygen suggesting a predominance of ether oxygen. The presence of only small amounts of long carbon chains was also confirmed by infrared analyses; however, strong absorption in the 7.3 micron region indicated the presence of considerable terminal CH₃ groups. This fraction had an average molecular weight of 400 before reduction with HI and 360 after reduction.

Adduct Paraffin Oil. The adduct paraffin oil, one of the smaller fractions representing only 1.4% of the reduced product, was composed largely of normal paraffins with smaller amounts of cycloparaffins and isoparaffins (table 3). The normal paraffins ranged from C₁₅ to C₃₀ carbon chains with an average chain length of C₂₃. (The average chain length determined by X-ray diffraction was C₂₂.) The naphthenic material contained 2 to 6 rings per molecule.

Ultimate analyses (table 2) showed that this fraction was highly saturated with hydrogen and contained 1.2% oxygen. Because of limited size of the fraction, oxygen functional groups were not determined by chemical methods. Infrared spectra of this fraction, shown in table 4, indicated the presence of very little oxygen functional groups. This suggested that most of the oxygen was ether oxygen. Strong absorption in the 13.7 and 13.9 micron region confirmed the presence of considerable

Table 4. Infrared Spectra of Wax and Oil Fractions Obtained From the Distillation Residue

Band Locations, Microns	Intensity ^a				Possible Interpretations
	Adduct Wax	Nonadduct Wax	Adduct Paraffin Oil	Nonadduct Paraffin Oil	
2.9	W	W	W	W	OH (bonded)
3.45	S	S	S	S	CH ₂ , CH ₃
5.70	M-W	M-W	W	W	C=O (ester)
5.78	M-W	M	W	M-W	C=O (ester)
5.95	None	M-W	W	W	C=O, aromatic
6.25, 6.35	W	M-W	W	M-W	C=C (aromatic), carboxylate ion
6.84	S	S	S	S	CH ₂ , CH ₃
7.30	M-W	S	M	S	CH ₃
7.55	W	M	W	W	-
8.10	W	M	None	None	Ester,
8.45	W	M	None	None	ketone, alcohol,
8.55	W	M	W	None	anhydride
11.25	W	M-W	M-W	W	-
11.5	W	M	W	M-W	Aromatic
12.7	M	M	M	M-W	-
13.45	None	None	None	None	Aromatic
13.7, 13.9	S	W	S	W	Alkyl chains

^aW - weak, M- medium and S - strong.

Table 5. Oxygen Functional Groups of Various Fractions

	Percent of Total Oxygen			
	Hydroxyl	Ester	Alkoxy	Ether, Carbonyl and Others ^a
Nonadduct wax	0	36	-	64
Nonadduct paraffin oil	2	27	3	68
Nonpolar resins	0	45	15	40
Polar resins	6	27	3	64

^aDetermined by difference.

normal paraffins. There was also some evidence for the presence of terminal CH₃ groups. The molecular weight of this fraction was 310 before reduction with HI.

Nonadduct Paraffin Oil. This fraction, which was the largest single fraction and amounted to 27.9% of the original reduced product, was predominantly naphthenic with smaller amounts of aromatic and paraffinic constituents (table 3). The naphthenic material had 1 to 6 rings per molecule with an average of 2 to 3 rings per molecule. The normal paraffinic and isoparaffinic constituents represented only a small portion of the total fraction; however, about 25% of the material was of aromatic composition.

Oxygen functional groups were determined by the methods described earlier and the results are shown in table 5. Of the 7.6% oxygen present in this fraction (table 2), the majority appeared to be present in the form of ether or carbonyl oxygen with smaller amounts of ester, hydroxyl and alkoxy functional groups. A predominance of ether oxygen was indicated by infrared analyses (table 4) since the absorption for carbonyl and other oxygen was weak. Also, weak absorption in the 13.7 and 13.9 micron region indicated the absence of long alkyl chains; however, strong absorption in the 7.3 region indicated the presence of considerable terminal CH_3 groups. This fraction contained very little nitrogen and sulfur and had an average molecular weight of 410 before reduction with HI and 350 after reduction.

