

Optical Activity of Petroleum

THOMAS S. OAKWOOD, D. S. SHRIVER,
H. H. FALL, W. J. MCALEER, AND P. R. WUNZ

Pennsylvania State College, State College, Pa.

THE question of the origin of petroleum has long been debated. In the history of this question, the fact of the optical activity of petroleum has occupied an important place. It was pointed out (1, 2) by Walden that "inorganic" hypotheses for explaining the origin of petroleum did not account for its optical activity. Because of the increasing certainty that all petroleum possessed optical activity, Engler (2) studied this occurrence in petroleum.

Fenske and his associates (4) have studied the distribution of optical activity in distillation fractions of a great variety of crude oils.

From the reported work, some generalizations may be made:

1. Optical activity appears in petroleum distillates at molecular weight of approximately 220, and increases thereafter passing through a maximum at molecular weight at about 400.

2. The maximum rotation is reached in fractions having about the same boiling points, regardless of the source of the petroleum.

3. Raw petroleum and its fractions are commonly dextrorotatory although there are a few reports of levorotatory distillation fractions (3).

The present study was undertaken with the idea of getting as much knowledge as possible concerning the character of the optically active substances of petroleum. It has been suggested repeatedly that sterols are responsible for the optical activity of petroleum since these yield dextrorotatory hydrocarbons on pyrolysis under pressure. It is notable that the saturated steroidal hydrocarbons lie in the correct molecular weight range to appear in the maxima of rotation for petroleum fractions, and they are all reported to have specific rotations of $+20^\circ$ to $+28^\circ$.

It is considered that the optically active compounds of petroleum may retain, besides the necessary asymmetry, other structural elements which would allow their precursors in nature to be recognized. And it is easily conceivable that such a relationship, once established, could cast considerable light on the process by which a precursor was changed into the substances now found in petroleum. This was the ultimate purpose of the work here reported.

EXPERIMENTAL

Materials. Two refinery samples were used for the bulk of the work reported. Crown oil was a 5-gallon sample separated by distillation only, from Cordale distillate, Jackson County, Tex. The sample had A.P.I. gravity of 15.9° and the Saybolt Universal viscosity was 1800 seconds at 100° F. California oil was a 1-gallon sample of the phenol raffinate of a neutral produced from a mixture of California crude oils.

The silica gel used was purchased from the Davison Chemical

The fact of the optical activity of petroleum has been of great importance in the question of the origin of petroleum, but there is little knowledge of the chemical nature of the optically active compounds of petroleum. The work reported was undertaken to isolate and, if possible, to identify such compounds. Methods for concentrating the optical activity have been developed, including distillation, chromatography, and partial chemical oxidation. Two refinery samples in the lubricant range, having different origins in nature and different refining histories, were studied. Each of these, by the same kinds of separations, yielded crystalline mixtures which appear to be similar in their gross nature, if not the same. These mixtures have average molecular weights near 400; they contain about 88% carbon and 12% hydrogen; their melting points lie in the range 126° to 132° C.; and their specific rotations at comparable melting points are $+32.7^\circ$ and $+36.8^\circ$. The data show that the mixtures are composed of saturated naphthenic hydrocarbons having four or five rings, but sufficient work has not been done to justify detailed conclusions as to the structures.

Corp.; it was 28-200 mesh and marked as commercial desiccant. The activated alumina was purchased from the Aluminum Ore Co., Grade F-20, 80-200 mesh. The pentane was mixed pentanes, purchased from the Phillips Oil Corp. It was dried and distilled before use; some samples were treated with fuming sulfuric acid, washed, dried, and distilled.

The rotations of the oil samples were measured at room temperature in 1-dm. tubes, using a Franz Schmidt and Haensch polarimeter which could be read within $\pm 0.01^\circ$. A sodium arc bulb was used as the light source. Since

most of the oil samples were highly viscous, the rotations were measured in hexane or chloroform solutions which were of such concentrations that the observed rotations were at least 2° . The specific rotations were found to be independent of the solvent used.

Silica Gel Treatment. Silica gel treatment of the oil was carried in batches. Crown oil (500 grams) was diluted with a liter of pentane, and 1 kg. of silica gel was added with vigorous stirring in 15 minutes. After additional stirring for an hour, the gel was filtered and washed with pentane. The filtrate and washings were evaporated and the oil was weighed. This process was repeated until a small loss (2 to 3 grams) was noted. There were obtained 260 grams of nearly white oil, $\alpha_D + 5.5^\circ$. The oil adsorbed on the gel was desorbed with methanol; it was quite viscous, highly colored and had $\alpha_D + 1^\circ$.

In the same manner California oil gave an unadsorbed oil with $\alpha_D + 3.2^\circ$.

