Hydrogenolysis of Colorado Oil-Shale Kerogen

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A knowledge of the constitution of the complex organic material, or kerogen, in Colorado oil shale would aid in developing methods of converting this abundant natural resource to liquid fuels and other related products. Because kerogen is only partially soluble in any known solvents, an initial step in determining its major organic constituents is the degradation of the kerogen to soluble products and the identification of the types of constituents in these products.

This report describes the procedure used by the U.S. Bureau of Mines to degrade Colorado oil-shale kerogen into hydrogenolysis products, the yields of the soluble fractions obtained, and some of their properties.

Hydrogenation is one of several methods used to convert complex, organic materials of high molecular weight into simpler soluble products that are more amenable to analysis and separation into type constituents for identification. Orchin (*4*), Biggs (*2*), and Weller (*10*) have described the catalytic hydrogenation of coal and the examination of the products with respect to the constitution of coal. As a working hypothesis to explain the results of his coal studies, Weller (*9*) postulated that coal (or asphalt) may split thermally to form reactive fragments when heated with certain catalysts and hydrogen under pressure, and the reactive fragments thus formed may either polymerize to form benzene-insoluble products or be stabilized by the addition of hydrogen to form benzene-soluble products. Similar reasoning was used as a basis for this work on oil-shale kerogen.

EXPERIMENTAL

The kerogen concentrate used in this study was prepared from a rich oil shale (Sample SBR48-699) from bed EF of the Green River formation in the U.S. Bureau of Mines oil-shale mine near Rifle, Colo. This shale assayed 78 gallons of oil per ton and contained approximately 39% organic material. The oil shale was crushed to pass a 100-mesh-per-inch screen and was treated with 5% acetic acid solution to remove mineral carbonates which cemented the shale together. The residual product was then extracted with benzene to remove a small amount of benzene-soluble bitumen (approximately 2% in the raw shale), which was not considered as kerogen in this study. The resulting concentrate contained approximately 50% kerogen (analyses are shown in Table III). The first part of the study involved the treatment of 10- to 15-gram portions of the kerogen concentrate with hydrogen at different temperatures and pressures in the presence of catalysts. Emphasis was placed on obtaining maximum conversion of kerogen to benzene-soluble material with minimum production of gas. The following catalysts were used with hydrogen for different periods, temperatures, and pressures: tungsten-nickel sulfide, stannous chloride, stannous chloride plus ammonium chloride, stannous chloride plus ammonium chloride and powdered zinc, Adkins catalyst (*1*), nickel chloride, nickel chloride plus powdered zinc, and nickel chloride plus ammonium chloride. The highest conversion of kerogen to benzene-soluble material with the lowest yield of gas was obtained by heating a mixture of 2.6 parts of kerogen concentrate and 1 part by weight of stannous chloride dihydrate with hydrogen at 4200 pounds per square inch gage (hot pressure) at a temperature of 355 °C. for 4 hours. Under these conditions, 88.6% of the kerogen carbon was converted to benzene-soluble material, and 9.3% of the carbon was converted to gas.

On completion of the preliminary study, the optimum conditions stated above were used for preparing the hydrogenolysis products. Two hundred grams of the pulverized kerogen concentrate were mixed with 78 grams of catalyst in an oblong stainless steel tray; the dry mixture was treated for 4 hours in a stationary, tube-shaped hydrogenation chamber. After cooling, the hydrogen and product gas were bled off, the apparatus was opened, and the sample was weighed to determine the gas formed. In a number of runs the hydrogen and gas were bled through a liquid nitrogen trap to collect condensable gases, which were analyzed by mass spectrometer. The hydrogenated kerogen concentrate was extracted with benzene to remove benzene-soluble material and then with trichloroethylene to remove additional soluble material remaining in the residue. A total of 8150 grams of kerogen concentrate was treated, and the products were combined.

The average element balance of hydrogenolysis products for the combined runs, based on the carbon in the original kerogen was: benzene-soluble material, 80.0%; trichloroethylene-soluble material, 5.6%; gas, 7.6%; and organic residue remaining in the spent shale, 6.8% (Table I). As shown, 89.4 (83.0 + 6.4) % of the nitrogen, 92.1% of the sulfur, and 83.8 (56.2 + 27.6) % of the oxygen were removed and did not appear in the soluble hydrogenolysis products. The total hydrogen in the products shows an increase of approximately 10% including hydrogen that was added to the organic compounds only. Hydrogen consumed in removing the sulfur, nitrogen, and oxygen was not determined.

Table I. Element Balance of Hydrogenolysis Products from Oil-Shale Kerogen[a]

	% of Total Element in Kerogen				
	C	H	N	S	O
Kerogen	100.0	100.0	100.0	100.0	100.0
Benzene-soluble fraction	80.0	91.3	9.4	7.2	11.7
Trichloroethylene-soluble fraction	5.6	6.4	1.2	0.7	4.5
Gas[b]	7.6	10.8	6.4	0.0[c]	56.2[d]
Residue	6.8	2.2	83.0[e]	92.1[c]	27.6[f]
Total	100.0	110.7	100.0	100.0	100.0
Added hydrogen	...	+ 10.7	...	...	...