Aromatic Oil. The aromatic fraction, which represented 9.3% of the total reduced product, was separated into 3 additional fractions; namely, iso-octenes, benzene, and 2-propanol eluted material (figure 1). These fractions are referred to as mono/di, tri, and tetra nuclear aromatics, respectively. Piperonal chloride color tests indicated that the iso-octene eluted material, which was the major aromatic fraction (table 1), was predominantly mono/di nuclear aromatics. This was confirmed by mass spectra data shown in table 6, which indicated that the material was mostly indanes and tetralins with smaller amounts of the other series of aromatic compounds. The benzene series had large peaks at m/e 268 and m/e 259. The m/e 268 peak was a parent peak that lost an ethyl radical to form m/e 259 and may represent the molecular weight of 1 compound or several isomeric compounds. A molecular weight of 268 indicated that 15 carbon atoms in alkyl groups larger than n-propyl were attached to the benzene ring. Considering all possible substitutions and eliminating some by infrared analyses, 3-ethylpropyl substitution appeared most likely. In addition to tri-substituted benzenes (Mol. wt. 288) there was evidence of di-substituted benzenes (Mol. wt. 216), di-substituted indanes (Mol. wt. 258)/di-substituted tetralins (Mol. wt. 272), and di- and tri-substituted indenenes (Mol. wt. 256, 326). These substitutions are shown diagrammatically in figure 2. The location of the substituted groups is not known; however, there is some evidence for the presence of symmetrical tri-substituted benzenes. Also, it is not meant to imply that other series of aromatics with the same "X-number" are not present, but the ones indicated appeared to be the best possibilities. It was assumed that the aromatic compounds isolated were degraded from kerogen and were not formed during the oxidation or reduction procedures. Therefore, each substituted group may represent a ruptured ring or ring system and suggests the presence of carbon skeleton structures in kerogen similar to that present in these compounds. Ring systems that would be readily ruptured by KMnO_4 to produce similar substitution on aromatic nuclei after reduction are cyclopentanone, cyclopentanol, cyclopentene or others.

Table 6. Constitution of Aromatic Oil Fractions From the Distillation Residue

	Volume, % ^a	
	Iso-octene eluted ^b	Benzene eluted ^c
Benzenes	12	16
Indanes and tetralins	41	29
Indenes and dihydronaphthalenes	14	16
Naphthalenes	10	10
Acenaphthenes	8	10
Acenaphthylenes	5	3
Anthracenes and phenanthrenes	10	11
Total	100	100

^aDetermined from mass spectra.

^bThe ratio of calculated to observed total ionization was 0.65.

^cThe ratio of calculated to observed total ionization was 1.09.

Resins. The resinous material obtained from the original product consisted of nonpolar (Mol. wt. 530) and polar resins (Mol. wt. 800) and represented 12 and 26% of the total material, respectively. Elemental analyses (table 2) of each fraction showed that they contained large amounts of oxygen and smaller amounts of nitrogen and sulfur. Oxygen functional groups were determined by the previous methods (table 5) and appeared to be present as ester and ether or carbonyl oxygen with smaller amounts of alkoxy oxygen. The polar resins contained some hydroxyl and little alkoxy oxygen. Infrared analyses of the two resin fractions are shown in table 7. Both fractions showed weak or no absorption in the 13.7 and 13.9 micron region, indicating few carbon chains with more than four methylene groups. Strong absorption in the 7.3 micron region indicated the presence of considerable terminal CH₃ groups. Absorption in the aromatic region was weak; consequently, these materials appeared to be composed predominantly of saturated cyclic structures. Infrared spectra showed evidence for hydroxyl, carbonyl and other oxygen functional groups, some of which was due to unreduced ester groups.