Distillation. Distillation of the unadsorbed oils was carried out in vacuo. The still was of standard Penn State design; the packed section was 21×2.5 cm. and was filled with protruded metal packing. The still pot, sealed to the still pipe, carried a sealed-in thermometer well and was heated by a Glas-Col mantle. A typical distillation of Crown oil (800 grams) gave 34 fractions of nearly equal size and a small residue. Fractions 22 to 31, inclusive (228.9 grams), had $\alpha_D^{28} + 10.3^\circ$ to $+ 11.9^\circ$ and n_D^{20} , 1.5082 to 1.5113. Combustion analysis showed carbon, 87.6%, hydrogen, 12.3%, and the molecular weight was 392 (micro-Rast, average of four determinations).

The California oil (1465 grams) gave ten fractions (450 grams) and a large residue. Fraction 4 had $\alpha_D + 9.1^\circ$.

Chromatographic Separation. Chromatographic separation of the distilled oil fractions was carried out by packing a glass tube 9 feet by $\frac{3}{4}$ inch with activated alumina and pouring the oil into the column. After the oil (41 grams, $\alpha_D + 10.7^\circ$) had passed into the alumina, pentane was added and the eluate was collected in fractions, the pentane evaporated, and the oil weighed. Since no convenient diagnostic test was found, successive eluate frac-

tions were combined as was convenient and necessary to measure the rotations. Table I shows typical results.

This pattern has always been observed in more than 200 such separations. The recovery of the oil taken in cases such as these is usually about 90%, depending on the effectiveness of the silica gel treatment; the recovery is often 98%, if large amounts of eluent are used. The amount of eluent used depended on the practical considerations, chiefly the time consumed. It is important to note that pentane alone was used as solvent and that nearly all the optical activity passed through the alumina readily with this solvent.

Table I. Chromatographic Separation of Distilled Oil Fractions

(Crown oil α_D 12.0°, 22.34 grams original sample)

Fraction No.	Weight of Oil, Grams	Running Total Weight, Grams	α_D^{25}
1	8.10	8.10	1.50
2	3.56	11.66	4.80
3	1.96	13.62	11.10
4	1.35	14.97	16.10
5	1.08	16.05	20.00
6	1.13	17.18	23.40
7	0.45	17.65	15.30
8	0.06	17.69	...

The fractions having rotations $\alpha_D + 20^\circ \pm 2^\circ$ were combined with others obtained by repeating the above process and rechromatographed. In this way 23.6 grams of oil (Crown) was obtained with $\alpha_D + 27^\circ$, observed rotation $+ 6.63^\circ$, $c = 24.6$ in hexane and 15 grams of oil, $\alpha_D + 27.8^\circ$ was obtained from California oil.

Partial Oxidation of Oil Fractions. These were carried out with chromic anhydride in acetic acid. Preliminary work showed that the hydrocarbon recovered from a chromic acid oxidation of gel-treated lubricant fractions had higher rotation than the original material taken. This was taken as evidence that part of the optically active substances of petroleum oxidized more slowly than the optically inactive substances. The following experiment shows the utility of this observation in concentrating the optical activity of petroleum.

A solution of 14.3 grams of oil ($\alpha_D = +27^\circ$), obtained from Crown, was dissolved in 900 ml. of glacial acetic acid and placed in a flask equipped with a mechanical stirrer. A solution of 10 grams of chromic anhydride in 100 ml. of 90% acetic acid was added to the oil solution in 35 minutes, keeping the reaction mixture at 90° with good stirring. The reaction mixture was stirred and heated for 20 hours, when 20 ml. of methanol was added; the acetic acid was distilled at reduced pressure, and the residue was steam distilled. The cooled distillation residue was extracted thoroughly with ether, and the ether extract was washed successively with water, 5% sodium hydroxide solution, and 5% sodium bicarbonate solution. Evaporation of the ether solution gave 11.0 grams of neutral material; the bicarbonate and sodium hydroxide washes gave acidic material amounting to 4 grams.

The neutral material from the oxidation was dissolved in pentane and chromatographed over alumina. The pentane eluate was divided into seven fractions having a total weight of 8.7 grams. The adsorbed material remaining on the column was eluted with ether-methanol to give five fractions of total weight 2.2 grams.

The pentane eluate fractions 5 (2.9 grams), 6 (0.70 gram), and 7 (0.04 gram), were semicrystalline. By crystallizing these from acetone, 0.78 gram of well-crystallized material was obtained. This material had a melting point of 126° to 132° C.; $\alpha_D^{26} + 36.8^\circ$, $c = 2.2$ in hexane; analysis, found: carbon, 87.8%; hydrogen, 11.7%.