[a] Average for 8150 grams of kerogen concentrate.

[b] Calculated from mass-spectrometer analysis.

[c] Hydrogen sulfide combined with tin chloride catalyst to form tin sulfide recovered in residue.

[d] Calculated from CO_2 determined by mass spectrometer, other oxygen values obtained by difference.

[e] Ammonia combined with hydrogen chloride from catalyst to form NH_4Cl.

[f] Probably formed water.

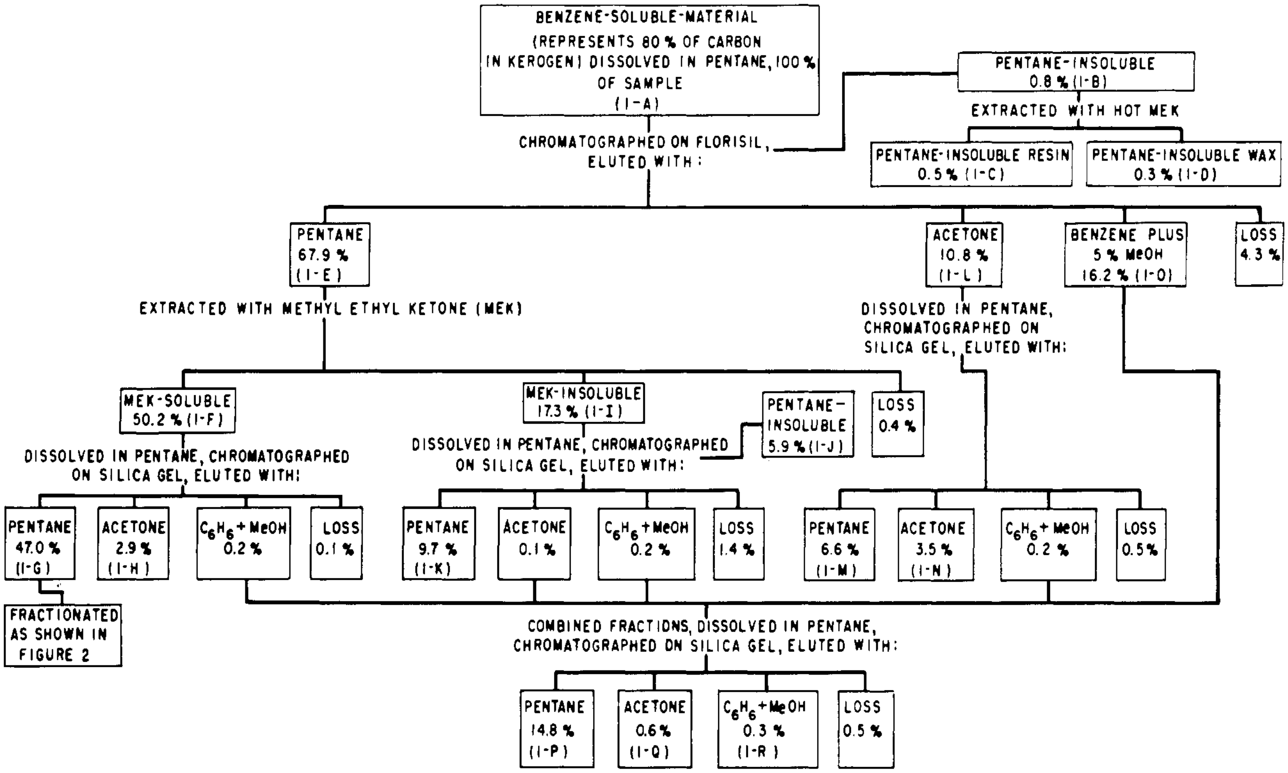


Figure 1. Chromatographic separation of benzene-soluble hydrogenolysis material from Colorado oil shale

These data indicate that the sulfur, nitrogen, and oxygen removed were in vulnerable positions or at weak linkages in the kerogen, which yielded more readily to hydrogenolysis. Sulfur was removed as hydrogen sulfide, which reacted with the tin chloride catalyst to form tin sulfide and hydrochloric acid. The latter reacted with ammonia in the product gas to form ammonium chloride. The tin sulfide and ammonium chloride were deposited in the spent shale or residue. Over half of the oxygen (56.2%) appeared in the hydrogenolysis gas in the form of carbon dioxide, and 27.6% could be accounted for only by the formation of water. The balance of the oxygen (approximately 16%) remained in the soluble products. Oxygen in constituents of the gas was calculated from mass-spectrometer analyses and oxygen in other products was obtained by difference from ultimate analyses.