Table 7. Infrared Spectra of Resin Fractions Obtained From the Distillation Residue

Band Location, Microns	Intensity ^a		Possible Interpretation
	Nonpolar Resins	Polar Resins	
2.9	M-W	M-W	OH (bonded)
3.45	S	S	CH ₂ , CH ₃
5.75	S	S	C=O (ester)
5.95	W	None	C=O, aromatic
6.25, 6.35	M-W	W	C=C (aromatic), carboxylate ion
6.84	S	S	CH ₂ , CH ₃
7.30	S	S-M	CH ₃
8.10	W	S-M	Esters, ketones,
8.9	S	None	alcohols, anhydrides
11.4	W	None	Aromatic
11.5	None	W	Aromatic
13.45	S	None	Aromatic
13.7, 13.9	W	None	Alkyl chains

^aW - weak, M - medium and S - strong.

Polar Oil and Pentane-insoluble Material. No analytical data were obtained for these fractions.

Composition of the Original Acids. Approximately 59% of the original acid fraction was identified by a previous study (4). In the present study, the remaining 41% was characterized as shown in table 8. These complex acids, whose molecular weights have a maximum of more than 1200, consisted of small amounts of straight-chain and aromatic acids, but were predominantly saturated cyclic and heterocyclic acids.

There was evidence that the oxidation product contained appreciable amounts of ether oxygen. Fractions of the material obtained by the reduction of the oxidation product contained 7 to 19% oxygen, of which 40 to 70% may be ether oxygen. A quantitative estimate was obtained from the remainder of the reduced product and a comparison of the oxygen present in the original kerogen from which these products were obtained. The total oxygen accounted for in the reduced product equaled 22% of the oxygen present in the original kerogen, which indicated that at least 10 to 15% of the oxygen present in kerogen may be ether oxygen.

Table 8. Composition of Acid Fraction Obtained from Kerogen by Alkaline Permanganate Oxidation

	Percentage of Reduced Product ^a	Percentage of Total Acids ^b
Normal paraffin acids (C ₂ to C ₈)	-	59
Normal paraffin acids (C ₁₆ to C ₃₈)	2	1
Isoparaffin acids	2	1
Cycloparaffin acids (1 to 6 rings)	34	14
Aromatic acids (1 to 2 rings)	15	6
Heterocyclic acids	<u>47</u>	<u>19</u>
Total	100	100

^aDetermined from mass spectra.

^bBased on analyses obtained from data presented in this report and a previous report (4).

By choosing other oxidation conditions different yields of complex acids could have been obtained. For example an 8-step-oxidation procedure produced 4% oxalic acid, 17% CO₂, 2% volatile acids and 77% complex organic acids. About 50% of the organic acids had molecular weights from 1200 to 1400 and did not undergo the reactions used in this study. Consequently, the oxidation used in the present study appeared to be a compromise between the two extremes and no attempt was made to obtain maximum yield of any one type of constituent.

SUMMARY AND CONCLUSIONS

The oxidation product obtained from Colorado oil-shale kerogen consisted of n-paraffinic, isoparaffinic, aromatic, naphthenic and heterocyclic structures; the naphthenic and heterocyclic types predominated.

The n-paraffins ranged from C₂ to C₃₈ compounds. The cycloparaffins contained 1 to 6 rings per molecule with di- and tri-nuclear material being most prevalent. Also, mono/di-nuclear aromatics appeared to predominate over compounds having more rings. The aromatic fraction contained nuclei with 3-ethylpropyl substitution at two and three points. The presence of this type of compound in the degradation products suggested that the permanganate oxidation cleaved 5-membered ring systems such as cyclopentene, cyclopentanone, or cyclopentanol that were substituted on benzene, tetralin, indane or indene nuclei. This structure has not been identified previously in kerogen degradation products.

Evidence was found for the presence of ether oxygen in the original kerogen. The four major fractions obtained by the reduction of the oxidation product still contained appreciable amounts of oxygen, most of which was unreduced ester and ether

oxygen. This indicated that Colorado kerogen contains some cyclic or bridge ether oxygen. It seems unlikely that stable ether groups would have been formed during any of the treatment procedures.

In general, these data show that Colorado oil-shale kerogen is predominantly a cyclic material, highly saturated with hydrogen and contains oxygen, nitrogen and sulfur atoms associated with ring structures. There is evidence for the presence of some aromatic and long-chain structures, each representing small portions of the kerogen. The nature of the oxidation products suggests that the kerogen is composed mostly of ring systems connected through short carbon chains, bridges or hetero atoms and is not composed of highly condensed ring structures (2 to 3 rings predominate). These conclusions are in agreement with those obtained from previous studies (4,5,6).