In analogous fashion, 13.0 grams of oil, α_D^{27} , 26°, from California oil was oxidized with 13 grams of chromic anhydride.

There was obtained 9.0 grams of neutral material and 3.5 grams of acids. Chromatography of the neutral material gave 13 fractions. Although some of these were partly crystalline, it was necessary to repeat the oxidation in order to obtain well-crystallized material, m.p. 121° to 126, $\alpha_D^{27} + 32.7^\circ$, $c = 3.5$ in hexane observed rotation. A mixture of this material with that obtained in the first experiment had a melting point of 126° to 131° C. It was difficult to crystallize the material obtained from California oils.

CHARACTERISTICS OF CRYSTALLINE SUBSTANCES

Crystallization was carried out beginning with 1.16 grams, m.p. 130° (all melted), α_D , 37.8°, which was dissolved in 150 ml. of hot 95% alcohol. Cooling gave (I) 0.82 gram, m.p. 131–134° C. $\alpha_D + 38.5^\circ$. Recrystallization of (I) gave (II), 0.77 gram, m.p. 138–143°, α_D 38.5°. Recrystallization of (II) gave (III) 0.63 gram, m.p. 145–147°, α_D 36.4°. (III) gave (IV), 0.39 gram, 149–154°, α_D 38.4°.

Crystallization from acetone led to similar results except that the melting range of the crystalline material after five crystallizations was 160–167° C. with $\alpha_D + 39.2^\circ$.

Chromatographic separation was carried out using a sample of 0.58 gram of crystalline material, $\alpha_D + 38^\circ$, m.p. 113–119°. This was dissolved in 60 ml. of pentane and separated into 13 fractions through a column of alumina, 8 feet by 3/4 inch, using pentane as eluent. The first five fractions (0.03 gram) of 25 ml. of pentane each, were tiny and none crystallized. The next eight fractions were all crystalline. Each was crystallized from alcohol; the crystals were filtered and dried, and the filtrates were evaporated and weighed. The data are shown in Table II. Fractions 7 and 11 were mixed and the melting point of the mixture was 133–143° C.

Table II. Chromatography of Optically Active Crystallizate

Charge: 0.58 gram
Adsorbent: activated alumina
Column: 8 ft. \times 3/4 inch

Fraction No.	Weight, Gram	Crystals		Filtrate Solids	
		Weight, gram	M. P., ° C.	Weight, gram	M. P., ° C.
1	0.00
2	0.01
3	0.00
4	0.00
5	0.01
6	0.08	0.02	118–121	0.06	98–108
7	0.09	0.01	130–134	0.08	115–121
8	0.05	0.01	131–137	0.04	117–121
9	0.11	0.04	133–138	0.07	116–118 5
10	0.08	0.02	136–142	0.06	110–125
11	0.08	0.03	137–142	0.05	118–123
12	0.04	..	146–153	..	121–130
13	0.06	0.02	139–142	0.04
Recovery	0.61

Ultraviolet absorption spectrum showed no absorption peaks. Infrared absorption spectrum has not yet been satisfactorily obtained because the material is quite transparent. The preliminary work indicates that the substance does not have the absorption of the steroidal skeleton (5).

Oxidation was carried out on crystalline material with chromic anhydride in acetic acid. A sample of 1.40 grams of material α_D^{27} 38°, m.p. 118–122° C. was dissolved in 600 ml. of glacial acetic acid. The solution was stirred and heated to 94° and a solution of 18 grams of chromic anhydride was added dropwise. After 8 hours' stirring and heating, the reaction mixture was worked up as previously described. There was recovered 0.93 gram of crystalline material which had m.p. 122–128° C. The acidic material recovered from this oxidation was negligible in amount, and the loss of starting material was known to be partly mechanical.

The ability of the crystalline material to withstand such vigorous oxidizing conditions is quite unusual. In a similar oxidation of the saturated steroidal hydrocarbon cholestane, carried out according to the work of Windaus and Neukirchen (6), it was possible to recover but 24% of the starting material and it was found possible to obtain a weight of oxidation products amounting to 50% of the weight of the starting material.

DISCUSSION

Prior to the work reported here, but little information is to be found in the literature concerning the chemical nature of the rotatory substances of petroleum. Fenske noted the stability of the rotatory power of lubricant fractions toward heat, sulfuric acid, aluminum chloride, decolorizing clays, and engine service.