The product gas contained excess hydrogen from hydrogenolysis. Accordingly, the composition of the evolved hydrogenolysis gas shown in Table II is expressed on a hydrogen-free basis and consisted predominantly of ethane (35.9%), propane (10.9%), and carbon dioxide (46.0%). Hydrogen sulfide reacted with the tin catalyst and was not recovered in the gas.

Table III shows the ultimate composition of kerogen and the following products: benzene-soluble oil or natural bitumen from the raw shale, shale oil from the N-T-U (Nevada-Texas-Utah) retort, and benzene-soluble and trichloroethylene-soluble hydrogenolysis material. The ultimate compositions of these materials are different. The origin of the benzene-soluble bitumen and its relation to kerogen are not known, but shale oil is a mixture of pyrolysis products of both the bitumen and kerogen. However, the low percentage of natural bitumen in the shale does not alter the composition of the shale oil significantly. In comparison with kerogen, marked decreases in the sulfur, nitrogen, and oxygen contents of the shale oil and the sulfur and nitrogen contents of the hydrogenolysis products

Table II. Composition of Gas Produced by Hydrogenolysis of Colorado Oil-Shale Kerogen.[a]

Constituent[b]	Vol. %[c]
Methane	2.7
Ethane	35.9
Propane	10.9
Ethylene	0.3
n-Butane and isobutane	2.3
Carbon dioxide	46.0
Nitrogen	1.5
1-Butene, 2-butene, and isobutene	0.1

[a] Carbonates removed from shale with acetic acid; hydrogenolysis at 355° C.

[b] Determined by mass spectrometer.

[c] Calculated as hydrogen-free, represents 7.6% of carbon in kerogen.

Table III. Ultimate Analyses of Kerogen and Oil-Shale Products[a]

				Hydrogenated Products	
	Kerogen	Extracted Bitumen[b]	N-T-U Oil[c]	Benzene-soluble[d]	Trichloro-ethylene-soluble[e]
C	78.28	82.59	84.53	83.93	81.03
H	10.55	11.04	11.32	13.00	12.28
S	1.34	1.19	0.75	0.12	0.18
N	2.59	0.81	1.77	0.36	0.57
O[f]	7.24	4.37	1.63	2.59	5.94
H/C atomic ratio	1.62	1.60	1.61	1.86	1.82

[a] Ash-free basis.

[b] Benzene-soluble bitumen extracted from raw oil shale; not considered as kerogen in this study.

[c] Shale oil from N-T-U retort comprising approximately 60% of kerogen.

[d] Benzene-soluble material comprising 80% of carbon in kerogen.

[e] Trichloroethylene-soluble material comprising 5.6% of carbon in kerogen.

[f] By difference.

Table IV. Properties of Fractions Separated from Benzene-Soluble Hydrogenolysis Material[a]

Fract. No.	Fraction	%[b]	Ultimate Analysis, % H	C	N	S	O[c]	Mol. Wt.	H/C Atomic Ratio
1-A	Benzene-soluble material	100.0	12.78	84.00	0.36	0.12	2.74	...	1.83
1-B	Pentane-insoluble fraction	0.8							
1-C	Insoluble resin	0.5	13.13	83.85	0.40	0.21	2.71	3,000+	1.88
1-D	Insoluble wax[d]	0.3	13.70	83.66	0.28	0.08	2.28	847	1.97
1-E	Pentane-eluted from Florisil[e]	67.9	12.97	83.73	0.09	0.09	3.12		1.86
1-F	MEK-soluble fraction	50.2	13.27	85.73	0.02	0.07	0.91		1.86
1-G	Pentane-eluted, silica gel	47.0	13.52	85.74	0.01	0.04	0.69	464	1.89
1-H	Acetone-eluted, silica gel[f,g]	2.9	10.32	84.95	0.11	0.07	4.55	377	1.46
1-I	MEK-insoluble fraction	17.3	12.65	82.83	0.32	0.10	4.10		1.83
1-J	Pentane-insoluble[h]	5.9	12.52	81.39	0.69	0.17	5.23	4,165	1.85
1-K	Pentane-eluted, silica gel[g]	9.7	13.06	83.86	0.17	0.07	2.84	2,225	1.87
1-L	Acetone-eluted, from Florisil[e]	10.8	11.68	84.06	1.20	0.20	2.86		1.67
1-M	Pentane-eluted, from silica gel[f,g]	6.6	12.58	84.62	0.90[i]	0.01	1.89	1,255	1.78
1-N	Acetone-eluted, from silica gel[f,g]	3.5	10.64	83.59	1.51[i]	0.02	4.24	436	1.53
1-O	Benzene + 5% MeOH, from Florisil[e]	16.2	12.84	84.81	0.77	0.10	1.48		1.82
1-P	Pentane-eluted, from silica gel[f,g]	14.8	12.92	84.85	0.66[j]	0.02	1.55	2,320	1.83
1-Q	Acetone-eluted, from silica gel[g]	0.6	11.62	80.48	1.14[k]	0.20	6.56	686	1.73

