

Some Chemical Reactions of Colorado Oil Shale Kerogen

Oil shale kerogen is a largely nonbenzenoid material with a limited amount of unsaturation and ability to undergo typical aromatic substitution reactions. Reactivity to various reagents indicates one double bond or active hydrogen atom for 16 to 22 carbon atoms. Perhaps kerogen is composed of polymeric or other units each containing 16 to 22 carbon atoms

COLORADO oil shale kerogen is an infusible, insoluble polymeric material, generally thought to be a nonaromatic hydrocarbon in chemical combination with compounds containing oxygen and small amounts of nitrogen and sulfur. Controlled permanganate oxidation gives only aliphatic carboxylic acids and oxides of carbon (10, 11). Ultimate analysis differs in different samples of shale; Colorado oil shale gives fairly consistent results (3, 4).

| Method of Concentrating Kerogen | % C | % H | % N | % S | % O Diff. | C/H |
|----------------------------------|------|------|-----|-----|-----------|-----|
| Acetic acid leach and sink float | 78.0 | 10.3 | 2.6 | 1.2 | 7.9 | 7.6 |
| HCl, HF leach | 78.4 | 10.4 | 2.6 | 1.2 | 6.4 | 7.4 |

The chemical literature contains little information relative to oil shale. Chlorination has been described (6), but the increase in weight reported is small. Selenium oxychloride reacted with oil shale and increased the weight of the shale by 21%, indicating the presence of unsaturated hydrocarbon (6). Kerogen is not appreciably attacked by acid or alkali; fusion with caustic gives a very low yield of water-soluble organic acids. Hydrogenation of Colorado oil shale has been reported (8). Thermal cracking of oil shale has only recently been scientifically investigated. Oxidation of oil shale is the only other chemical reaction extensively examined. Oxidants include nitric acid (9), hydrogen peroxide (2), a mixture of potassium hydroxide and potassium nitrate (5), alkaline potassium permanganate (10, 11), oxygen (7), and air (7). Permanganate, the most extensively employed, has given products indicative of the original nature of kerogen. Stepwise oxidation with a deficiency of permanganate converts about 80% of the organic material to nonbenzenoid, alkali-soluble "regenerated humic acids" (10, 11). There may be two kinds of kerogen, as not all the kerogen is oxidized with equal ease, and kerogen is a nonbenzenoid material.

The present work was undertaken to expand knowledge of the chemical nature of kerogen. Chlorination and air oxidation have been investigated, as well as

hydrobromination, sulfonation, and nitration of Colorado oil shale kerogen. The reactivity toward various reagents was definitely established. Other reagents failed to react. Kerogen may be a heterogeneous material and the reaction product analyses are perhaps only average values.

Oil Shale Samples

The samples were of rich shale having a Fischer assay of 67 gallons per ton;

those used in the air oxidation experiments assayed approximately 30 gallons per ton. All samples were from the Bureau of Mines oil shale mine near Rifle, Colo. (Green River formation).

The shale, sieved to 100 to 200 mesh, was treated for 4 hours at room temperature with 1 to 1 hydrochloric acid prior to reaction of the kerogen. Reaction with acid is slow at first, but eventually the inorganic carbonates dissolve. This procedure eliminates inorganic carbon and renders ultimate analyses of the final products more meaningful (Table I).

Experimental

Chlorination. Chlorine gas was swept for 3 hours over a few grams of acid-treated oil shale in a 2-inch horizontal glass cylinder. A bed of the shale particles (maximum 1/8 inch thick) was spread out on the bottom of the cylinder. During the early part of the experiment the temperature of the shale bed rose to 60° C. and hydrogen chloride was evolved. Analysis indicated 18.96% chlorine. In a second experiment in a

column packed with oil shale the reaction became so violent that carbonization ensued.