ACKNOWLEDGMENT

This work was conducted under a cooperative agreement between the Bureau of Mines, United States Department of Interior, and the University of Wyoming.

LITERATURE CITED

- (1) Adams, Roger, "Organic Reactions," vol. VI, pp. 469-509, John Wiley and Sons, Inc., New York, N. Y., 1951.
- (2) Blatt, A. H., "Organic Synthesis," Collective vol. II, pp. 320-1, John Wiley and Sons, Inc., New York, N. Y., 1943.
- (3) Mair, B. J., Marculartis, W. J., Rossini, F. D., Anal. Chem. 29, 92 (1957).
- (4) Robinson, W. E., Cummins, J. J., J. Chem. Eng. Data 5, 74-80 (1960).
- (5) Robinson, W. E., Cummins, J. J., and Stanfield, K. E., Ind. Eng. Chem. 48, 1134-38 (1956).
- (6) Robinson, W. E., Heady, H. H., and Hubbard, A. B., Ind. Eng. Chem. 45, 788-91 (1953).
- (7) Schreiber, R. S., "Organic Synthesis," vol. 31, pp. 31-2, John Wiley and Sons, Inc., New York, N. Y., 1951.

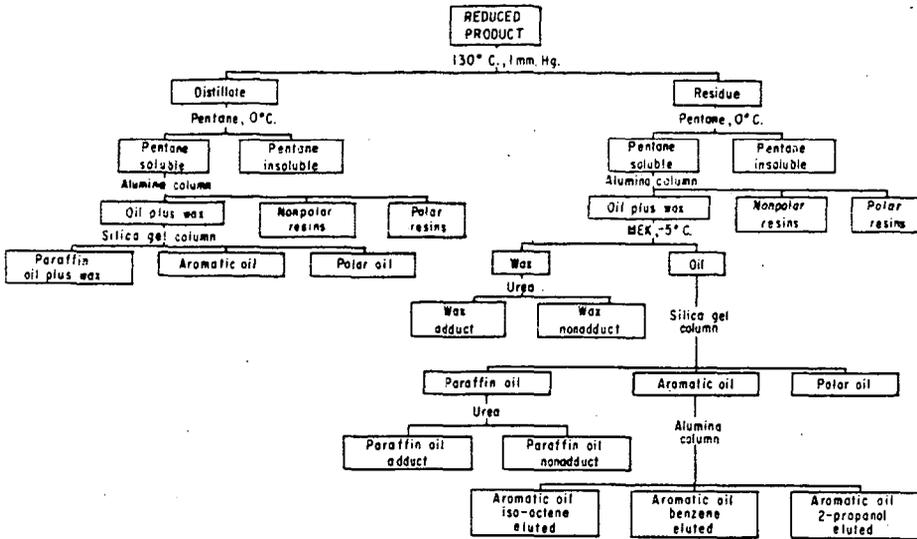


FIGURE 1.- FRACTIONATION OF REDUCED PRODUCT

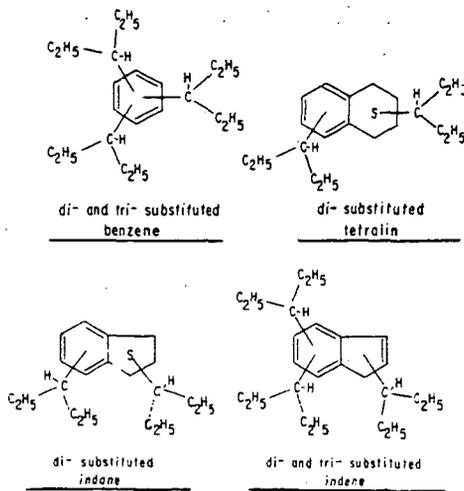


FIGURE 2.- POSSIBLE STRUCTURES PRESENT IN THE MONO/DI-NUCLEAR AROMATIC OIL.