[a] Obtained by hydrogenolysis of Colorado oil-shale kerogen and extraction with benzene.
[b] Percentages based on total benzene-soluble material (80% of carbon in kerogen).
[c] Oxygen determined by difference.
[d] Melting point, 66° to 68° C.; N_d 1.483; carbon chains of 54 to 57 indicated by x-ray.
[e] Bromine number determinations indicated saturation.
[f] Infrared analyses indicated presence of aromatic nuclei, condensed structures, short carbon chains, and C = O groups.
[g] Trinitrofluorenone complex of Tetralin isolated and identified by x-ray.
[h] Contained 16.6% ash resulting from formation of tin-organic complex with catalyst; results calculated ash-free.
[i] Nitrogen 50 to 53% basic.
[j] Nitrogen 24% basic.
[k] Nitrogen 15% basic.

Table V. Properties of Wax Fractions Separated from Benzene-Soluble Hydrogenolysis Material[a]

Fract. No.	Fraction	%[b]	Ultimate Analysis, % H	C	N	S	O[c]	M.P., °C.	Mol. Wt.	N_d	H/C Atomic Ratio
2-A	0° C. wax, crystallized from MEK	13.7									
2-B	Acetone-soluble fraction	4.1									
2-C	Urea adduct[d,e]	1.8	14.34	84.39	0.02	0.04	1.21	58–59	430	1.442	2.04
2-D	Urea nonadduct	2.3									
2-E	Thiourea adduct[d,f]	1.0	12.74	81.91	0.26	0.10	4.99	46–49	564	1.468	1.87
2-F	Thiourea nonadduct[d,e,f,g]	1.3	13.31	83.78	0.18	0.20	2.53	33–36	762	1.479	1.91
2-G	Acetone-insoluble fraction[h,i]	9.0									
2-H	Thiourea adduct[i,j]	0.9	13.13	82.34		0.50	4.03	16–17	936	1.493	1.91
2-I	Thiourea nonadduct[i,j,k]	8.1	12.95	82.83	0.05	0.50	3.67	11–13	1028	1.491	1.88
2-K	– 17.8° C. wax crystallized from MEK	2.5									
2-L	Urea adduct[d,e]	0.8	14.10	83.86	0.07	0.09	1.88	40–43	381	1.452	2.02
2-M	Urea nonadduct[j]	1.7	13.90	84.80	0.04	0.06	1.20	20–22	648	1.478	1.97

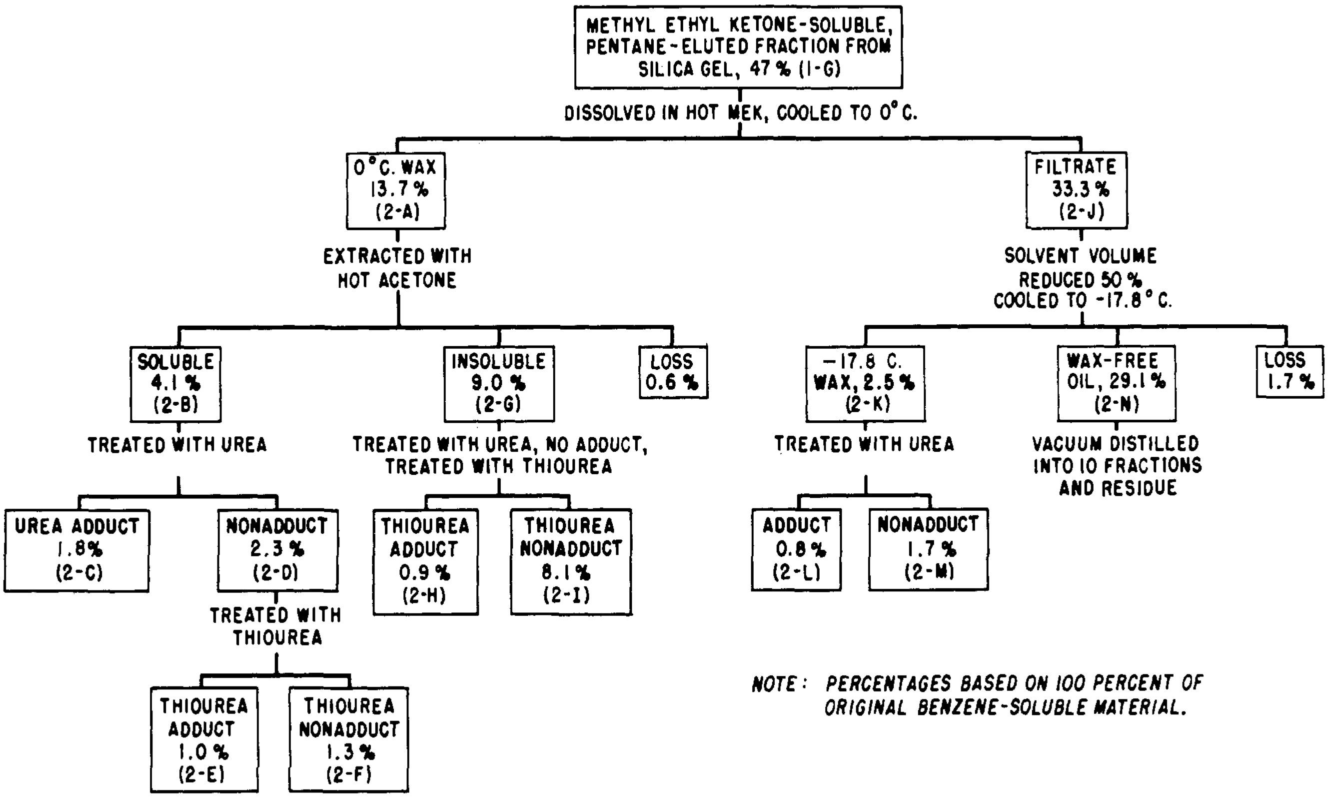
[a] Obtained by hydrogenolysis of Colorado oil-shale kerogen and extraction with benzene.
[b] Percentages based on total benzene-soluble material (80% of carbon in kerogen).
[c] Oxygen determined by difference.
[d] Infrared analyses indicated presence of straight chains and ester groups.
[e] X-ray indicated straight chains.
[f] Branched chains probably present.
[g] Saponification number 1060.
[h] Treated with urea but no complex formed.
[i] Microcrystalline.
[j] Infrared analyses indicated both branched and straight chains.
[k] Trinitrofluorenone complex of Tetralin isolated and identified by x-ray.