A third sample of shale was chlorinated with chlorine gas while suspended in refluxing carbon tetrachloride. Filtration gave an amber filtrate and the residue was therefore washed with carbon tetrachloride to remove all soluble material. The residue after drying in vacuum contained 21.85% chlorine. Only 2.20% chlorine remained in the sample after treatment with a tertiary amine, indicating elimination of hydrogen chloride from the chlorinated kerogen and a deficiency of aromatic ring chlorine.

Chlorination in water solution at room temperature (addition of hypochlorous acid) gave a light tan product which contained 10.8% chlorine.

Hydrobromination. In a manner similar to that used for the chlorination experiments 67-gallon-per-ton oil shale previously treated with acid and sieved to 100 to 200 mesh was exposed to an atmosphere of anhydrous hydrogen bromide. Analysis indicated 13.46% bromine in the product. In benzene suspension the product formed contained 12.33% bromine.

Nitration. Two grams of acid-treated oil shale sieved to 100 to 200 mesh was nitrated in a 1 to 1 mixture of concentrated nitric acid and concentrated sulfuric acid at 50° to 54° C. The product when washed and dried contained 3.45% nitrogen.

A second experiment at 90° to 95° C. gave a product with 3.25% nitrogen.

Sulfonation. Sulfonation was performed with fuming sulfuric acid or chlorosulfonic acid. The chlorosulfonic acid was most suitable when the following procedure was used.

Table I. Ultimate Analyses of Oil Shale

| Shale Sample | % C | % H | % Cl | % N | % S | % Ash |
|-------------------|-------|------|------|------|------|-------|
| 67 gal./ton shale | 30.55 | 3.76 | 0.14 | 0.88 | 2.04 | 56.31 |
| Acidized | 37.76 | 5.13 | 1.54 | 1.30 | 2.39 | 49.45 |

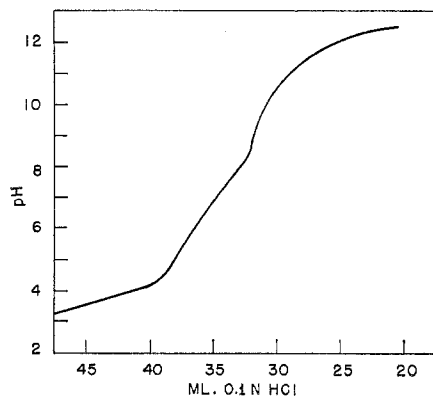


Figure 1. Typical acidification curve for sodium salts of water-insoluble acids shows similarity to polyfunctional weak acids

Twenty grams of oil shale, treated with 1 to 1 hydrochloric acid and sieved to 100 to 200 mesh, was added to 100 ml. of methylene chloride containing 6 ml. of chlorosulfonic acid. Reaction began immediately, as shown by evolution of acidic vapors. After spontaneous reaction had proceeded for 1 hour, the mixture was heated to refluxing temperature for an hour. The reaction vessel was then allowed to stand undisturbed overnight. The mixture was filtered and washed with methylene chloride until the washings were colorless. The residue was washed with dilute hydrochloric acid and then with water, then transferred to a flask and heated to boiling with dilute alkali. The dark brown solution was filtered and the remaining sulfonated shale was washed well with water. When dry, the product weighed 10.4 grams and contained C, 37.84%; H, 4.97%; S, 6.06%; Cl, 0.34%; ash, 40.50%. This sulfonated shale is an ion exchange material having a capacity of 1.683 meq. per gram, similar to sulfonated coal. When converted to its magnesium salt it is a low capacity desiccant capable of taking up 5.6 weight % of moisture upon standing in air.

Air Oxidation. Oil shale assaying approximately 30 gallons per ton, which had been ground and sieved to 30 to 50 mesh and elutriated of fines, was air-oxidized in a heated static bed. When air was passed through the bed at temperatures well above 200° C., the oxidation could be controlled only by limiting the supply of air, and a hot zone proceeded through the bed. Oxidation was carried out with a hot zone at 245° to 255° C. beginning at the bottom of the bed where air was admitted and advancing upward as combustion proceeded. Oxidation with a hot zone temperature of 375° C. completely oxidized the organic matter to oxides of carbon and volatile acids. The exit gas stream for the latter oxidation was shown by Orsat analysis to contain approximately 2% oxygen.