The work described here provides partial information as to the kinds of molecules which are responsible for much of the optical activity of petroleum. The following statements summarize the new information gained:

1. The optical activity of petroleum is due, in large part, to substances composed only of carbon and hydrogen.
2. Most of the rotation is due to a hydrocarbon mixture, containing no aromatic rings, but several alicyclic rings.
3. The isolation of a crystalline hydrocarbon fraction having $[\alpha_D + 38^\circ]$, relatively high melting point, consisting of 87.8% carbon and 11.7% hydrogen, and having molecular weight 392 has been accomplished.
4. The isolation of similar crystalline materials of high rotatory power from oils of diverse origins by the same separation process lends evidence to the idea that the rotatory power of all petroleum is due to the same substance(s) or to closely related substances.

The information available at this time leads to the notion that the crystalline material separated, consists of a mixture of closely related substances. Separation of the mixture by crystallizing from solvents or extensive chromatography gives fractions of changing melting points but of the same rotations, within the error of the determination.

The separation of other samples and efforts to determine structures of the crystalline materials are being continued.

ACKNOWLEDGMENT

This work was mostly done as a part of the work of A.P.I. Research Project 43b. The cooperation of the Advisory Committee of this project is especially appreciated. The senior author owes the encouragement and inspiration to undertake this work to the late Frank C. Whitmore.

LITERATURE CITED

- (1) Engler, C., and Hofer, H. V., "Das Erdöl," Vol. I, p. 176, S. Hirzel, Leipzig, 1913.
- (2) *Ibid.*, pp. 175-219.
- (3) *Ibid.*, pp. 205-6.
- (4) Fenske, M. R., *et al.*, *Anal. Chem.*, **20**, 434 (1948); *IND. ENG. CHEM.*, **34**, 638 (1942) and **36**, 383 (1944).
- (5) Huckabay, W. G., The Magnolia Petroleum Corp., Dallas, Tex., private communication.
- (6) Windaus, A., and Neukirchen, K., *Ber.*, **52**, 1915 (1919).

RECEIVED for review June 25, 1952.

ACCEPTED September 28, 1952.

Contribution from the Whitmore Laboratories, Department of Chemistry, The Pennsylvania State College.

Evidence of Catalytic Action in Petroleum Formation

BENJAMIN T. BROOKS

405 Lexington Avenue, New York 17, N. Y.

IN RECENT papers (7, 8, 10) on this subject, it has been suggested that chemical changes catalyzed by acid silicates, particularly certain types of clays, have played an essential role in petroleum formation. The idea that some form of catalysis has played such a role is not new but the suggestion has sometimes been made without supporting evidence. Frost (22) has pointed out that clays such as fuller's earth at temperatures of 150° to 200° C. can effect isomerization, disproportionation of hydrogen, and polymerization of unsaturated hydrocarbons. Although instances of such reactions in the presence of fuller's earth have been known for a long time, Frost suggested that such catalyzed reactions have occurred in petroleum formation. In the present paper it is pointed out that such catalytic action is not limited to fuller's earth (or montmorillonite) but is shown by a wide variety of sedimentary silicate rocks. Evidence is also submitted, supporting the suggestion made in earlier papers, that the multiplicity of hydrocarbons and the types of hydrocarbons occurring in petroleum, i.e., paraffins, isoparaffins, cycloparaffins, and aromatics, can be plausibly accounted for by carbonium ion reactions such as were postulated by Whitmore (56) in acid-catalyzed polymerizations and by Bartlett (1) and others (36, 39) in hydrocarbon alkylations. Such a method of petroleum formation also receives support from the work of Greensfelder and his associates (27) and of Thomas (48, 50) on catalytic cracking. They concluded that the reactions taking place in catalytic crack-

ing are best explained by carbonium ion reactions induced by acid-type catalysts. The formation of cycloparaffins and aromatics at the low temperatures which must be considered as prevailing in petroleum formation, has hitherto had no plausible explanation.

In a recent paper by Cox, Weaver, Hanson, and Hanna (16) it was suggested that under conditions where excess alkali is present acid-silicate catalysis could not take place. In the discussion of their paper Weaver expressed the opinion that a condition of alkalinity prevailed in the early mud stages of source beds and that acid silicates could result in later stages of consolidation, lithification, and recrystallization, as well as under other more special conditions. In the present paper it is pointed out that the presence of alkali, sodium bicarbonate, in large proportions in the Green River oil shale beds may account for the fact that the organic matter, so-called kerogen, in these shales has persisted without conversion into petroleum. Whether substantial proportions of alkali occur in other oil shales containing little or no petroleum is not yet known. It may be significant that in the Green River formations petroleum does not occur in appreciable quantities except in a relatively thin bed of sandstone known locally as the "mahogany marker." The shale body is essentially a magnesian marl.

Any theory of petroleum origin must take into account the physical conditions under which the original source beds were laid down and the evidence for the physical conditions prevailing in