are apparent. The oxygen contents of the latter were also reduced but to a lesser extent.

The fractionation of the hydrogenolysis products into classes of compounds was accomplished by solvent extraction; chromatography on Florisil and silica gel; fractional crystallization from methyl ethyl ketone and acetone (*8*); vacuum distillation; formation of complexes with urea, thiourea, and 2, 4, 7-trinitrofluorenone (*5, 6, 11*); and acid and base extractions. Most of the results reported in this paper concern the benzene-soluble material. The study of the trichloroethylene-soluble material was limited by its complex nature and constituents of high molecular weight.

After Soxhlet extraction of the benzene-soluble material from the hydrogenolysis product, benzene was removed by distillation, and the extract, representing 80% of the kerogen carbon, was dried in a vacuum oven. It was a dark-brown, viscous material with a slight odor. A weighed portion of this material was dissolved in pentane and centrifuged to remove a small fraction of pentane-insoluble organic material (fraction 1-B, Figure 1) composed of resinous material (fraction 1-C) and a small amount of wax (0.3% of benzene-soluble material) containing chains up to 57 carbons in length (fraction 1-D). The dissolved material was then chromatographed on Florisil equal to approximately 400 times the weight of nitrogen in the sample (*7*) and eluted with pentane, acetone, and a mixture of benzene plus 5% methanol. Silica gel and the same eluents were used to classify the material further. Yields and properties of the fractions are shown in Table IV.

The benzene-soluble material was separated into a fraction composed largely of hydrocarbons, which was very low in sulfur and nitrogen but contained oxygen due



NOTE: PERCENTAGES BASED ON 100 PERCENT OF ORIGINAL BENZENE-SOLUBLE MATERIAL.

Figure 2. Fractionation of waxes in methyl ethyl ketone–soluble hydrogenolysis material from Colorado oil shale

especially to the presence of long-chain esters, and fractions that were comparatively high in nitrogen and oxygen but low in sulfur. The original pentane-eluted fraction (1-E) representing about 68% of the benzene-soluble material was fractionated with methyl ethyl ketone and silica gel as shown in Figure 1. Because of the hydrocarbon-like properties and quantity of fraction (1-G), it was studied more thoroughly than the other fractions. This fraction was resolved into the following general classes of materials: straight-chain waxes (including some esters) containing chains up to 33 carbons in length with an average molecular weight of 430; branched-chain waxes and esters with average molecular weights ranging from 564 to 762; microcrystalline waxes with average molecular weights of 936 to 1028; straight-chain waxes and esters with an average molecular weight of 381; branched-chain waxes with an average molecular weight of 648; a small fraction of straight-chain wax, 54 to 57 carbons in length, with a molecular weight of 847; and a wax-free oil. The procedure used to fractionate the waxes (8) is outlined in Figure 2, and yields and properties are summarized in Table V.