Oxidation at 200° and atmospheric

pressure is general throughout the bed, as shown by the absence of a hot zone and the presence of 18 to 19% oxygen in the exit gas stream. The principal products are water, oxides of carbon, and water-insoluble regenerated humic acid. A small amount of volatile acid is produced. Extent of oxidation at 200° C. is indicated in Table II.

The water-insoluble acids were very hard, solid, amorphous substances, soluble in dimethyl formamide and sparingly soluble in pyridine, ethylenediamine, and diethylene glycol. They are practically insoluble in water and many common organic solvents, including acetone, but dissolve readily in certain solvent pairs such as 50% acetone in water. Their sodium salts are water-soluble and were extracted from the oxidized shale residue by digestion in hot aqueous alkali. When allowance was made for inert matter in the acids as shown by ash analysis, the equivalent weight of several samples ranged between 123 and 153. A typical acidification curve is shown in Figure 1.

Other Reactions. An attempt to acetylate acid-treated 67-gallon-per-ton oil shale with acetic anhydride in the presence of stannic chloride did not give the expected Friedel-Crafts reaction, but a substance containing 6.58% chlorine and 5.80% tin was produced.

Maleic anhydride failed to react with 67-gallon-per-ton acid-treated oil shale.

Discussion and Conclusions

Colorado oil shale kerogen undergoes reactions typical of unsaturated substances. As chlorination involves substitution as well as addition, it cannot be used to measure the degree of unsaturation. If the chlorine reacted only by addition and to the same extent as hydrogen bromide, chlorine in the chlorinated shale would be 12.12%. From this we can conclude that the 18.96% chlorine actually obtained includes 6.84% which reacted by substitution. Experiments with hydrogen bromide indicate formation of a hydrobrominated kerogen containing 23.9% hydrogen bromide. This represents addition to approximately one double bond for each 16 carbon atoms in the kerogen. Such conclusions are not entirely accurate because of uncertainty as to the exact amount of kerogen in the sample of shale used and the difficulty of obtaining complete reaction in a heterogeneous system, but the value is significant. The failure of maleic anhydride to react with kerogen perhaps indicates the absence of conjugated double bonds.

Although kerogen is generally thought of as nonbenzenoid in nature, it undergoes some substitution reactions typical of aromatic compounds. It nitrates (under conditions suitable for producing nitrobenzene from benzene) to give a

Table II. Air Oxidation of Oil Shale Is General throughout the Bed at 200° C. and Atmospheric Pressure

| Oxidation Time, Hours | Loss during Oxidation, Wt. % | Water-Insoluble Acids, G./100 G. Kerogen | CO ₂ Evolved, Grams | Carbon Evolved as CO ₂ , Wt. % Shale | 0.1N NaOH to Render 1 Gram of Oxidized Shale Neutral to Phenolphthalein, ml. |
|-----------------------|------------------------------|--|--------------------------------|---|--|
| 34.5 | 1.35 | 8.2 | 24 | 0.89 | 2.82 |
| 70.7 | 3.25 | 29.5 | 48 | 1.62 | 4.90 |
| 168.0 | 5.65 | 33.0 | 72 | 2.19 | 6.50 |
| | | | 96 | 2.58 | 8.04 |

material which contains approximately one nitro group for each 16 carbon atoms. Kerogen is readily sulfonated with chlorosulfonic acid to give alkali-soluble sulfonic acids and an insoluble sulfonated oil shale residue containing approximately one sulfonic group for each 21.5 carbon atoms (assuming that the sulfonated residue represents a typical sulfonated kerogen).

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