Two wax fractions were obtained by cooling the methyl ethyl ketone–soluble portion of the pentane-eluted material from silica gel (fraction 1-G representing 47% of the benzene-soluble material) to 0° and –17.8°C., respectively (*8*). The waxes were treated with urea and thiourea to remove adducts of straight-chain and branched-chain compounds, respectively (*6*, *11*), leaving cyclics and other nonadducts in the filtrate.

Based on x-ray diffraction the urea adduct (fraction 2-C) from the 0°C. wax contained paraffin waxes with chain lengths as long as 33 carbons. Infrared spectra indicated the presence of straight chains and some ester groups. The thiourea adduct (2-E) and nonadduct (2-F) fractions showed some of the same properties as the preceding fraction in that chain lengths up to 33 carbons were indicated in the thiourea adduct and chains of 6 carbons or more in length evidenced considerable branching. Also, all fractions appeared to contain ester groups. These were further indicated by oxygen in the fractions and the fact that long-chain esters form urea complexes, as reported by Zimmerschied and coworkers (*11*). Saponification number determinations confirmed this assumption. For example, the saponification number of the thiourea nonadduct fraction (2-F) was 1060.

The acetone-insoluble portion of the 0°C. wax (2-G), which was microcrystalline in character, was treated with urea, but no complex was formed, showing that long carbon chains were essentially absent. The wax was then treated with thiourea, and two fractions were obtained. Infrared spectra analyses showed that the thiourea adduct (2-H) was highly branched but contained some straight chains. The thiourea nonadduct fraction (2-I) contained some cyclics. It was treated with trinitrofluorenone and the trinitrofluorenone complex of Tetralin was isolated and identified by x-ray diffraction.

The wax fraction separated at –17.8°C. (2-K) was also treated with urea in a similar manner. Adduct (2-L) and nonadduct (2-M) fractions were obtained; in general, they were similar to the fractions obtained from fractions 2-D and 2-G. The former was composed essentially of straight-chain compounds and the latter of essentially branched-chain compounds. The small amounts of these fractions limited further study.

Table VI. Properties of Adduct-Forming Portions of Hydrocarbon Fractions Obtained by Vacuum Distillation of Wax-Free Oil[a]

Fract. No.	Cut Temp., °C.	%[b]	% of Sample H	% of Sample C	H/C Atomic Ratio	Mol. Wt.	Sp. Gr.[c]	n_D^{20}	Calculated Average Formula[d]	Amt. of Each Formula in Fraction,%[e]
1	99	0.5	...	...	...	291	...	1.4343	$(CH_3)_2(CH_2)_{19}$	30
									$(CH_3)_3(CH_2)_{17}CH$	70
2	123	1.1	14.99	84.72	2.12	254	0.776	1.4348	$(CH_3)_3(CH_2)_{14}CH$	100
3	144	1.3	15.01	85.22	2.11	260	0.788	1.4396	$(CH_3)_3(CH_2)_{15}CH$	100
4	150	1.0	14.54	84.20	2.07	273	0.798	1.4432	$(CH_3)_3(CH_2)_{15}CH$	100
5	163	1.1	14.62	84.38	2.08	279	0.801	1.4452	$(CH_3)_2(CH_2)_{18}$	60
									$(CH_3)_3(CH_2)_{16}CH$	40
6	190	1.3	14.44	84.40	2.05	297	0.809	1.4488	$(CH_3)_3(CH_2)_{19}$	40
									$(CH_3)_3(CH_2)_{17}CH$	60
7	270	1.2	15.22	84.22	2.17	340	0.816	1.4531	$(CH_3)_2)CH_2)_{22}CH$	25
									$(CH_3)_3(CH_2)_{20}CH$	75
8	229	0.8	14.94	84.00	2.13	380	...	1.4581	$(CH_3)_3(CH_2)_{23}CH$	100
9	254	0.4	...	...	...	412	...	1.4699	$(CH_3)_{2-3}(CH_2)_{27}$[f]	100
10	262	0.2	...	...	...	441	...	....	$(CH_3)_2(CH_2)_{29}$[f]	100
Residue	...	Trace	...	...	...	...	...	...	...	...

[a] Fractions 1 to 8 distilled at 0.8 to 0.9 mm. of mercury pressure; fractions 9 and 10 distilled at 35 microns of mercury absolute pressure.
[b] % of wax-free oil (wax-free oil is 29% of benzene-soluble material).
[c] 25°/25° C.
[d] Average groups per molecule based on infrared analysis.
[e] Calculated percentage of each formula in fraction.
[f] Infrared data extrapolated to obtain results because molecular weights are out of instrument range.

Table VII. Properties of Non-Adduct-Forming Portions of Hydrocarbon Fractions Obtained by Vacuum Distillation of Wax-Free Oil[a]

Fract. No.	Cut Temp., °C.	%[b]	% of Sample H	% of Sample C	H/C Atomic Ratio	Mol. Wt.	Sp. Gr.[c]	n_D^{20}	Calcd. Av. Formula[d]	Amt. of Each Formula in Fraction,%[e]
1	99	2.0	13.45	84.55	1.90	253	0.846	1.4625	$(CH_3)_4(CH_2)_{12}(CH)_2$	40
									$(CH_3)_5(CH_2)_{10}(CH)_3$	60
2	123	4.7	13.20	84.61	1.87	265	0.848	1.4663	$(CH_3)_4(CH_2)_{13}(CH)_2$	40
									$(CH_3)_5(CH_2)_{11}(CH)_3$	60
3	144	5.0	13.46	85.53	1.89	269	0.856	1.4701	$(CH_3)_4(CH_2)_{13}(CH)_2$	20
									$(CH_3)_5(CH_2)_{11}(CH)_3$	80
4	150	3.8	13.10	83.90	1.87	281	0.861	1.4730	$(CH_3)_4(CH_2)_{14}(CH)_2$	30
									$(CH_3)_5(CH_2)_{12}(CH)_3$	70
5	163	3.8	13.02	84.69	1.85	297	0.869	1.4761	$(CH_3)_4(CH_2)_{15}(CH)_2$	20
									$(CH_3)_5(CH_2)_{13}(CH)_3$	80
6	190	6.4	13.34	85.57	1.87	320	0.871	1.4782	$(CH_3)_5(CH_2)_{15}(CH)_3$	85
									$(CH_3)_6(CH_2)_{13}(CH)_4$	15
7	270	7.3	13.18	84.96	1.86	361	0.876	1.4812	$(CH_3)_5(CH_2)_{18}(CH)_3$	50
									$(CH_3)_6(CH_2)_{16}(CH)_4$	50
8	229	7.3	13.22	85.28	1.86	390	0.883	1.4843	$(CH_3)_5(CH_2)_{22}(CH)_3$	
									$(CH_3)_6(CH_2)_{18}(CH)_4$	
9	254	8.6	13.16	85.18	1.85	452	0.887	1.4865	$(CH_3)_{4-5}(CH_2)_{27-28}$[f]	
10	262	8.1	13.30	85.54	1.87	476	0.891	1.4888	$(CH_3)_5(CH_2)_{29}CH$[f]	
Residue	...	33.0	12.72	85.80	1.78	740	...	1.504	$(CH_3)_{4-5}(CH_2)_{48}$[f]	

[a] Fractions 1 to 8 distilled at 0.8 to 0.9 mm. of mercury pressure; fractions 9 and 10 distilled at 35 microns of mercury absolute pressure.
[b] % of wax-free oil (wax-free oil is 29% of benzene-soluble material).
[c] 25°/25°C.
[d] Average groups per molecule based on infrared analysis.
[e] Calculated percentage of each formula in fraction.
[f] Infrared data extrapolated to obtain results because molecular weights were out of instrument range.

The wax-free oil (2-N), which amounted to 29.1% of the benzene-soluble material, was vacuum-distilled into 10 fractions and a residue. These were treated with urea and separated into two general classes consisting essentially of straight-chain compounds (urea adduct-forming material) and branched-chain and possibly cyclic compounds (non-adduct-forming material). Based on infrared spectra, the average CH_2 and CH_3 contents and formulas for each fraction were calculated (Tables VI and VII). As the agreement between two regions of the spectra was fair for the CH_3 determinations but less satisfactory for the CH_2 determinations, the formulas represent only the order of magnitude. Taking this into consideration, the properties presented in Table VI indicate that the fractions were, for the most part, straight-chain paraffins with molecular weights ranging from 254 to 441. Table VII presents similar properties of the non-adduct-forming portions of the vacuum-distilled fractions and the residue. These properties indicate that the non-adduct-forming portions of the vacuum-distilled fractions contained branched-chain hydrocarbons with molecular weights ranging from 253 to 740.

Because of the number and different types of compounds present in the pentane-eluted fraction (1-E) and the lack of knowledge of the steps involved in their formation, it is not possible to establish their precursors. It is evident, however, that the long-chain waxes, for example, do not exist as such in the kerogen or they could be extracted with solvents. Therefore, they must exist as a part of the molecule attached in such a way that they are cleaved free by pyrolysis or hydrogenolysis, as they are present in both shale oil (*8*) and hydrogenolysis products. To establish whether the branched-chain and cyclic compounds exist similarly in the kerogen molecule will require additional study.

The two high-nitrogen fractions, representing 10.8% (1-L) and 16.2% (1-O) of the benzene-soluble material obtained by chromatographing the benzene-soluble material on Florisil, were then chromatographed on silica gel to produce three principal fractions (1-M, 1-N, and 1-P) and a small fraction (1-Q). Molecular weights for these samples ranged from 436 for fraction 1-N to 2320 for sample 1-P. Treatment with perchloric and hydrochloric acids (*3*) showed that

Table VIII. Properties of Trichloroethylene-Soluble Hydrogenolysis Material[a]

Fraction	%[b]	Ultimate Analyses, % H	C	N	S	O[c]	H/C Atomic Ratio	Mol. Wt.	Structures Indicated by Infrared Spectra
Trichloroethylene-soluble material		12.28	81.03	0.57	0.18	5.94	1.63		
Acid extract	21.0								
Trichloroethylene-soluble	(5.5)	12.29	82.44	0.35	0.32	4.60	1.79	1076	Long chains, branched chains, carbonyl and possibly esters
Chloroform-soluble	(0.7)	...	...	...	...	...	...	2000+	Branched chains, carbonyl and possibly esters, hydroxyl groups
Insoluble	(14.8)	11.51	81.98	0.67	0.77	5.07	1.78		No infrared pattern
Base extract	0.4							1500+	Long chains, branched chains, amides
Neutral fraction	74.2	12.41	81.65	0.38			1.82	1053	Long chains, branched chains, amides
Loss	4.4								
Total	100.0								

[a] Obtained by hydrogenolysis of Colorado oil-shale kerogen and extraction with trichloroethylene; represents 5.6% of carbon in original kerogen.
[b] Based on 100% of trichloroethylene-soluble material.
[c] By difference.

approximately 50% of the nitrogen in the first two fractions (1-M and 1-N) and 24% of the nitrogen in the third fraction (1-P) was basic. Basic nitrogen indicates such structures as piperidines and quinolines. Neutral nitrogen indicates pyrrole and carbazole structures.

Infrared spectra analyses of the same fractions indicated the presence of aromatic nuclei, condensed structures, short carbon chains, and carbonyl groups. A portion of each fraction yielded an insoluble complex with trinitrofluorenone (5) in which the trinitrofluorenone complex of Tetralin was identified by x-ray diffraction. No significant separations were obtained by extractions of these fractions with dilute or concentrated acids and bases.

Different results were obtained by oxidizing fractions 1-M and 1-P with hot, alkaline potassium permanganate. Oxidation of sample 1-M for 8 weeks consumed approximately 21 grams of potassium permanganate per gram of carbon and converted 77% of the carbon to carbon dioxide, 0.6% to volatile acids—e.g., acetic acid—7.2% to oxalic acid, and 14.8% to nonvolatile-nonoxalic acids; 0.4% was unoxidized. Attempts to prepare identifiable derivatives of the nonvolatile-nonoxalic acids were unsuccessful. Sample 1-P was more resistant to oxidation and consumed only 5 grams of potassium permanganate per gram of carbon. Analyses of these oxidation products showed that 11.1% of the carbon was converted to carbon dioxide, 0.4% to volatile acids, 5.2% to oxalic acid, and 9.0% to nonvolatile-nonoxalic acid; 74.3% was unoxidized.

While the oxidation results were difficult to interpret, the data substantiated some of the infrared analyses in that the high-nitrogen material (representing 27 weight % of the benzene-soluble material) appeared to be a mixture of complex compounds composed of aromatic nuclei, condensed structures, and carbon chains. Except for Tetralin detected in all fractions, no individual compounds were identified.

The trichloroethylene-soluble material, representing 5.6% of the carbon in the kerogen, was extracted with 20% sodium hydroxide and 20% sulfuric acid. The base extract of only 0.4% was insignificant. The acid extract, amounting to 21%, was separated further into the following fractions: trichloroethylene-soluble, 5.5%; chloroform-soluble, 0.7%; and insoluble material, 14.8%. Infrared spectra analyses of the soluble portions of the acid extract indicated both straight and branched chains and considerable evidence of two types of carbonyl groups. Similar analyses of the neutral fraction (representing 74% of the trichloroethylene-soluble material) indicated long chains, carbonyl groups, ether linkages, and possibly amides. Tetralin was isolated from the neutral fraction by preparing trinitrofluorenone complex; the neutral material was very resistant to oxidation by hot alkaline permanganate solution. Some of the properties of these fractions are shown in Table VIII. The base and acid extractions were difficult to perform because of the formation of emulsions that required extractions with additional trichloroethylene and neutralization to break them. Tetralin was probably present because it had not been removed during the benzene extraction.

CONCLUSIONS

This study showed that a high percentage of Colorado oil-shale kerogen can be converted to soluble products by hydrogenolysis and that these products are amenable to partial separation into type compounds, a number of which are indentifiable. However, no definite structures in kerogen were established because of the uncertainty of the degradation reactions involved and the possibility that polymerization and other side reactions occurred during the treatment and because the final products were not completely identified.

Elucidation of the structure of kerogen based on hydrogenolysis requires a more comprehensive study of the reactions involved and the resulting products by employing additional catalysts under a wider range of temperatures and pressures than were used in this study.

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